



Impact of polymer modulus/chain mobility on water accumulation at polymer/metal oxide interfaces

Alper Karul^a, Kar Tean Tan^b, Christopher C. White^b, Donald L. Hunston^b, Steve T. Marshall^c, Bulent Akgun^d, Sushil K. Satija^d, Christopher L. Soles^e, Bryan D. Vogt^{a,*}

^a Department of Chemical Engineering, Arizona State University, Tempe, AZ 85284, USA

^b Building and Fire Research Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

^c Department of Chemical Engineering, University of Colorado, Boulder, CO 80309, USA

^d Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

^e Polymers Division, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

ARTICLE INFO

Article history:

Received 11 February 2009

Received in revised form

11 April 2009

Accepted 19 April 2009

Available online 7 May 2009

Keywords:

Moisture

Interfaces

Thin films

ABSTRACT

Moisture is known to accumulate at the interface between polymers and metal oxides, leading to detrimental effects on physical properties such as modulus and adhesion. Direct measurement of the interfacial moisture profile has been carried out with neutron reflectivity, while thickness dependent swelling of a thin film series has also been also utilized to indirectly assess the interfacial moisture content. In this work, the moisture adsorption on the clean surfaces is compared to that observed when the surface is coated with a series of polymer films. The mechanical properties of the polymer appear to impact the quantity of moisture adsorbed at the interface; surprisingly less moisture accumulates at the interface if the coating is rubbery (larger intrinsic mobility of polymer chains). For glassy polymers, the total accumulation at the interface is identical to the adsorption on the clean metal oxide surface. This result potentially provides an understanding of solvent distribution in glassy nanocomposites by measuring moisture adsorption onto the bare filler materials prior to incorporation into the polymer matrix.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

The incorporation of nanosized inorganic fillers into polymeric materials can provide tremendous improvements in transport, thermal, and mechanical properties for applications in membrane, packaging and structural materials as examples [1–4]. One key property of these nanocomposite materials is their large internal interfacial area between the filler and polymer; the nature of this interface is critical to the performance of the nanocomposite [5]. Generally, only the interactions between the filler and polymer are considered in assessing nanocomposite performance; however, most applications require the material to withstand different environmental factors. This is particularly true for membrane applications where transport through the material is required; for example, separation of carbon dioxide from flue gas for CO₂ sequestration to minimize global release of greenhouse gases will be dependent on how CO₂ interacts with the polymer–filler interface [6]. Structural applications also require knowledge of moisture

interactions with the nanocomposite; accumulation of moisture at the internal interfaces could lead to mechanical failure [7]. However, direct measurement of the distribution of these small molecules within nanocomposites is challenging.

Recently, several research groups have demonstrated that the thermal behavior of nanocomposite is identical to a thin film whose thickness is the same as the average distance between filler particles [8–11]. The accumulation of small molecules such as water [12,13] or ethanol [14] at polymer–inorganic filler interfaces can be readily determined using neutron reflectivity in thin film geometry. Thus, films can be used to estimate the behavior of nanocomposite materials exposed to different environmental conditions. Unfortunately, this measurement is significantly limited by the availability of neutron sources; therefore, alternative methodologies are sought. Nguyen and coworkers were able to estimate the moisture accumulation at buried interfaces of supported polymer coatings using FTIR, but this requires multiple assumptions and measurements to differentiate between bulk and interfacial sorption [15]. Similar deconvolution schemes have been used based upon thickness dependent swelling of ultrathin films; the thickness dependence is attributed to the interfacial accumulation or depletion, which is independent of film thickness [16].

* Corresponding author. Tel.: +1 480 727 8631.

E-mail address: bryan.vogt@asu.edu (B.D. Vogt).

The extension to understanding the interfacial sorption by examining a polymer-free surface has not been discussed to date. The work herein seeks to address the question does the coating of a surface with a polymer film cause a deviation in the adsorption properties of the surface? Adsorption on surfaces has been a staple of surface science [17], and numerous techniques are available to characterize the adsorption of small molecules on surfaces. Previous studies on asphalt showed a qualitative relationship between moisture susceptibility and the surface energy of the filler [18]. Here, the quantitative relationship between surface adsorption of moisture and the interfacial moisture in a model polymer nanocomposite is examined.

