polymer communications

The density profile at a polymer/solid interface

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The density of an amorphous polymer near its interface with a flat solid surface was investigated using neutron reflectometry. Bulk poly(methyl methacrylate) with a monodisperse molecular weight in contact with a silicon single crystal wafer was the first system studied, and the emphasis was placed on the temperature dependence of the interface density profile. The temperature range studied encompassed the glass transition temperature of the polymer and a reversible change in the density profile was discovered.

(Keywords: density profile; interface; neutron reflectometry)

Introduction

Adhesion, durability and many other important features of an interface between a polymer and a solid surface depend strongly on the conformations of the polymer molecules in the interface region. Of particular interest is the first few tens of nanometres away from the solid surface. Lack of knowledge in this area makes fibre matrix interface strength one of the most elusive factors in controlling the performance of polymer matrix composites. The quality of protective polymer coatings is one of many other questions where an improved knowledge of the interface would be highly beneficial.

Considerable theoretical efforts in predicting the polymer density and chain conformation near a surface have been made in recent years[1-10]. However, experimental data in this area are still sparse. In this communication, the results of the first part of a series of experiments probing polymer/solid interfaces are reported.

For polymers with monodispersed molecular weight the molecules near a flat surface will deviate from a Gaussian coil configuration if the space filling requirement is satisfied. Qualitatively, one can easily envisage that these molecules must be distorted such that their dimension perpendicular to the surface, hereafter referred to as the z axis, must be decreased from that of the Gaussian coil; the dimensions along the interface (the x–y plane) must be increased. In other words, the chains near the interface flatten out to resemble a pancake. Recent results from theoretical calculations indeed support the above notion of chain distortion[1,2,10]. The segment density of the bulk, not of individual chains, must be determined by the balance of the loss in entropy due to the chain distortion and the cohesive enthalpy as well as the adhesive enthalpy between the polymer and the substrate. In addition, at nanometre scale polymer segments can no longer be considered as flexible thin threads, instead semi-rigid rods are a better model. The local packing of these semi-rigid rods near a flat surface is another factor that could affect the polymer density near a flat surface. It is the objective of this work to probe the polymer density near a flat surface and its temperature dependence from the analysis of neutron reflectivity measurements.

Experimental

Materials. Deuterated poly(methyl methacrylate) (PMMA) with a polydispersity of 1.10 and a number-average molecular weight of 135000 was synthesized via a group transfer polymerization method. The polymer is ~57% syndiotactic, 37% atactic and 6% isotactic. The glass transition temperature (T_g) was found to be 115°C as determined by d.s.c.

A silicon single crystal wafer with a (1 0 0) surface was used as the substrate. The neutron reflectivity result from the silicon/air surface indicated a roughness of 4 Å root mean square. A PMMA film (0.5 mm thick) was prepared in vacuum at 150°C in direct contact with the polished surface of the wafer. This polymer/silicon sample was then placed between two spring-loaded aluminium plates in contact with a heating block. A steel ring (0.5 mm thick) was placed around the PMMA film while sandwiched between the two aluminium plates. The sample assembly was in its vertical position during the neutron measurements. Both the incident and the reflected neutrons passed through the sides of the silicon crystal. All the neutron measurements were performed in a vacuum of 1.33×10^{-2} Pa. The sample temperature was measured via a thermocouple placed within the aluminium block contacting the polymer, and the distance between the probe and the polymer was < 1 mm.

Reflectivity measurements. The BT-7 reflectometer at the reactor of the National Institute of Standards and Technology was used for all the measurements. A graphite monochromator was used to select neutrons of

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wavelength $\lambda = 2.35$ Å with width $\Delta\lambda/\lambda \cong 0.01$. Slit collimators reduced the incident beam divergence to ~0.016°. The detector acceptance angle was set at ~0.075° for the reflectivity (the specular component) measurements and ~0.012° for the transverse scan[11] (the off-specular component).

Results and discussion

The PMMA film will detach from the substrate once the temperature falls below 80°C, presumably due to the build-up of thermal stress. Hence the lowest temperature used in this work was >80°C. The highest test temperature was limited to 144°C to avoid thermal degradation even though the thermal stability of PMMA synthesized via the group transfer method exceeds by far that obtained for free radical polymerized PMMA in which degradation begins around 150°C.

