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Vapor sorption in thin supported polymer films studied by white light interferometry

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Abstract

In the present study, we apply a white light interferometric methodology to study sorption of moisture and methanol vapor in thin films of poly(2-hydroxyethyl methacrylate) [PHEMA] and poly(methyl methacrylate) [PMMA], supported on oxidized silicon wafers. The measured equilibrium thickness expansion of each film, exposed to different activities of the vapor penetrant, is used to determine the sorption isotherm of the system. Results for relatively thick films (100 nm < L_o < 600 nm) are compared with corresponding literature data for bulk, free-standing films, obtained by direct gravimetric methods. Furthermore, PMMA films of thicknesses lower than 100 nm were employed in order to study the effect of the dry film's thickness, and of substrate, on fractional swelling.

Keywords: Vapor sorption; Poly(2-hydroxyethyl methacrylate); Poly(methyl methacrylate)

1. Introduction

Moisture and organic vapor sorption in, and concurrent swelling of, ultrathin supported polymer films is important in many applications, such as coatings, microelectronics manufacturing and chemical sensors (e.g. [1,2]). Conventional gravimetric methods are not always suitable for studying these phenomena in ultrathin supported films. Accordingly, various techniques have been applied, such as quartz crystal microbalance for mass uptake measurements [1,3–5] and specular X-ray reflectivity [1,4,6–8], ellipsometry [9,10], or interferometry [11] for monitoring thickness changes due to sorption. The latter type of measurements is also used to estimate mass or volume fraction of the sorbed penetrant, assuming unidirectional swelling due to the constraining rigid support [1,4,6,7,9–11]. In certain cases the sorption isotherms deduced by the application of the above techniques in supported films have been compared with the corresponding data deduced by conventional methods in free-standing, bulk films. The results indicate that the former type of films may sorb differently from the latter [9–11]. Moreover, studies on ultrathin supported films of different thicknesses L_o (<100 nm), mainly focused on moisture absorption, indicate that equilibrium fractional swelling, due to exposure to a constant vapor activity, is thickness-dependent [1,3,4,6–8]. For relatively hydrophobic poly(4-*tert*-butoxycarbonyloxystyrene) films supported on hydrophilic SiO_2 substrate, an enhancement of fractional swelling with decreasing film thickness was observed [6]. A similar, although weaker, effect was observed for the same polymer supported on Al_2O_3 [7] as well as for a polyimide supported on SiO_2 [8]. This behavior was attributed to the accumulation of excess water near the polymer–hydrophilic substrate interface, and the interpretation was supported by water distribution profiles determined by specular neutron reflectivity measurements [6,7]. Furthermore, treatment of the Al_2O_3 substrate surface with a hydrophobic

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agent reduced the degree of interfacial water at the buried interface [7]. In general, the water concentration profile near the substrate is thought to depend on the relative hydrophobicity (hydrophilicity) of the polymer and substrate. Thus, fractional swelling of hydrophilic poly(vinyl pyrrolidone) supported on SiO_2 was found to be independent of thickness, while treatment of the SiO_2 surface with hydrophobic hexamethyldisilizane (HMDS) resulted in decreasing fractional swelling with decreasing film thickness [4].

Other physical properties of ultrathin supported films, such as diffusivity and glass transition temperature, have also been found to differ from those of the bulk, due to the significant contribution of interfacial effects to the properties of the film, when the latter's dimensions approach the radius of gyration of the polymer's molecule. For example, the glass transition temperature of ultrathin PMMA films was found to increase with decreasing film thickness for films supported on silicon dioxide substrate [12–14]. In contrast, the T_g of PMMA films supported on gold [13] or silicon dioxide treated with HMDS [12] substrates was found to decrease with decreasing film thickness. In the case of polystyrene, the T_g of supported films [15] (as well the solvent-induced T_g of polymer brushes [16]) has also been found to be thickness-dependent. Although these phenomena are not completely clarified, the prevailing interpretation is based on the concept that a supported film consists of three layers [15,17]. The polymer layer near the free surface (polymer–air interface) is characterized by enhanced mobility and reduced packing density as compared to the bulk polymer. The middle layer behaves like bulk polymer. The properties of the layer near the solid substrate depend on the strength of polymer–substrate interactions. As the film thickness decreases, the contribution of the top and bottom layers becomes increasingly significant and determines the thickness dependence of the apparent T_g of the film. Thus, in the case of strong polymer–substrate interactions, leading to restricted chain mobility in the layer near the solid substrate, the properties of this layer are the determinant factor and the T_g of the film increases with decreasing thickness. On the other hand, in the case of weak polymer–substrate interactions the free surface effect dominates, and T_g decreases with decreasing thickness. In line with the three layer model are molecular simulation studies [18] showing that, for dimensions lower than 30σ (where σ is the monomer diameter), free-standing films exhibit a decrease in the T_g with decreasing thickness, but the behavior of supported films depends on polymer–substrate interactions. In particular, T_g decreased with decreasing thickness for a weakly attractive substrate (having the same interaction strength parameters as the polymer), but the extent of reduction was less than that of the simulated free-standing film. In contrast, an increase in T_g was found for a strongly attractive substrate (having a polymer–surface interaction strength twice as that between polymer segments).

