Characterization of Local Elastic Modulus in Confined Polymer Films via AFM Indentation

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The properties of polymers near an interface are altered relative to their bulk value due both to chemical interaction and geometric confinement effects. For the past two decades, the dynamics of polymers in confined geometries (thin polymer film or nanocomposites with high-surface area particles) has been studied in detail, allowing progress to be made toward understanding the origin of the dynamic effects near interfaces. Observations of mechanical property enhancements in polymer nanocomposites have been attributed to similar origins. However, the existing measurement methods of these local mechanical properties have resulted in a variety of conflicting results on the change of mechanical properties of confined polymers. Here, an atomic force microscopy (AFM)-based method is demonstrated that directly measures the mechanical properties of polymers adjacent to a substrate with nanometer resolution. This method allows us to consistently observe the gradient in mechanical properties away from a substrate in various materials systems, and paves the way for a unified understanding of thermodynamic and mechanical response of polymers. This gradient is both longer (up to 170 nm) and of higher magnitude (50% increase) than expected from prior results. Through the use of this technique, we will be better able to understand how to design polymer nanocomposites and polymeric structures at the smallest length scale, which affects the fields of structures, electronics, and healthcare.

1. Introduction

The properties of polymers near an interface are altered relative to their bulk value due both to chemical interaction and geometric confinement effects. For the past two decades, the dynamics of polymers in confined geometries (thin polymer film or nanocomposites with high-surface area particles) has been studied in detail, allowing progress to be made toward understanding the origin of dynamic effects near interfaces. Observations of mechanical property enhancements in polymer nanocomposites have been attributed to similar origins. However, the measurement methods of these local mechanical properties have resulted in a variety of conflicting results on the change of mechanical properties of confined polymers.

It has been widely reported that adding small amounts of nanoparticles to polymers results in dramatic changes in physical properties, ranging from thermal stability to diffusion to stiffness and strength. For example, where the nanofillers comprise less than 5% of the nanocomposites, the modulus enhancement can reach up to 80%. Such a significant increase in properties cannot be explained by linear property combination of polymer matrix and nanofillers. The results are thus attributed to “interphase polymer” with enhanced properties due to chemical and geometric confinement of polymer chains near the nanoparticle–polymer interfaces. While quantitative evidence of the existence of such a domain of polymers for the dynamic properties ($T_g$) has been...
reported,[1,10–15] similar data have been relatively lacking for mechanical properties of interphase polymer.[16] In the design of nanocomposites and structures, the information about the intensity and thickness of interphase layer is essential, yet in many cases, such information is unavailable for the specific material systems.[17] which indicates the demand of a consistent and simple method that can be applied to any given material system for the characterization of interphase properties.

In the last two decades, the study of confined polymer interphase suggested large deviation of properties for the glass transition temperature ($T_g$).[1,2,10–15,18–21] Utilizing fluorescence dye-label measurements, it has been observed by Torkelson and co-workers[1,10–12] that the different interaction mechanisms between confined polymer films and inorganic substrates lead to the shifting of $T_g$ in different directions and degrees. For example, when poly(methyl methacrylate) (PMMA) is combined with a silica substrate, the local $T_g$ in ultrathin films increased slightly; however, when polystyrene (PS) thin films were supported on the same silica substrate, a significant $T_g$ decrease was observed. It is believed that the increased $T_g$ in PMMA/silica system is largely due to hydrogen bonding between the hydroxyl groups of PMMA chains and silica surface, which lead to the loss of mobility of polymer molecules in interphase region (Figure 1). However in PS thin films, the absence of hydrogen bonding opens an opportunity for the free surface, where the $T_g$ drops due to increased chain freedom, to play the dominant role in the overall $T_g$ change of the entire film. The study of local $T_g$ change made the concept of interphase widely accepted, and also suggested the possibility to study other local physical properties in a similar manner.

![Figure 1. Mechanisms of interphase: PMMA chains attached substrate via stronger hydrogen bonding (denoted by “—”) and weaker van der Waal’s Forces (denoted by “—”).](image)

To date, there are several methods have been proposed to investigate mechanical property distribution near polymer interfaces, those methods include indirect methods, such as Brillouin light scattering (BLS),[22] film buckling,[23] and bubble measurements of biaxial creep via AFM topography tests,[24] as well as direct measurement, such as AFM indentation and nanoindentation,[25–31] where sometimes conflicting conclusions were derived. The thickness of the interphase domain has been reported to have a wide range of values, from several nanometers to hundreds of nanometers in different material systems.[16,32–36] And in thin polymer films, some methods suggested strongly increased modulus, while others showed decreased modulus. The mechanisms causing the interphase, its extent, and magnitude of property changes imparted is still an open discussion in the literature. Thus, new experimental methods and simulation techniques are needed to address this issue of fundamental concern in polymer physics.