The reflectivity results at six different temperatures were fitted with theoretical models of the density profile using a matrix method calculation[5,12]. Two variables were allowed, one being the square of the critical angle in Q (Q_c^2, in Å^{-1}), which is linearly proportional to the polymer density away from the interface, the other being the width of the interface region. An error function profile was assumed. Q is the magnitude of the wavevector transfer between the reflected (or scattered) beam and the incident beam. More explicitly, $Q_c^2 = 16\pi N\bar{b}$ where N is the number density and $\bar{b}$ the average scattering length. The fitted results are listed in *Table 1*.

Figures 1a, b and *c* show both the measured and the theoretically fitted reflectivity results using a matrix method[5] at 92.6, 117.8 and 144.0°C, respectively. The fit between the experiment and the calculation is very good. Attempts were made to include other possible detailed features of the interface, e.g. an oxide layer between the polymer and the wafer, a maximum in the polymer density near the interface as predicted by some molecular mechanics calculations[1,2]. However, the experimental results did not require the inclusion of any additional fine interface structure to obtain a fit. This, however, does not preclude the existence of some fine interface structures.

The density profiles resulting from the fits for all six temperatures are given in *Figure 2*. The x-axis origin of each profile, or the location of the interface, was shifted by an arbitrary amount to highlight the changes in the profile shape with temperatures. The change from a step function to a gradual profile across the T_g (115°C) is clearly demonstrated in this figure. The other remarkable feature is the recovery of the step profile as the temperature was lowered back to 80.6°C. The transition from a step-like profile to a gradual profile took place between 101.1°C and 117.8°C. More measurements with finer temperature increments between these two temperatures are needed to locate the transition temperature more accurately and to determine the nature of the transition. The results given in both *Figure 2* and *Table 1* indicate that the width of the polymer/solid interface region increases with temperature. Measurements at higher temperatures are also needed to find out whether there is an upper limit for the interfacial width as the temperature is further raised. The current value of the transition width is far less than the radius of gyration of 99 Å calculated for a 135000 molecular weight[13] molecule. In other words, the transition region is within the first layer of molecules at the interface. It will be interesting to carry out additional experiments with different molecular weights to examine the possible relation between the molecular weight and the transition zone width. The width of the interface at temperatures below 80°C is similar to that of the silicon/air interface.

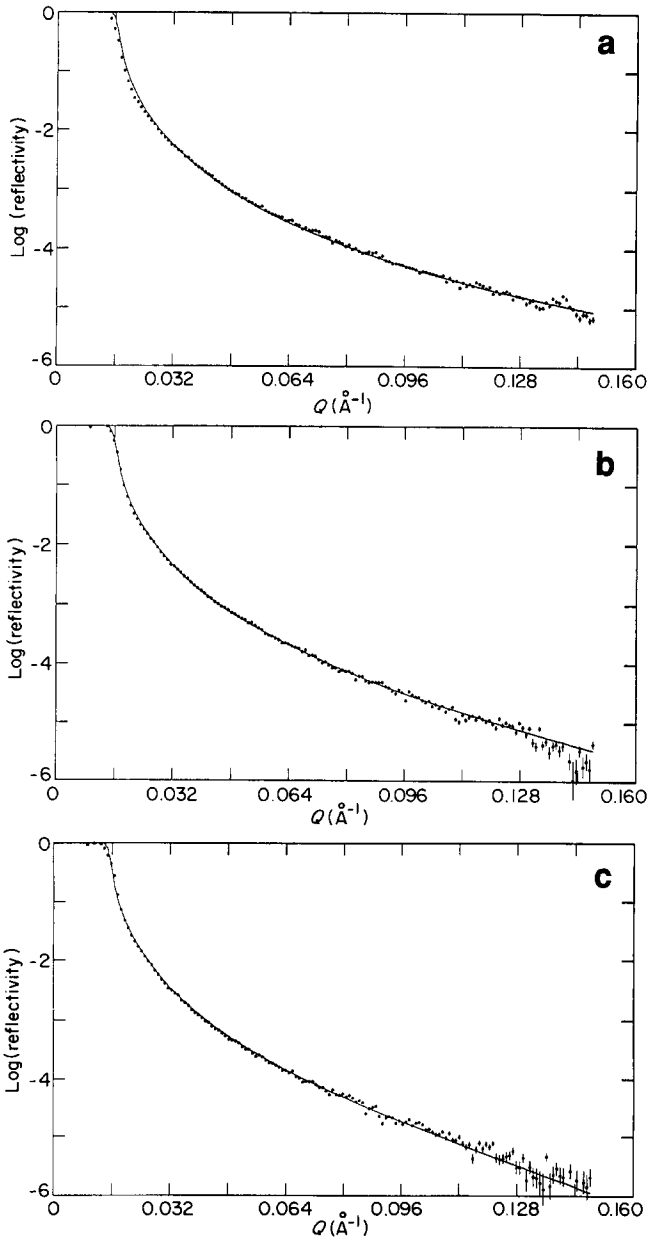

Figure 1 (a) Reflectivity curve from a deuterated PMMA/silicon interface at 92.6°C: (●) experimental points; (—) theoretical fit. (b) Same as (a) except the temperature was 117.8°C. (c) Same as (a) except the temperature was 144.0°C

