Polymer 53 (2012) 4002–4009

Contents lists available at SciVerse ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Enthalpy recovery and structural relaxation in layered glassy polymer films

Thomas M. Murphy [a], D.S. Langhe [b], M. Ponting [b], E. Baer [b], B.D. Freeman [a], D.R. Paul [a,*]

[a] Department of Chemical Engineering and Texas Materials Institute, The University of Texas at Austin, Austin, TX 78712, United States
[b] Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH 44106, United States

ARTICLE INFO

Article history:
Received 29 May 2012
Received in revised form
3 July 2012
Accepted 8 July 2012
Available online 16 July 2012

Keywords:
Physical aging
Enthalpy relaxation
Confinement

ABSTRACT

Recent studies of physical aging in confined polymer glasses have revealed that aging behavior in confinement often differs from bulk behavior. This study used DSC to characterize physical aging and structural relaxation in bulk polysulfone (PSF) and co-extruded multilayered films of PSF and an olefin block copolymer (OBC) that have average PSF layer thicknesses of 640 nm, 260 nm, and 185 nm. The films were aged isothermally at 170 °C, and the recovered enthalpy upon reheating was measured over time. The films with 640 nm and 260 nm PSF layers had aging rates very similar to that of bulk PSF, while the film with 185 nm PSF layers had an aging rate slightly greater than the bulk value. The cooling rate dependence of the limiting fictive temperature (T_f') in multilayered and bulk PSF samples was also characterized. Values of T_f' were similar for all films at each cooling rate. The results of this work are in general agreement with our previous gas permeation aging study of multilayered PSF films aged at 35 °C, in which the effect of layer thickness on aging behavior was minimal. This stands in contrast to studies with thin, freestanding PSF films, which exhibit accelerated aging relative to bulk and have aging rates that depend strongly on film thickness.

1. Introduction

Glassy polymers typically exist in a non-equilibrium state in which properties such as specific volume, enthalpy, and entropy are in excess of equilibrium values. Compared to the “rubbery” or “liquid” equilibrium state above the glass transition temperature, T_g, the molecular mobility of the polymer chains is greatly reduced in the glassy state. However, some chain mobility remains, which allows for relaxation of the excess volume as the polymer approaches equilibrium [1]. Fig. 1 shows a simplified view of the enthalpy of a glass-forming polymer as a function of temperature. Upon holding a non-equilibrium glassy polymer at a fixed annealing temperature, T_a, densification will occur over time, and many of the polymer's properties will change. For example, the enthalpy of the sample will decrease. The time-dependent property changes resulting from this densification process are known as physical aging [2]. For glassy engineering thermoplastics at typical service temperatures (i.e., well below T_g), aging is often slow, and equilibrium is practically never achieved on experimentally-accessible timescales [1,2]. The fictive temperature, T_f, is a concept used to characterize the instantaneous state of a glass [3–5]. As indicated in Fig. 1, it is the temperature at which the extrapolated equilibrium line would be intersected by a line drawn through the point representing the current enthalpy value of the sample and having the same slope as that of a sample in the glassy state (i.e., the same heat capacity). If a material is in equilibrium, the fictive temperature and annealing temperature will be the same. For a non-equilibrium glass annealed isothermally below T_g, the fictive temperature will be greater than the annealing temperature, with the difference between the two being a reflection of the departure of the sample's enthalpy from equilibrium. The fictive temperature concept is often used in phenomenological models of structural relaxation and physical aging, such as the Tool-Narayanaswamy-Moynihan (TNM) model, to capture the dependence of the relaxation time on the instantaneous structural state of the polymer [4]. A review by Hodge provides a thorough description of enthalpy relaxation and the models used to describe it [6]. A general review of physical aging (not limited to enthalpy relaxation), written by Hutchinson, also describes enthalpy relaxation studies and theoretical treatments of the aging process [2].

Historically, differential scanning calorimetry (DSC) has been widely used to study physical aging and dynamic structural relaxation (i.e., relaxation that occurs during cooling or heating while the polymer is below T_g) of glassy materials. Early studies by Petrie in the 1970s helped establish DSC as a viable and useful technique for studying physical aging in polymer glasses [7,8]. Much recent work pertaining to physical aging and enthalpy relaxation has

---

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

0032-3861/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.polymer.2012.07.012

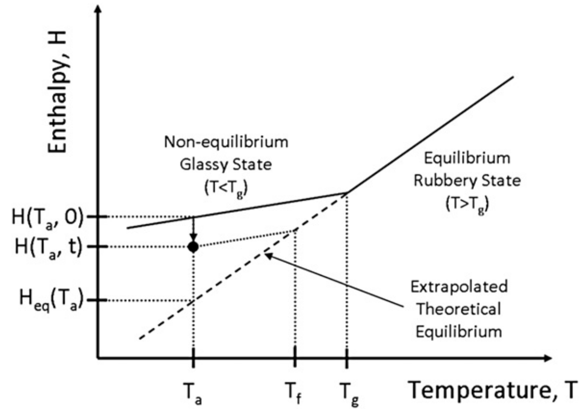


Fig. 1. Qualitative enthalpy vs. temperature diagram for a glass-forming polymer.

focused on aging in confined geometries such as polymer thin films [9], nanocomposites [10–14], and molecular glass-formers confined in nanopores [15].

