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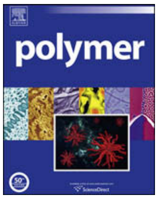

Impact of thickness on CO_2 concentration profiles within polymer films swollen near the critical pressure

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ABSTRACT

The isothermal swelling of polymer thin films by a supercritical fluid does not increase monotonically with increasing chemical potential (pressure), but rather a maximum in swelling is generally observed near the critical pressure. A reactive templating approach utilizing the condensation of silica within hydrophilic domains of a swollen amphiphilic polymer film enables visualization of the qualitative concentration profile of CO_2 by the changes in the size of hydrophobic domains (pores) with cross sectional TEM microscopy; specifically, isothermal swelling of poly(ethylene oxide-propylene oxide-ethylene oxide) films by CO_2 at 60 °C is examined. Films that contain thickness gradients are used to avoid any uncertainties in the impact of thickness due to variations in the temperature or pressure during the silica modification. A uniform pore size (local swelling) is observed for all film thicknesses when the pressure is outside of the anomalous maximum in the film swelling, except for a small increase at the buried interface due to preferential adsorption of CO_2 to the native silicon oxide surface of the substrate. However at this swelling maximum, a gradient in the pore size is observed at both interfaces. These swelling gradients at interfaces appear to be responsible for the anomalous maximum in thin films. As the film thickness increases beyond 350 nm, there is a decrease in the maximum swelling at the free interface.

1. Introduction

Supercritical carbon dioxide has been proposed as alternative green solvent for the processing of polymeric materials due to being environmentally benign with tunable solvent quality through manipulation of the fluid density through temperature and/or pressure [1,2]. However, most polymers are not soluble in CO_2 [3], but generally can be appreciably swollen [4]. The sorption of CO_2 into polymers leads to changes in their physical properties including a decrease in the glass transition temperature (T_g) [5], an increase in the diffusivity of the polymer chains [6], and changes in the phase behavior of multicomponent polymeric systems [7–9]. The improvements in the transport properties of CO_2 swollen polymers enable improvements in processing of some otherwise intractable materials [10].

The potential for significant improvements in physical properties exists through the incorporation of nanofillers to create polymer nanocomposites. These nanocomposites have been proposed for use in a host of applications ranging from lightweight structural materials to membranes for separations [11,12]. Their processing can be difficult due to the presence of the filler materials, especially when the nanomaterial is highly asymmetric such as in the case of carbon nanotubes. CO_2 has been recently explored as a green alternative for aiding in the processing of polymer nanocomposites [13]. However, it is still unclear how CO_2 interacts within these nanocomposites. One report for PMMA–clay nanocomposites showed that swelling can be solely attributed to the PMMA and is consistent with neat PMMA [14]; but the changes in viscosity of polymer-fumed silica nanocomposites swollen with CO_2 is dependent upon the surface chemistry of the nanofillers [15]. Thus, an improved fundamental understanding of the physical interactions between CO_2 and polymer nanocomposites would be useful. Recently, several groups have reported on the equivalence of polymer thin films and nanocomposites in regards to the thermophysical properties [16,17]. Therefore, thin films provide an attractive surrogate to probe the fundamental properties of polymer nanocomposites as both films and nanocomposites exhibit large surface area to volume ratios. Understanding interfaces in thin films can provide insight into the behavior of analogous polymer nanocomposites. Additionally, CO_2 processing of polymeric thin films has been shown to be advantageous for some photoresist systems [18] and in the fabrication of low-*k* dielectric films [19] for microelectronics. In these applications, precise control

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of the structure is required at the nanoscale. Thus, it is important to understand where CO_2 goes in these thin films, especially in regards to the polymer interfaces.

These interfaces are thermodynamically distinct from the bulk of the polymer and provide a different potential for absorbing species. Supported polymer thin films can exhibit apparent changes in the solubility of solvents. In particular, water in polymer thin films has been examined extensively using neutron reflectivity [20,21] and to a lesser degree using ion scattering [22]. An accumulation (or depletion) of water at the polymer–substrate interface measured with reflectivity can be directly correlated to changes in the apparent solubility with decreasing film thickness [23]. A qualitatively similar phenomenon has been observed for the swelling of polymer thin films with carbon dioxide [24,25]. However, film swelling in this case is not monotonic; an anomalous maximum in the swelling is observed at a CO_2 activity near unity [24–26]. Unlike water, the distribution of CO_2 within the films is difficult to quantify directly as the neutron contrast between most polymers and CO_2 is low.