In the present work we apply a white light interferometric methodology to characterize the swelling behavior of thin supported films due to the sorption of methanol and water from the vapor phase. Films prepared from two polymers of different hydrophilicities are used: poly(2-hydroxyethyl methacrylate) [PHEMA] and poly(methyl methacrylate) [PMMA]. Data on the thickness expansion of relatively thick polymer films ($100\ \text{nm} < L_o < 600\ \text{nm}$), upon exposure to various activities of moisture and methanol vapor, are used to estimate the sorption isotherm of the system. Results are then compared with corresponding literature data obtained by direct gravimetric methods for bulk, free-standing films. Furthermore, PMMA films of thicknesses lower than 100 nm were employed in order to study the effect of the dry film's thickness, and of substrate, on fractional swelling.

2. Experimental

PMMA (MW ~ 120,000; density: 1.188 g/ml at 25 °C) and PHEMA (MW ~ 300,000; density: 1.15 g/ml at 25 °C) in the form of powder were purchased from Sigma–Aldrich. The radius of gyration R_g of each polymer's molecule was estimated, by group contribution methods [19], to be 8.7 and 14.8 nm for PMMA and PHEMA, respectively. Propylene glycol methyl ether acetate (PGMEA), ethyl lactate and methanol (MeOH) were also purchased from Sigma–Aldrich and used without further purification.

Polymer films, supported on oxidized silicon wafers, were prepared by spin-coating from 0.5–8% w/w solutions of PMMA in PGMEA, and of PHEMA in ethyl lactate. In certain experiments, partial hydrophobization of the support was effected by deposition, via spin-coating, of a few nanometers thick HMDS layer on the SiO_2 surface. The measured contact angles of water on bare, and HMDS-treated Si/SiO_2 substrate were $39 \pm 1°$ and $67 \pm 2°$, respectively. All supported films were heated on a hot plate for 15 min to 160 °C (PMMA) or 120 °C (PHEMA), in order to remove residual solvent and then were stored in a desiccator until further use. Dry film thicknesses L_o in the range 25–600 nm were used, corresponding to a range of $3–69R_g$ for PMMA and $2–40R_g$ for PHEMA.

For the measurement of changes in polymeric film thickness due to absorption/desorption of vapors, a home-made experimental set-up [20] has been used, consisting of the following sub-systems (i) a white light interferometry unit, (ii) a delivering sub-system for controlled concentrations of the vapor penetrant, (iii) a temperature controlled measuring chamber and (iv) a PC for the control of the sub-systems, and the data acquisition and processing.

The main parts of the white light interferometry unit are a light source, a spectrophotometer and a bifurcated optical fiber. A splitter optical fiber is connected to a vis–NIR light source (Avantes AvaLight HAL Tungsten-Halogen) through SMA connectors. The delivered optical power is equally divided into two beams: one directed to the slave channel of a PC driven double spectrophotometer, with a resolution of approximately 0.4 nm (Ocean Optics USB SD2000), and another connected to a bifurcated optical fiber. The outer part of the bifurcated optical fiber guides the light vertically onto the supported polymer film. The support is a Si wafer covered with a thermally grown, at 110 °C for 200 min, silicon dioxide layer of a final thickness of 1060 nm. Both the SiO_2 and the polymer used are transparent in the vis–NIR spectrum and