2. Experimental

2.1. Materials

Poly(4-hydroxystyrene) (PHOST, $M_w = 8$ kg/mol) was obtained from DuPont Electronic Materials and used as-received. A series of poly(*n*-alkyl methacrylates) was also examined: poly(methyl methacrylate) (PMMA), poly(*n*-butyl methacrylate) (PnBMA) and poly(*n*-octyl methacrylate) (PnOMA) were obtained from Scientific Polymer Products. Silicon wafers with thermal oxide and quartz crystals were utilized as substrates. The thermal oxide was prepared using typical microelectronics processing techniques [19] and grown to approximately 15 nm. X-ray porosimetry was used to check the porosity of analogous films. The porosity of the thermal oxide was below the detection limit of the measurement. Thus, we consider the thermal silicon oxide layer as dense and nominally impervious to moisture. For the PHOST films, the quartz crystals were capped with a sputtered silica layer. For the polymethacrylate films, the quartz crystal surface was chromium oxide. Both surfaces were cleaned using UV–ozone prior to film coating. PHOST films were formed by spin coating from 0.2 wt% propylene glycol methyl ether acetate (PGMEA, Aldrich), followed by a baking at 120 °C for 2 h under vacuum to remove residual solvent. The polymethacrylates were spin coated from toluene (Aldrich) and baked at 120 °C for 1 h under vacuum. The concentration of the solutions was varied from 0.1 wt% to 5 wt% to obtain a large range of film thickness.

2.2. Measurements

To measure the moisture uptake, quartz crystal microbalances (QCM) were used. For the PHOST films, the mass uptake of moisture into the films was measured using a quartz crystal microbalance (Q-Sense) with dissipation (QCM-D). The crystals were 5.0 MHz quartz resonators with SiO_x coated gold electrodes. For the polymethacrylate films, the uptake was measured using a Maxtek RQCM. The crystals were 5.0 MHz quartz resonators with chromium coated gold electrodes. The moisture was introduced into the QCM sample chamber through a flow system that bubbles dry air through distilled water, exposing the polymer film to ca. 100% RH. Under these conditions, the amount of water absorbed into the film can be determined from the change in the resonance frequency using the Sauerbrey equation [20], relating the frequency shift, Δf , to the change in mass, Δm .

$$\Delta f = -\frac{2f_0^2 \Delta m}{nA(\mu_q \rho_q)^{0.5}} = -C_f \frac{\Delta m}{nA} \quad (1)$$

where f_0 is the measured resonant frequency or overtone, n is the number of the overtone, A is the electrode area (0.25 cm²), μ_q and ρ_q are the shear modulus (2.95×10^6 N/cm²) and the density (2.65 g/cm³) respectively of the quartz, and C_f is the integral sensitivity constant (57 Hz cm²/μg).

To quantify the distribution of water within the polymer films, neutron reflectivity (NR) measurements were performed on the NG-7 reflectometer at the Center for Neutron Research at the National Institute of Standards and Technology (Gaithersburg, MD) in the following configuration: wavelength (λ) = 0.4768 nm and wavelength spread ($\Delta\lambda/\lambda$) = 0.025. NR is capable of probing the neutron scattering density at depths of up to several thousand Å, with an effective depth resolution of several Å. Deuterium oxide (Aldrich, 99.9% pure) was utilized to enable direct quantification of the water distribution within the film. All measurements were performed at 23 °C ± 2 °C.

3. Results and discussion

Fig. 1 shows the adsorption of moisture on a blank SiO_x coated quartz crystal. The adsorption is initially quite rapid and then decreases as surface sites are progressively filled. At equilibrium, approximately 76 ng/cm² of water is adsorbed onto the surface. This modest adsorption of moisture is expected due to the hydrophilic nature of the SiO_x glass surface. When this surface is coated by an ultrathin PHOST film (4.9 nm thick), the total uptake increases to approximately 98 ng/cm² of water in the thin film. Previously, we reported approximately 5 vol% swelling in thick PHOST films where the interfaces did not impact the moisture uptake [16]. Assuming a density of 1 g/cm³ for the sorbed water [21], the moisture uptake in the 4.9 nm thick PHOST film results in 20% swelling. This uptake is significantly larger than the bulk sorption for saturated water vapor into PHOST. Such a difference was speculated to be a result of moisture accumulation at the PHOST–silicon oxide interface; linear swelling of PHOST films of a similar thickness was reported to be 20% from reflectivity measurements [16]. To extract bulk from interfacial sorption, neutron reflectivity was used to quantify the uptake at the interface [16] and moisture accumulation at the PHOST–silicon oxide interface was found to account for the changes in the swelling of the thin films. However, comparisons to the blank substrate have not been explored. As shown in Fig. 1, there is a 22 ng/cm² difference between the blank crystal and the 4.9 nm PHOST film in the sorption at equilibrium. Interestingly, this difference would result in a linear swelling of 4.5%, which is in good agreement to previous measurements of ‘bulk’ moisture swelling of PHOST [16]. Thus, the interfacial moisture was found to be independent of the polymer interfacial chemistry. This independence of the polymer coating appears to also be independent of even the presence of a polymeric coating [16]. These results suggest that moisture content at polymer–inorganic interfaces can be predicted via simple adsorption measurements on the inorganic surface. This