Table 1 Curve fitting results for the PMMA/silicon interface

Temperature (°C)	Width (Å)	Q_c^2 (Å^{-2})	Density (g cm^{-3})[a]
92.6	3.06	3.688×10^{-4}	1.242 (1.170)
101.1	1.50	3.626×10^{-4}	1.221 (1.168)
117.8	14.61	3.503×10^{-4}	1.180 (1.164)
125.0	17.60	3.437×10^{-4}	1.157 (1.158)
144.0	21.00	3.283×10^{-4}	1.105 (1.147)
80.6	1.00	3.669×10^{-4}	1.235 (1.174)

[a]Measured polymer density with the calculated bulk density in parentheses

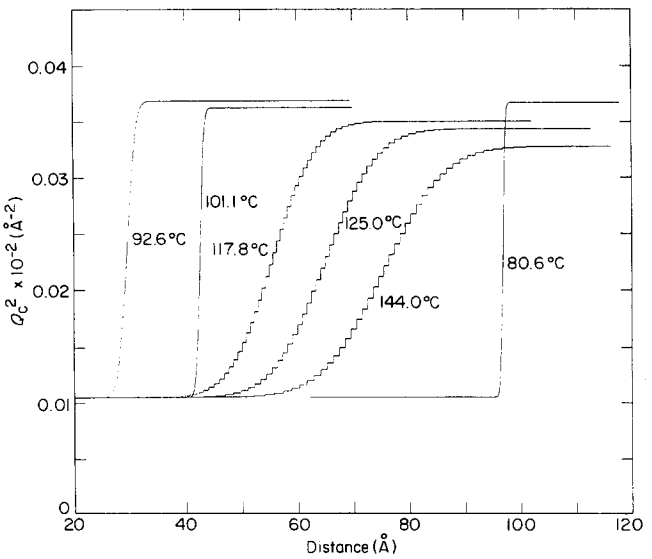

Figure 2 Density profiles of a deuterated PMMA/silicon interface at six different temperatures during a heating and subsequent cooling cycle. The origin of each profile on the x-axis, or the locations of the interface, was shifted by an arbitrary amount to illustrate the change in the profile shape. The ordinate is Q_c^2 and is linearly related to the local polymer density by a constant factor

The restoration of a step profile at cooling demonstrates that the transition is reversible. In addition, this observation also rules out the segregation of impurities or a low molecular weight fraction as a possible mechanism for the step-to-gradual profile transition, since it is highly improbable that the impurities of the lower molecular weight species, once migrated to the interface at high temperatures, will diffuse back toward the bulk upon cooling.

The measured polymer density calculated based on Q_c^2 is given in *Table 1*. The calculated bulk densities based on a literature value[13] of 1.188 g cm^{-3} at 25°C are also given. The thermal expansion coefficients of 2.6×10^{-4} and 5.8×10^{-4} for temperatures below and above T_g, respectively, were used for the density calculation. It seems that the measured densities at temperatures below 144°C are greater than the bulk values, whereas the value at 144°C is less than the calculated bulk value. However, the magnitude of the error in the measured density is large. The magnitude of the experimental error involved in the determination of Q_c^2, hence the asymptotic density values of *Table 1*, can be estimated as follows. The major source of experimental error is the sample position relative to the incident beam. Based on a conservative estimation this uncertainty in sample position can result in an uncertainty in Q of 0.001 Å^{-1}. By shifting the abscissa of the reflectivity results by ± 0.001 Å and by fitting the shifted data with the fitting routine, we find that the upper limit of the error in the density is $\pm 6\%$. Accordingly, the difference between the measured density deduced from Q_c^2 and the calculated bulk density is just within the range of experimental error. Therefore, further experiments with better resolution need to be done to confirm that the densities of PMMA near the surface at low temperatures are indeed higher than the bulk density calculated from the thermal expression.