Koh and Simon used DSC to study the structural relaxation of ultrathin polystyrene (PS) films arranged in stacks [9]. When aged at the same temperature, the ultrathin films (62 nm and 38 nm) required less time to reach equilibrium than bulk films. Thus, physical aging in these thin films was accelerated relative to that in bulk samples. The depressed T_g values in the thin films were cited as the reason for the accelerated aging. When both ultrathin and bulk films were aged at a constant value of $T_g–T_a$ (thus accounting for T_g depression in ultrathin films), rates of aging were similar. The DSC thermograms for the thin films also showed a reduced height in the heat capacity overshoot peak and a broader glass transition relative to those observed in bulk films. Modeling studies indicated that the thinner films had a broader distribution of relaxation times than the corresponding bulk films.

Boucher et al. studied enthalpy recovery in poly(methyl methacrylate) (PMMA)/silica nanocomposites using DSC [12]. Addition of silica nanoparticles did not affect T_g. Physical aging of the nanocomposites was accelerated relative to that of bulk PMMA when aged at 80 °C (i.e., $T_g - 43$ °C). Higher ratios of silica particle surface area to PMMA volume correlated with more rapid physical aging. A recent paper from Cangialosi et al. considered both PMMA-silica and PS-silica nanocomposites and observed accelerated aging in both systems [11]. A decoupling between the segmental mobility (as determined by broadband dielectric spectroscopy) and both the calorimetric T_g and physical aging rate was observed. A model based on the diffusion of free volume holes to the silica/polymer interface was used to rationalize their observations.

Flory et al. investigated the enthalpy relaxation and T_g of nanocomposites of PMMA and both unmodified and amino-functionalized single-wall carbon nanotubes (SWNT) [14]. The T_g of unmodified SWNT nanocomposites was the same as that of pure PMMA, while the amino-functionalized nanocomposites showed a T_g increase of ∼17 °C. The physical aging of both nanocomposite systems was reduced relative to that of neat PMMA when aged at the same distance from T_g, as judged by their approach to a constant recovered enthalpy value.

Simon, Park, and McKenna used DSC to study the physical aging of ortho-terphenyl (o-TP) confined in a nanoporous matrix [15]. The confined o-TP exhibited accelerated aging relative to bulk, and the equilibrium state reached by the confined glasses was different from that of the bulk material. Simon et al. were able to model the aging behavior by accounting for isochoric glass formation (i.e., the o-TP "sticks" to the walls of the nanopores and cannot undergo volume changes, thus leading to tensile stresses in the confined o-TP glass).

A study by Langhe et al. explored physical aging of PS layers in multilayered films of PS and polycarbonate (PC) using DSC [16]. The PS/PC films had PS layer thicknesses ranging from 50 to 500 nm. The T_g of the PS layers in these films was independent of layer thickness and essentially the same as that of bulk PS. Isothermal aging studies at 80 °C showed that aging rate decreased as layer thickness decreased. A film with 50 nm PS layers had an aging rate 50% lower than that of bulk PS. The fraction of interphase material (i.e., material surrounding the PS/PC layer interface containing both PS and PC), which increases as layer thickness decreases, was inversely correlated with aging rate. The increased T_g of the interphase material was hypothesized to lead to longer relaxation times, thus reducing the aging rate. It was also suggested that the interphase material could impose mechanical constraints on PS layer relaxation that become more important as the interphase fraction increases. The enthalpy relaxation occurring during cooling these films at different rates was also studied, but the enthalpy recovered upon reheating the sample after cooling did not depend on layer thickness and was similar to that of bulk PS.

Many other recent physical aging studies, using techniques such as gas permeability tracking [17–27], fluorescence spectroscopy [28–31], dielectric spectroscopy [28,32–37], and ellipsometry [38–42], have been aimed at understanding physical aging in confined systems. A concise review of some of these recent studies is provided by Priestley [43]. In most of these studies, the aging behavior of polymers in confinement is different from that of bulk polymers.

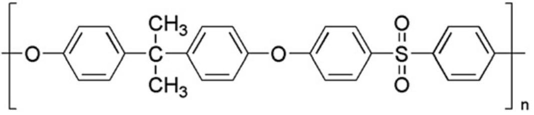
Our previous work on physical aging in multilayered polysulfone (PSF) films at 35 °C, which used gas permeability to track physical aging, revealed that the rate of aging in these films is similar to that in bulk films [25]. This work, in which some of the same multilayered film systems from our previous study are used, employs DSC to further explore enthalpy relaxation in these films at temperatures closer to the T_g of PSF.

2. Experimental

2.1. Materials

Polysulfone (UDEL P-3700, Solvay Advanced Polymers) was the primary material of interest in this work. PSF is used as a gas

Table 1
Materials used to produce layered films.

Polymer	Density[a]	T_g	T_m	X_c[b]
UDEL P-3700 Polysulfone (PSF) 	1.24	186 °C	–	–
Infuse 9007 (OBC)	0.866	−60 °C	120 °C	8%

[a] Density values taken from manufacturer data sheets; reported in units of g/cm³.
[b] Crystallinity determined by DSC and reported in wt.%.