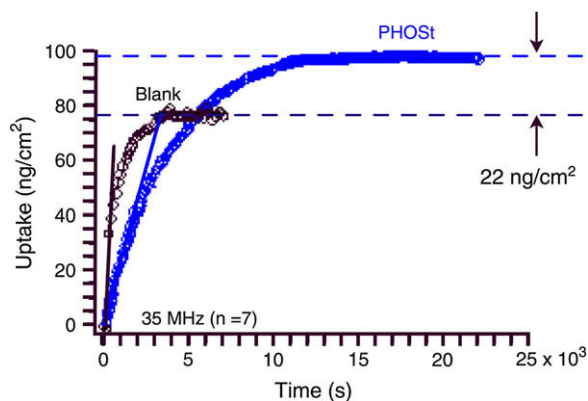


Fig. 1. Moisture uptake on a blank SiO_x coated crystal and 4.9 nm thick PHOST film on the same crystal. The difference in swelling between the two samples is consistent with the bulk swelling of PHOST.

would dramatically ease the experimental burden of measuring the concentration of small molecules at buried polymer interfaces.

To further investigate this phenomenon of surface adsorption matching the interfacial moisture accumulation, a 300 nm chromium layer was used as the capping layer on the gold electrode of the quartz crystal. The polycrystalline nature of the chromium leads to a significant increase in the surface roughness in comparison to the SiO_x surface examined previously. The chromium also oxidizes upon exposure to air resulting in a hydrophilic chromium oxide surface that is presented to the polymer film.

In addition, the impact of the modulus of the polymer coating on moisture accumulation has not been investigated to date, but it has been suggested that the polymer modulus plays a role in determining the interfacial moisture content [22]. Therefore, a series of poly(*n*-alkyl methacrylates) are utilized in this work: poly(methyl methacrylate) (PMMA), poly(*n*-butyl methacrylate) (PnBMA) and poly(*n*-octyl methacrylate) (PnOMA). As the alkyl chain length is increased, the glass transition temperature decreases monotonically from 105 °C for PMMA to 15 °C for PnBMA to –20 °C for PnOMA. Differences in moisture uptake between glassy and rubbery are assessed from using a series of different film thicknesses for each polymer.

The equilibrium moisture uptake into ca. 10 nm films is shown in Fig. 2. PMMA has the highest uptake, followed by PnBMA and PnOMA. This trend is expected as increasing the alkyl chain length also tends to make the polymer more hydrophobic. The difference in equilibrium sorption of saturated water vapor between the PMMA and blank crystal is approximately 10 ng/cm², which corresponds to ≈1% swelling. This swelling is nominally consistent with the reported bulk solubility of moisture at saturation in PMMA [23]. This is the same result as we previously discussed for the PHOST film, reinforcing the notion that the accumulation of interfacial moisture is independent of polymer chemistry. However, the adsorption on these chromium coated crystals is 3 times as much as measured for the smooth hydrophilic SiO_x surface. It is also important to note that Kent and coworkers found a significant moisture concentration within molybdenum oxide coatings when exposure to D₂O using neutron reflectivity. Thus, both the increased surface area from both roughness and intrinsic porosity likely contribute to the enhanced water uptake in the chromium oxide coatings in comparison to the silicon oxide.

