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Abstract

This is the final report of a three-year, Laboratory-Directed Research and Development (LDRD) project at the Los Alamos National Laboratory (LANL). This project addresses fundamental questions concerning the behavior of polymers at interfaces: (1) What processes control the formation of an adsorbed layer on a clean surface? (2) What processes control the displacement of preadsorbed polymers? (3) Can one accurately predict the structure of polymer layers? To answer these questions, using neutron reflectivity, we have studied adsorbed layers of the polymer poly(methyl methacrylate) (PMMA) onto a quartz substrate. The polymer density profiles were derived from the neutron reflectivity data. We have shown that dry films exhibit behavior predicted by mean-field theory in that the equilibrated layer thickness scales with the molecular weight of the polymer. Also, we find that the profiles of the polymers in solution qualitatively agree with those predicted by reflected random walk (RRW) theories, yet the profiles are not in quantitative agreement.

Background and Research Objectives

Polymers are long chain-like molecules composed of repeated basic units called monomers. Polymers physi-sorb from a melted or glassy state so strongly onto solids that the attachment often seems irreversible. This strong binding is a result of the large number of direct segmental contacts per polymer chain that makes the energetic penalty per chain for desorption very high. This interaction affects a number of practical, industrial applications involving contact between polymer melts and solid surfaces, including melt processing and composite fabrication. In the case of melt processing one would like to minimize the amount of polymer sticking to molds, but in the case of composite materials it is quite desirable to have the bonding between the polymer and graphite, for example, be very strong. In spite of

this practical importance of polymer melts, the majority of experimental work cited in the literature focuses on adsorption of polymers from dilute solutions; there are relatively few basic studies of adsorption from melts or even concentrated solutions. In this work, we characterize the structure of layers adsorbed strongly from a melt onto smooth, flat solid substrates under well-controlled contacting conditions. Once we have measured this structure, we then compare our results to the appropriate theoretical predictions.

Importance to LANL's Science and Technology Base and National R&D Needs

One of the core competencies of the laboratory is Nuclear and Advanced Materials. Topics that fall under that category include process technology and chemical and physical characterization. This project is aimed at understanding polymers at interfaces. This directly relates to process technology in that the binding or sticking of polymers to interfaces during molding can be problematic in industrial applications. Likewise, when composite materials are made from polymers, the adhesion between the polymer and strengthening material (such as graphite fibers) is essential to forming a material with the desired properties.

Furthermore, using neutron reflectometry to study polymers at interfaces is at the forefront of methods for characterization of soft condensed matter including polymers. The neutron scattering facility at LANSCE is one of only two pulsed-spallation sources in the United States. This technique is unique in its ability to discern differences in structures in polymer mixtures at interfaces with a resolution of a few Angstroms.

Scientific Approach and Accomplishments

The equilibrium structure of a polymer melt at an inert, solid wall has been studied theoretically by applying mean-field methods. DeGennes (1) examined a single polymer chain with N monomer segments in a melt against a flat, impenetrable wall by a self-consistent field method. He showed that the wall's effect on the polymer is screened beyond distances of order of the size of a single monomer. This has simple consequences. For example, at equilibrium, an adsorbed chain with N monomers makes on the order of $N^{1/2}$ contacts with the surface.

Further theoretical studies of a melt at an interface were performed by Guiselin (2). For an equilibrated melt against an inert solid wall, Guiselin imagined suddenly fixing those

$N^{1/2}$ contacting polymer segments which were in contact with the wall. He showed theoretically that after removal of the unbound polymeric material, and swelling of the residual bound polymer layer in a good solvent for the polymer, a brush-like structure results with a height $h_{\text{swollen}} \sim N^{5/6}$. Guiselin went on to show that the density profile of the monomers takes on the functional form $\phi(z) \sim z^{-2/5}$, where z denotes the distance away from the surface. In addition, it was shown that the height of this same film when dried (i.e. when the solvent is removed) $h_{\text{dry}} \sim N^{1/2}$.

Both of the theories just noted, describe systems which have reached equilibrium. However, due to energetic considerations, it may take some time after initial contact with a melt before the system comes to equilibrium. In that case it may be possible to follow the progression of the polymer structure from initial contact to final equilibrium. In our studies, we have designed experiments to study both the non-equilibrium and the steady state cases.

The samples were prepared by dissolving PMMA in benzene, a good solvent for this particular polymer. Several solutions were made where PMMA with a different molecular weights was dissolved. Flat polymer films were then produced by spin coating the PMMA from the benzene solution onto flat quartz substrates. These films were ~ 1 micron in thickness. Then, the films were annealed for times ranging from 0 hours to 120 hours. The temperature chosen for the annealing was 165C which is above the melting point for the polymer. After annealing, the samples were rinsed several times to remove the excess, unbound polymer. The samples were then measured using neutron reflectometry (3).