Recently, we reported an indirect route to visualize the CO_2 concentration profiles using an *in-situ* reactive templating approach [27]. This is based upon the seminal work of Watkins and co-workers that demonstrated that reactions with CO_2 swollen polymers [28,29] can be used fabricate well defined nanoporous structures using amphiphilic templates [19]. After allowing an amphiphilic film to equilibrate with CO_2, the local swelling of the hydrophobic domains can be determined by the selective *in-situ* condensation of silica within the hydrophilic domains, which "locks" the swollen size into the templated structure. This process enabled the identification of long range gradients in the CO_2 concentration in polymer films swollen near the density fluctuation ridge [30] (near critical point). A gradient extending approximately 150 nm into the film from the free surface and a short (<10 nm) gradient at the buried interface is found for a 350 nm thick film prepared at CO_2 pressure corresponding to the anomalous swelling maximum [27].

However, the CO_2 swelling of polymer thin films appears to be dependent upon initial thickness [25,31]. For example, Koga et al. found that absolute swelling amount decreases as increasing film thickness at anomalous swelling and levels off when initial thickness h_0 approaches $8R_g$ (polymer radius of gyration) for deuterated polybutadiene (d-PB) polymer thin films [32]. In this work, the impact of film thickness on CO_2 concentration gradients is examined using the previously described *in-situ* reactive templating approach. To avoid difficulties in obtaining identical processing conditions, thickness gradient films produced using flow coating [33] are utilized to assess multiple thicknesses simultaneously. These results provide insight into CO_2 sorption at free and buried (polymer/native silicon oxide) interfaces near the anomalous swelling maximum.

2. Experimental section

2.1. Materials and synthesis

Polymer templates were prepared from solutions containing poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) (Pluronic F108, BASF), poly(*p*-hydroxystyrene) (PHOSt, $M_n = 8000$ g/mol, DuPont Electronic Materials), and *p*-toluenesulfonic acid (*p*-TSA, Aldrich) dissolved in a mixture of ethanol (Aldrich) and deionized water. The use of a hydrogen bonding polymer blend yields a highly ordered template that is not possible from the Pluronic alone [34–36]. This extended ordering simplifies the identification of any gradients in the film after reaction. Silicon wafers were utilized as substrates and were cleaned using UV/Ozone cleaner (Jelight Company Inc. Model 42) for a cleaning time of 5 min prior to film formation. A schematic of the flow coating [33] technique used to create a gradient polymer template film is illustrated in Fig. 1(a). The apparatus consists of a glass blade fixed above a movable stage. A bead of the polymer solution is deposited between the glass blade and substrate and then the stage is accelerated. The variation in frictional drag with respect to blade velocity determines the amount of the polymer solution left behind. A constant acceleration rate during the flow coating results in a film with a near linear gradient in thickness (Fig. 1b) until the blade decelerates.

The gradient polymer films are then placed in a closed stainless steel vessel (25 mL, Thar) preheated to 60 °C and pressurized slowly with CO_2 to desired pressure. The polymer film was then allowed to equilibrate with the CO_2. Reactive modification of the CO_2 swollen polymer template used a fixed quantity of precursors (10 μL of tetraethyl orthosilicate (TEOS, Aldrich) and 20 μL deionized water) for all syntheses. All the reactions were allowed to proceed for 30 min, then the reactor was slowly de-pressurized to avoid foaming of the resultant silica–polymer nanocomposite. To increase the robustness of the films for visualization, a post-synthesis aging in a sealed vessel with saturated water vapor at 90 °C for 2 h was used to enhance silica network formation followed by calcination at 450 °C for 5 h at a heating rate of 1 °C/min in air to remove the organic template.

2.2. Film characterization

Spectroscopic ellipsometry (SE) and transmission electron microscopy (TEM) were utilized to characterize the film

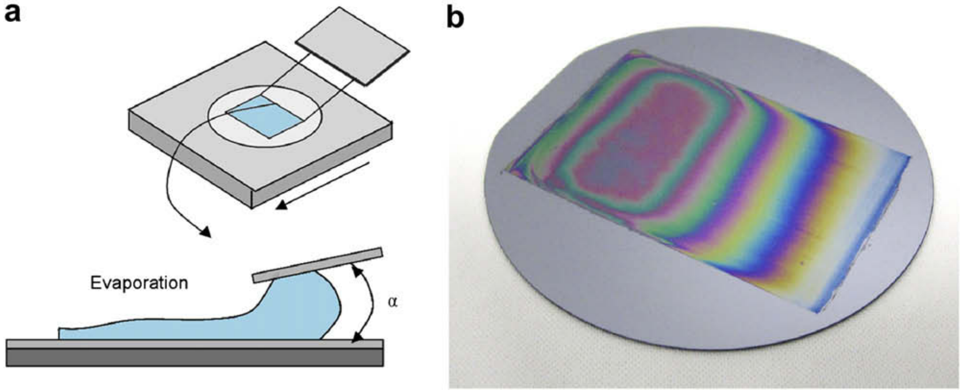

Fig. 1. (a) Schematic of the flow coating process, where α is the glass blade angle to the substrate. The substrate is moving in the direction of the arrow. (b) A gradient film coated by flow coater. Color variance indicates thickness difference.