However, the uptakes in the thin films of PnBMA and PnOMA are significantly less than that for the blank crystal. In contrast to the increasing hydrophobicity with the alkyl chain length, the moduli

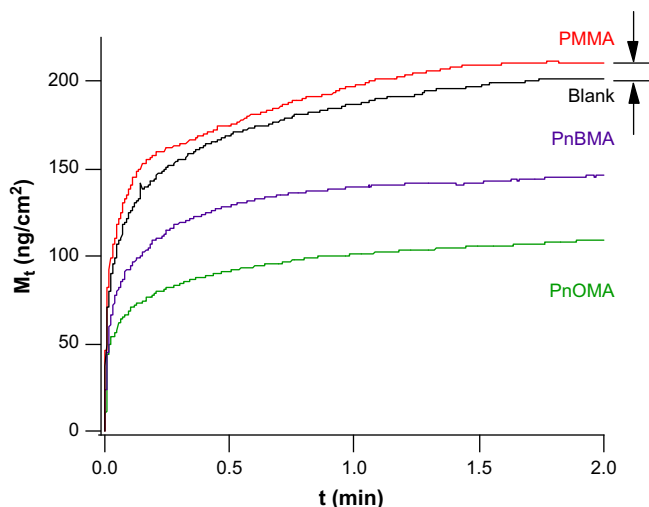


Fig. 2. Equilibrium moisture uptake into thin films of PMMA (11 nm), PnBMA (12 nm) and PnOMA (11 nm) supported on chromium coated quartz crystals.

of the PAMAs decrease from PMMA to PnBMA and PnOMA. The modulus is an indicator of the molecular mobility of the polymer. Thus, a decrease in modulus with increasing alkyl chain length is attributed to increased molecular mobility and the ability to vary molecular conformations at the interface. As the role of polymer chemistry on the interfacial moisture is minimal, these results suggest the importance of polymer rheological properties on the accumulation of moisture at a buried interface.

Additional information can be obtained by examining the thickness dependence of the moisture uptake as shown in Fig. 3. For the PMMA films, extrapolation of the uptake to zero thickness agrees reasonably well with the blank crystal, but appears depressed to a small extent (films less than 10 nm exhibit some deviation). From the slope of the thickness dependence of the sorption, the 'bulk' solubility of the film is estimated to be approximately 3.4% water at saturation for PMMA. This is consistent with measurements of water solubility in PMMA films using neutron reflectivity [23]. More interestingly, PMMA films on sapphire show strong coupling between the inorganic oxide and the ester groups of