In the effort to measure the gradient of modulus change in interphase, a nanoindentation-based method was recently developed by Watcharotone et al.[9] to quantitatively measure local interphase properties. The method performed nanoindentation on top of thin glassy polymer films (perpendicular to the substrate) with a series of different film thickness ranging from 300 nm to 1 μm. Modulus enhancement of up to two times of bulk polymer value was reported on the thinnest films. The nanoindentation method provides promising insight into the increased modulus in interphase polymer, but at the same time, interpretation of the data is a challenge and quantitative results on the modulus gradient as a function of distance from interface are not possible. In cases that mechanical properties on interphase inside smaller spatial regions are desired, AFM indentation is an ideal method to conduct the study[29,30] due to the nanometer level probe size. In addition to topography information, AFM instrumentation is able to provide local elastic properties,[15,25,27,28] and viscoelastic properties[31] in different polymer microdomains.[26] However, measurement of the local mechanical properties inside the polymer interphase near surfaces of stiff inorganic materials with nm resolution has not yet been published. In this paper, we present a new AFM-based methodology that is able to provide consistent and insightful information the local modulus change in the interphase directly, with minimum data interpretation.

## 2. Experimental Methods

### 2.1. Sample Preparation

Two sets of polymer/substrate systems were prepared for testing: PMMA on silica slides and PMMA on alumina plates. PMMA
The sample was made in sandwich form with silica or alumina substrate on the bottom, PMMA in the middle, and a 100 μm thick cover glass on the top. Substrates were ultrasonically cleaned in Acetone for 10 min, and fast dried. Small piles of PMMA powder were placed between two substrates and cover glass, and melted at 220 °C, then pressed under a small pressure (10–50 Mpa) to form the sandwich structure. After cooling, the samples were annealed at 135 °C (10 °C above \( T_g \)) for 24 h to release the internal stress caused by hot pressing.

2.2. AFM Indentations

In the nanoindentation approach, the entire polymer film from tip to substrate was probed in each test (Figure 2a), and only the effective modulus of the entire film can be extracted. By decreasing the film thickness, the interphase polymer takes higher volume fraction in the film. However, this method still remains an indirect measurement of interphase properties. To obtain a direct and quantitative method, here we section film/substrate samples and use an ultrafine AFM tip to probe parallel to the surface, resulting in data on the gradient of properties in the interphase directly (Figure 2b). The AFM tests were performed by running in PeakForce tapping mode. In this mode, the AFM tip used in this study is in conical shape, with radius of 10 nm. By taking the advantage of the small tip, the AFM is capable of performing numerous ultra-shallow indentations with indentation depth less than 5 nm in a compact area. The details of the experiments are described in methods section.

The surface modulus at the indentation point is derived from unloading curve by using the DMT model:[37,38]
\[ F = \frac{4}{3} \pi R d^3 + F_{\text{adh}} \]  

where \( F \) is the force on the tip, \( R \) is the tip radius, \( d \) is tip deflection, and \( F_{\text{adh}} \) is the adhesion force between tip and sample. In this equation, all of these variables are recorded during experiments, leaving the reduced modulus, \( E_r \), as the only unknown variable, which can be calculated by fitting the unloading curve using power function. From the reduced modulus, with the knowledge of tip modulus and Poisson’s ratio, the modulus of sample can be calculated using the following expression:

\[ E_s = \left( \frac{1 - \nu_{\text{sample}}^2}{E_{\text{sample}}} + \frac{1 - \nu_{\text{tip}}^2}{E_{\text{tip}}} \right)^{-1} \]  

The theoretical basis and effectiveness of AFM indentation on investigating Young’s modulus of soft materials have been widely discussed previously\(^{28,39–43}\) and it also has been used to successfully characterized the local mechanical properties change in micron-sized fiber reinforced composite materials\(^{30,44–46}\). Results from literature have demonstrated the ability of AFM indentation to accurately measure the polymers modulus in the magnitudes from tens of MPa to tens of GPa with spatial resolution as low as several nanometers.

The AFM used in this study is Bruker Dimension ICON with PeakForce QNM module installed. The samples were safely attached on a vertical holder by carbon tape. The sensitivity of silicon tip was first calibrated on alumina substrate, which is much harder than tip material. The AFM probe used in this study was Bruker TAP525 with 200 N m\(^{-1}\) spring constant and 10 nm tip radius. The resolution of image is 512 × 512 pixel, where each pixel corresponds to an independent indentation, with indentation depth around 3–5 nm. The loading and unloading curves for each indentation were automatically recorded by software. Modulus map as well as topography and adhesion maps were obtained simultaneously.

### 2.3. Ion Milling

However, the ability of AFM indentation to measure the local modulus on nanoscale level comes with the demand of an extremely smooth surface for testing. Due to the large discrepancy in stiffness of PMMA and the substrate, ordinary mechanical polishing is unable to create a sufficiently smooth surface for AFM modulus mapping. Broad beam ion milling was specifically designed to create a smooth surface over multiple domains with large stiffness difference. The instrument employed in this project is Leica EM TIC 3x, which uses three Argon ion beams to simultaneously polish an area up to 1 mm by 4 mm. A schematic of the ion milling set up and results for film sandwich sample are shown in Figure 2d, as well as the microscopy image and an AFM topography scan line of milled surface, demonstrating the extreme smoothness with less than 5 nm roughness over the range of 1 μm distance. The cover glass in the sandwich samples acts as a sacrifice layer to face the ion beam, and provide protection to PMMA films because the first 50 μm of material facing the ion beam is destroyed in the process (Figure 4d). The ion milling is performed in Leica TIC3X. It is first run at 5 kv for 3 h to quickly penetrate cover glass, and then the voltage is lowered to 4 kv for 5 h to finelly mill PMMA film and interphase. The milling temperature was set at −20 °C to safely eliminate any possible damage caused by overheating in milling process (see Section 1, Supporting Information). The hot-pressed samples were first fractured in the middle, and then mechanically polished to get a relatively smooth and straight edge on which ion milling can be performed.