The neutron reflectivity of a surface is defined as the ratio of the number of neutrons elastically and specularly reflected to the number of incident neutrons. When measured as a function of neutron wave vector transfer (or incident neutron energy), the reflectivity curve contains information regarding the profile of the in-plane average of the scattering length density (or simply scattering density) normal to that surface. The concentration of a given atomic species at a particular depth can then be inferred. Although similar information can be extracted from x-ray reflectivity data, an additional sensitivity is gained by using neutrons in those cases where elements with nearly the same number of electrons or different isotopes (especially hydrogen and deuterium) need to be distinguished. These properties make neutron reflectivity a powerful tool for the study of interfaces. In the simplest case, this technique yields both the layer thickness and the density profile.

Using neutron reflectivity, we could examine the non-equilibrium behavior of the films as a function of annealing time and check the scaling behavior of the dry films once an equilibrium state had been achieved. In some of the films which had reached a steady state structure, the samples were immersed in a good solvent and the reflectivity measurements were repeated to examine Guiselin's theory for the expected structure in solution.

Figure 1 shows the results of the annealing experiments for PMMA of molecular weight $M=345,000$ and $M=70,000$. Plotted is the layer thickness, h_{dry} , versus the annealing time for these two molecular weights. For both molecular weights, a very thin layer $\sim 10 \text{ \AA}$ thick, results from spin-casting and then rinsing the sample with benzene without subsequent annealing. In this situation one expects that a large number of possible absorption sites are not immediately covered with polymer upon initial contact. Subsequent collapse of the initially formed polymer loops onto the surface upon annealing allow the surface to obtain full coverage. Figure 1 may be fit to obtain the times scales for equilibration, $\tau_{\text{eq}} \sim M^{0.9}$.

Using the final thickness for several samples with molecular weights ranging from 13,000 to 1,200,000 we can test the data for agreement with Guiselin's theory for h_{dry} . Figure 2 shows a log-log plot of h_{dry} versus the degree of polymerization, N . In the range of $250 = N = 2160$ (ie. $25000 = M = 216000$ since each monomer has a molecular weight ~ 100) a regression analysis to the data give $h_{\text{dry}} \sim N^{0.47 \pm 0.05}$. In this range the data agree with the prediction $h_{\text{dry}} \sim N^{1/2}$. Figure 2 also indicates failure of the model for the lowest and highest molecular weight samples. For the highest molecular weight the reason is that the annealing time was too short for this sample. For the low molecular weight sample, the density at the surface as measured with neutron reflectivity is very low. This suggests that the film is patchy and only partially covers the surface. In that case, one would not expect the theory to apply.

Finally, we discuss the experiments designed to directly interrogate the structure of the immobilized melt layer swollen in a good solvent. Recall that in the case of an equilibrated melt, Guiselin's theory gives the polymer density profile $\phi(z) \sim z^{-2/5}$. Fits to the neutron reflectivity data where the polymer film is in contact with a good solvent qualitatively fit this model, but not quantitatively. Although a power law may be used to fit the data, the exponent found in these experiments is closer to $4/5$ than $2/5$. This is consistent

with not achieving full equilibrium in the annealing step. However, since the scaling law for the dry films is consistent with this same theory it is not totally clear that this is the case.

This work has shown for the first time in detail how the structure of a polymer film adsorbed from the melt evolves as it approaches equilibrium. Also, we have devised a set of experiments to test the Guiselin theory for both dry and swollen films. Further work on non-equilibrium polymer systems is in progress to examine how polymers exchange with one another after adsorption of a thin bound film. Further details of this work may be found in the publication below.

Publications

- [1.] Durning C.J., O'Shaughnessy B., Sawhney U., Nguyen D., Majewski J., and. Smith G.S, "Irreversible Adsorption of Poly(Methyl Methacrylate) Melts on Quartz," submitted to *Macromolecules*, Nov. 1988.

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- [1] deGennes P.G., "Conformations of Polymers Attached to an Interface," *Macromolecules*, 13(#5) pp. 1069-1075 1980
- [2] Guiselin O., "Irreversible Adsorption of a Concentrated Polymer Solution," *Europhys. Lett.*, **17**(3), 225(1992).
- [3] Smith G.S. and Majkrzak C.F., "Neutron Reflectometry," To be published in the International Tables for Crystallography, Volume C: Mathematical, Physical and Chemical Tables - second edition, Editors: E. Prince and A. J. C. Wilson.

Figure Captions

Figure 1: Dry residual adsorbed layer thickness, h_{dry} , versus annealing time. $M=345,00$ (circles); $M=70,000$ (triangles). The lines are exponential fits which gave time constants of 90 hours and 22 hours for $M=345,00$ and $70,000$, respectively.

Figure 2: Log-log plot of the dry residual layer height, h_{dry} , versus degree of polymerization (number of monomers), N , for samples annealed for long times. The dashed line is a regression result of the data with hollow symbols and has a slope of $0.47 \pm .05$.

Figure 1

Figure 2