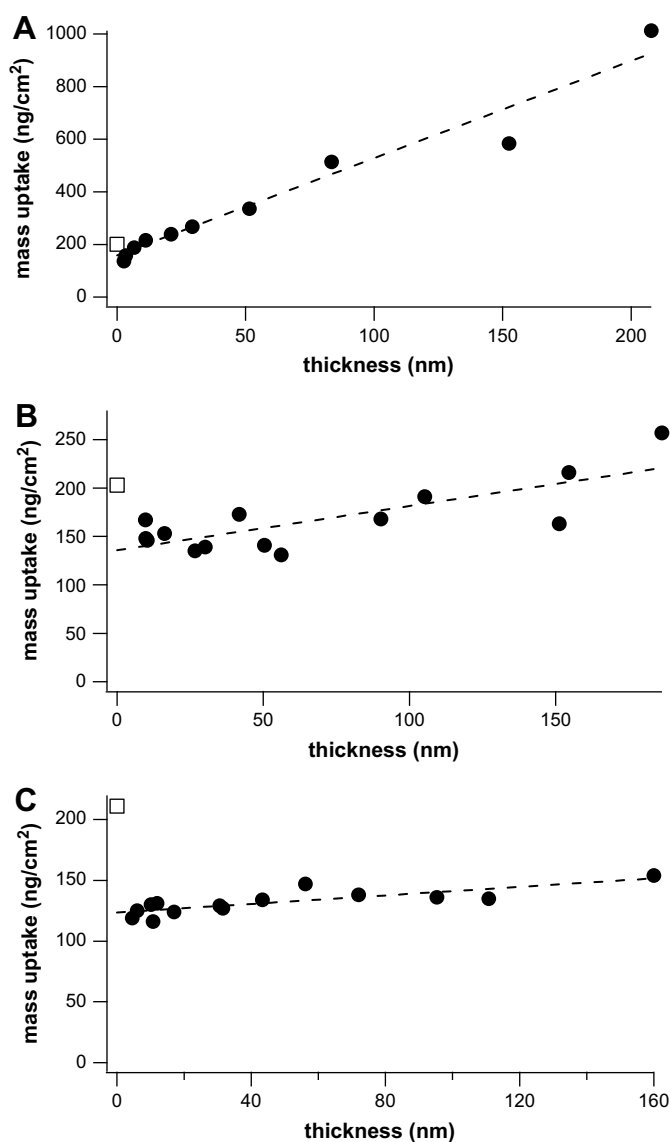


Fig. 3. Moisture uptake into thin films of (A) PMMA, (B) PnBMA, and (C) PnOMA films supported on chromium coated quartz crystals. (□) corresponds to the adsorption on the blank crystal. The dashed lines are linear fits to the data.

the methacrylate from infrared-invisible sum frequency generation (SFG) measurements [24]. This result illustrates the strong chemisorption of the PMMA to many metal oxide surfaces. However, this strong interaction appears insufficient to significantly suppress moisture accumulation at the interface. Thus for glassy polymers, adsorption on a surface and the sorption at the interface between a polymer and the same surface is nearly equivalent. This simple correlation provides a facile route to understand environmental factors in polymer nanocomposites; previous measurements of the interfacial moisture content used neutron reflectivity and thus very smooth, flat interfaces were required for the studies. For most practical applications, the interface between the filler and the polymer will be quite rough; therefore, a measurement on these more realistic systems is extremely useful. Additionally, specific interactions between the polymer and the substrate such as hydrogen bonding are insufficient to significantly alter the equilibrium moisture accumulation at the interface as the correlation holds for PMMA and PHOSt, which both have potential for hydrogen bonding with surface hydroxyls. Additionally, the moisture distribution at a buried glassy polymer–silica interface is statistically independent of the polymer from neutron reflectivity measurements for PHOSt, poly(*t*-butoxycarboxystyrene) and silane [16,25].

However, a different result is observed for the PnBMA and PnOMA films. Extrapolation to zero thickness yields an uptake significantly less than that of the blank crystal surface. The difference between the blank crystal adsorption and extrapolated zero thickness sorption increases as the alkyl chain length is increased from butyl to octyl. Thus, it appears that rubbery polymers suppress the accumulation of moisture at interfaces and this effect appears to be associated with the polymer modulus and/or chain mobility as the total accumulation at the interface decreases from PMMA to PnBMA to PnOMA. This decreased accumulation has implications in adhesion science where moisture is known to degrade performance [26]. A previous SFG study showed that surfaces of polymethacrylates with varying alkyl chain lengths behave differently in water [31]. In air, the methyl groups in ester chain of PnBMA and PnOMA tend to tilt more towards the surface normal; in water while the ester methyl group of PnBMA lies closer to the surface, the backbone movement of PnOMA would randomize the surface groups. However, such surface restructuring is absent at the PMMA surface. Note that there is a potential constraint effect at the polymer/substrate interfaces but the relatively unrestricted molecular movement in the low- T_g polymers (PnBMA and PnOMA) promotes molecular arrangement towards a thermodynamically stable molecular conformation such that the hydrophobic alkyl chains are closer to the interface. These results may explain why rubbery polymers are able to suppress the accumulation of moisture at interface and thus, are more resilient to moisture-induced failure [27]. The differences in the quantity of water at the interface are quite dramatic between the polymers, but these indirect measures of the interfacial moisture do not provide a direct measure of the distribution of moisture at the interface especially as the uptake on the chromium oxide may include bulk adsorption into voids.

To elucidate the interfacial moisture distribution in these different polymers, neutron reflectivity measurements were performed using thin films of the each poly(alkyl methacrylate) on a silicon wafer with a nominal 15 nm thermal oxide. The oxide layer enables the moisture at the interface to be quantified more easily, as was also the case for alumina surfaces [28]. One issue is the intrinsic roughness of the thermal oxide, which leads to a maximum in the moisture concentration near the interface as water is sorbed into the polymer coating, but not the silicon oxide. It is important to note that the preparation method for the silicon oxide coating is extremely important to the interactions of moisture within the oxide layer itself [29]. Fig. 4 presents the reflectivity curves for PMMA, PnBMA and PnOMA films before