The values of Q_c^2 just mentioned, or the asymptotic polymer density away from the interface in *Figure 2*, are determined by the position of the critical angle. The margin of error is within 6% as discussed. A much larger error is expected for the Q_c^2 in contact with the wafer. In *Figure 2* it is noticeable that the values of Q_c^2 in contact with the silicon wafer are exactly that of the wafer. This coincidence must be fortuitous since there is no obvious reason that the polymer density in contact with the silicon is so fine tuned that the neutron scattering length per unit volume matches that of the silicon wafer. This equality is likely a natural consequence of the fitting program used. One can take the value of Q_c^2 in contact with the wafer as a fitting parameter in addition to others. However the simplicity in the reflectivity curves (*Figures 1a–c*) does not warrant the use of more fitting parameters. This leads to a severe shortfall in the results given in *Figure 2*; the extent of polymer density depletion near the interface is largely undetermined. In other words, the neutron reflectivity results cannot provide a unique answer to the exact amount of the free volume near the interface. The fitting results reported herein are based on the simplest model, namely a one-layer model. This model itself may not be the correct one for the polymer/solid interface. However, the results especially regarding the change of the interface width with temperature must be qualitatively correct.

Specular reflectivity is only sensitive to density gradients perpendicular to the sample surface. In order to determine in-plane correlations, one must measure the scattering from wavevectors that have an off-specular component[11]. Typically, these off-specular or transverse scans are performed by changing the angle of incidence of the neutron beam onto the sample while keeping the exit angle fixed.

Transverse scans at all of the above temperatures were performed to examine the possible dependence of in-plane roughness on temperature. At each temperature the results were collected at $Q = 0.14$ and 0.23 Å^{-1}. Part of the data at $Q = 0.14$ Å^{-1} are given in *Figure 3*, and

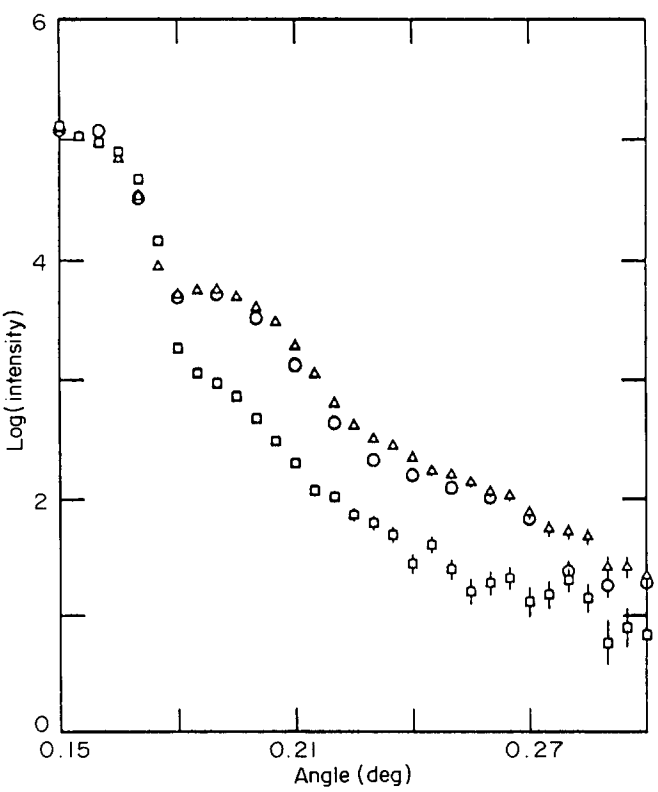

Figure 3 Results of a transverse scan from a deuterated PMMA/silicon interface at $Q = 0.014$ Å^{-1}: (○) 92.6°C; (△) 101.1°C; (□) 117.8°C

shows that the off-specular intensities decrease concurrently with the step to gradual profile transition along the z-axis. These off-specular results have not been treated quantitatively. Nevertheless, since the off-specular scattering decreases, the results of *Figure 3* suggest that the interface becomes smooth in the in-plane or $x-y$ directions as the interface thickness increases. This change of interface smoothness in the $x-y$ plane was also found to be reversible with temperature.

Conclusions

The neutron reflectivity results from a PMMA/silicon interface at six temperatures can be fitted with an error function profile normal to the interface. The fitted results indicate a transition in the interface density profile from an abrupt step to a more gradual profile at temperatures close to the T_g of the polymer. This transition is found to be reversible with temperature. The off-specular results suggest that the polymer density along the in-plane directions gets smoother as the profile normal to the interface becomes more gradual.

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