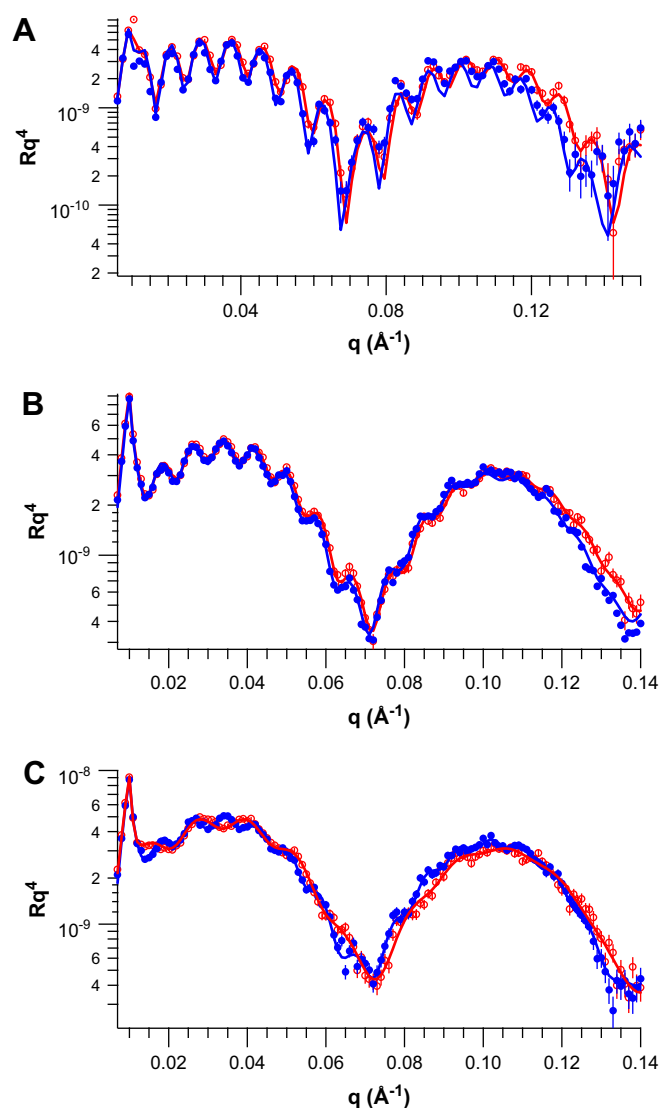


Fig. 4. Neutron reflectivity of (a) PMMA, (b) PnBMA, and (c) PnOMA film before (○) and after (●) exposure to 0.019 bar of D₂O vapor. The solid lines are the recursive fits of the data to a multilayer model using the Parratt formalism.

(red) and after (blue) exposure to D₂O vapor pressure of 0.019 bar. There are two distinct beating patterns in the reflectivity; the long period is a result of the thermal oxide thickness (≈ 15 nm), while the short period oscillations are from the combined polymer and thermal oxide thickness. One feature in these curves is a shift in the minimum associated with the nominal 15 nm thermal oxide layer to lower q ; this corresponds to an apparent increase in the thickness of this layer due to the accumulation of the high scattering length density D₂O at the interface as the scattering length density of the silica is intermediate to the D₂O and polymer. The extent of this shift is strongly dependent upon the polymer coating on the silicon oxide. The shift decreases as the alkyl chain in the methacrylate polymer is increased in length from methyl to butyl to octyl. This change is consistent with the extrapolated accumulation at the interface from the QCM uptake studies.

The real space D₂O concentration profiles through the film are calculated from the change in the scattering length density profiles between the dry and wet states. There are three components whose concentration must be determined. First, the concentration of the SiO₂ (from the finite roughness of the interface) as a function of distance into the poly(alkyl methacrylate) (PAMA) film was determined for the dry state as follows:

$$\phi_{\text{SiO}_2}(x) = \frac{Q_c^2(x) - Q_{c,\text{PAMA}}^2}{Q_{c,\text{SiO}_2}^2 - Q_{c,\text{PAMA}}^2} \quad (2)$$

where $Q_c^2(x)$ is the scattering length density at position x in the film, Q_{c,SiO_2}^2 is the scattering length density of the pure SiO_2 and $Q_{c,\text{PAMA}}^2$ is the scattering length density of pure PAMA, which is dependent upon the polymer being examined. With the assumption that the SiO_2 is immobile and impervious to D_2O (based upon negligible porosity), the water concentration profile is calculated as:

$$\phi_w(x) = \frac{Q_c^2(x) - (1 - \phi_{\text{SiO}_2}(x))Q_{c,\text{PAMA}}^2 - \phi_{\text{SiO}_2}(x) \cdot Q_{c,\text{SiO}_2}^2}{Q_{c,\text{D}_2\text{O}}^2 - Q_{c,\text{PAMA}}^2} \quad (3)$$

where $\phi_w(x)$ is the water concentration at position x in the film and $Q_{c,\text{D}_2\text{O}}^2$ is the scattering length density for pure D_2O . The extracted water concentration profiles near the interface are illustrated in Fig. 5. The interfacial water concentration decreases as expected from the sorption measurements in the series of thin films for the different polymethacrylates shown in Fig. 4. The modulus of the polymer decreases as the alkyl chain length is increased as discussed previously. Unlike the prior studies on varying the hydrophilicity of the polymer, which showed no dependence on the water content at a polymer/silicon oxide interface [16], the modulus of the polymer coating does impact the moisture content at interfaces. Additionally as an aside, the interfacial moisture content reported here for the PMMA film is less than found for glassy polymers–native oxide interfaces. First, the D_2O vapor was not at saturation in this case, which will decrease the interfacial concentration. However, this does not appear to fully account for the discrepancy between these samples. The thickness of the oxide layer between this study and prior reports using native oxide varies by an order of magnitude, thus the Hamacker constant will also be significantly altered [30]. This change appears to impact the distribution of D_2O at the polymer–silicon oxide interface. As the surface chemistry plays a significant role in the accumulation of moisture at buried polymer interfaces, we suspect that surface forces are also important in determining the equilibrium concentration at the interface.

One key observation from this study is that the interfacial moisture content for glassy polymers can be estimated from the

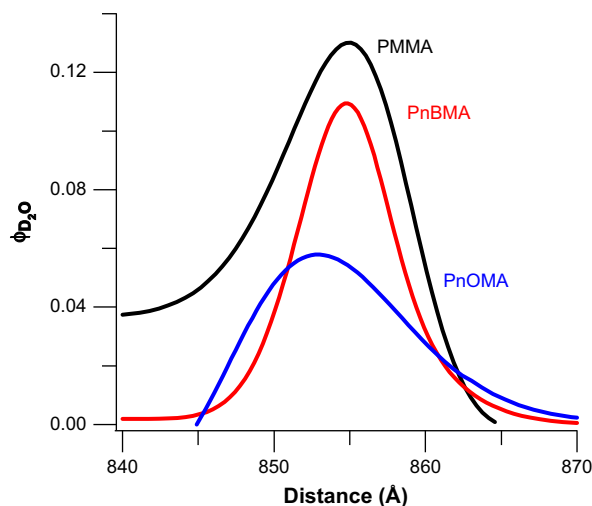


Fig. 5. D_2O concentration profiles obtained from the fit of the neutron reflectivity data. The accumulation of moisture at the interface is depressed as the alkyl chain length is increased from methyl to butyl to octyl. The maximum concentration at the interface between the thermal oxide and PnOMA is less than 50% that found for an identical oxide with a PMMA coating.

adsorption of water onto the analogous bare support surface. It is important to note that there may be some limitations to this generalization that the moisture adsorbed on the surface is identical to the interfacial concentration when coated with a glassy polymer. First from film thickness studies, the interfacial water concentration can exceed the adsorption at the free surface if the polymer is more hydrophilic than the surface [22]. Thus, interfacial depletion cannot be accurately predicted with this correlation. However, many cases exist where water is more strongly attracted to the filler than the polymeric matrix. Additionally, intrinsic porosity within the oxide itself must be considered if this is extended to other systems.

4. Conclusions

The impact of the polymer modulus/chain mobility on the distribution and accumulation of moisture near the buried interface of supported polymer films was systematically examined using a series of poly(*n*-alkyl methacrylates). For glassy polymers, the water at the interface can be accurately estimated from the adsorption of moisture onto the bare support. This provides a simple method of estimating the interfacial contribution to total sorption in polymer nanocomposites, which could be useful for understanding the performance of these materials for membrane separations. However for rubbery polymers, the interfacial moisture content is significantly suppressed in comparison to the adsorption on the bare substrate.

Acknowledgements

This work was partially supported by the National Science Foundation (CMMI-0653989). AK acknowledges the Fulton Undergraduate Research Initiative (FURI) at ASU and Science Foundation Arizona (SFAz) for providing financial support.

References

- [1] Alexandre M, Dubois P. *Materials Science & Engineering R-Reports* 2000;28:1–63.
- [2] Thostenson ET, Li CY, Chou TW. *Composites Science and Technology* 2005; 65:491–516.
- [3] Vaia RA, Giannelis EP. *MRS Bulletin* 2001;26:394–401.
- [4] Giannelis EP. *Advanced Materials* 1996;8:29.
- [5] Balazs AC, Emrick T, Russell TP. *Science* 2006;314:1107–10.
- [6] Merkel TC, Freeman BD, Spontak RJ, He Z, Pinnau I, Meakin P, et al. *Science* 2002;296:519–22.
- [7] O'Brien EP, White CC, Vogt BD. *Advanced Engineering Materials* 2006;8:114–8.
- [8] Bansal A, Yang HC, Li CZ, Cho KW, Benicewicz BC, Kumar SK, et al. *Nature Materials* 2005;4:693–8.
- [9] Rittigstein P, Priestley RD, Broadbelt LJ, Torkelson JM. *Nature Materials* 2007;6:278–82.
- [10] Priestley RD, Rittigstein P, Broadbelt LJ, Fukao K, Torkelson JM. *Journal of Physics-Condensed Matter* 2007;19.
- [11] Sen S, Xie Y, Bansal A, Yang H, Cho K, Schadler LS, et al. *European Physical Journal-Special Topics* 2007;141:161–5.
- [12] Kent MS, Smith GS, Baker SM, Nyitray A, Browning J, Moore G. *Journal of Materials Science* 1996;31:927–37.
- [13] Wu WL, Orts WJ, Majkrzak CJ, Hunston DL. *Polymer Engineering and Science* 1995;35:1000–4.
- [14] Gallagher PD, Satija SK, Karim A, Douglas JF, Fetters LJ. *Journal of Polymer Science Part B Polymer Physics* 2004;42:4126–31.
- [15] Nguyen T, Byrd E, Bentz D. *Journal of Adhesion* 1995;48:169–94.
- [16] Vogt BD, Soles CL, Jones RL, Wang C-Y, Lin EK, Wu W, et al. *Langmuir* 2004;20:5285–90.
- [17] Bent BE. *Chemical Reviews* 1996;96:1361–90.
- [18] Bhasin A, Little DN, Vasconcelos KL, Masad E. *Transportation Research Record* 2007;37–45.
- [19] Miki H, Noguchi M, Yokogawa K, Kim BW, Asada K, Sugano T. *IEEE Transactions on Electron Devices* 1988;35:2245–52.
- [20] Sauerbrey G. *Zeitschrift fur Physik* 1959;155:206.
- [21] Vogt BD, Soles CL, Lee H-J, Lin EK, Wu WL. *Langmuir* 2004;20:1453–8.
- [22] Vogt BD, Soles CL, Lee H-J, Lin EK, Wu W. *Polymer* 2005;46:1635–42.
- [23] Tan KT, Vogt BD, White CC, Steffens KL, Goldman J, Satija SK, et al. *Langmuir* 2008;24:9189–93.

- [24] Rao A, Rangwalla H, Varshney V, Dhinojwala A. *Langmuir* 2004;20:7183–8.
- [25] Kent MS, McNamara WF, Fein DB, Domeier LA, Wong APY. *Journal of Adhesion* 1999;69:121–38.
- [26] Buchwalter SL, Brofman PJ, Feger C, Gaynes MA, Lee KW, Matienzo LJ, et al. *IBM Journal of Research and Development* 2005;49:663–75.
- [27] Brown HR. *Annual Review of Materials Science* 1991;21:463–89.
- [28] Vogt BD, Prabhu VM, Soles CL, Satija SK, Lin EK, Wu W. *Langmuir* 2005;21:2460–4.
- [29] Iler RK. *The chemistry of silica: solubility, polymerization, colloid and surface properties and biochemistry*. Wiley Interscience; 1979.
- [30] Israelachvili J. *Intermolecular and surface forces*. London: Academic Press; 1992.
- [31] Wang J, Woodcock SE, Buck SM, Chen C, Chen Z. *Journal of American Chemical Society* 2001;123:9470–1.