### 3. Results and Discussion

The AFM indentation modulus mapping results of PMMA/silica interphase are shown in Figure 3a, including the 3D topography, adhesion, and modulus maps over the same 1 μm by 1 μm area. The examination area was selected at the silicon/polymer interface to include silicon, PMMA interphase, and the part of bulk PMMA. The topography map exhibits the extreme flatness of the surface over three domains, where the silicon/PMMA boundary is invisible; the adhesion map clearly shows the boundary since the adhesion force on the PMMA is significantly higher than on the silicon. The modulus map similarly demonstrates the boundary of PMMA and silicon substrate. The interphase polymer with increased modulus can also be clearly seen as a bright yellow strip adjacent to the boundary. The true modulus value of the silicon substrate cannot be obtained in these experiments, as it is out of the range of the AFM tip. The AFM apparent modulus of bulk PMMA is around 3.5 GPa, and data were further processed by normalization with respect to this bulk PMMA modulus to exhibit changes in interphase.

Figure 3b gives representative scan lines of topography, adhesion, and modulus, from which quantitative data can be gathered. The topography scan line shows that the roughness over 1 μm area is less than 2 nm. From the adhesion scan line, the adhesion force suddenly increases moving from silicon to polymer. The exact location of the boundary is determined by taking the average value of the adhesion over the PMMA surface, and the intersection of this average line and the adhesion curve. This boundary line is then projected onto the modulus and topography scan lines. On the modulus scan line, the measured modulus was normalized by the modulus of the PMMA bulk sample. The average modulus value from multiple scan lines on three different scan areas are given in Figure 3c. In the interphase region, the modulus starts from 150% of bulk PMMA modulus, and then gradually decreases away from substrate. After 100 nm, modulus variation is no more than 2% from average bulk PMMA modulus.

For comparison with PMMA/silica interphase, PMMA/alumina was examined. The modulus and topography
mappings are given in Figure 4a. Because of the significant hardness difference between alumina and AFM tip (Silicon), scanning on alumina substrate severely damages the tip, and a map including both substrate and polymer cannot be acquired. Therefore in this sample, after identifying the boundary of PMMA and alumina on the adhesion map, following the same method described above, the tests were completely performed on the PMMA immediately adjacent to the alumina substrate. Once again, the ion milled PMMA surface was extremely smooth, with roughness less than 1 nm. The modulus-enhanced interphase can also be observed. The detailed scan lines averages are given in Figure 4b. The maximum modulus is on the left boundary with about 40% increase from bulk PMMA's modulus, and the gradient extends for approximately 170 nm before falls to less than 2% increase of the bulk value.

The modulus changes for interphase polymer obtained by AFM mechanical mapping are consistent with the results of previous nanoindentation results, both in magnitude and extent \cite{3,47,48}. Additionally, in those results PMMA/alumina presented a higher magnitude of the overall film modulus, consistent with the longer extent of the interphase domain observed in the AFM data. It has also been observed that local $T_g$ changes occur in the range of approximately 100 nm. \cite{1,10–14,49} However, opposite trends were observed for local $T_g$ values: PMMA/silicon showed a moderate $T_g$ increase, while PMMA/alumina exhibited a $T_g$ decrease in the interphase region, an indication of increased molecular chain mobility. This opposite sense of the modulus and $T_g$ changes indicate differences in the impact of underlying mechanisms on $T_g$ and modulus. One possible conclusion from these results is that geometric confinement, which is the same for both systems, plays a larger role in the local mechanical properties of the interphase compared to the chemical interactions, which differ for the two systems.
In AFM indentation, when the distance from indentation point to the boundary of film and substrate is comparable to the dimension of AFM tip and indentation depth, the stress field discontinuity (shown in Figure 5a) caused by stiffness difference of film and substrate will interfere with the measured modulus. Similar to the substrate effects observed in nanoindentation,[3,50] the degree of the artificial modulus changes is influenced by several factors, including stiffness of the substrate materials, the roughness of interface, misalignment of sample surface, and polymer surface adhesion, etc.[51,52] In this paper, with the fixed boundary condition between film and substrate, the results of FE simulation (Figure 5b) reveal that when indentation is more than 15 nm away from the boundary, the substrate-induced modulus error decreases to less than 10% for various indentation depths. To remove the substrate influences, in Figure 3 and 4, cut-off lines are shown. Even excluding the first 15 nm from the substrate, about 35% modulus enhancement form PMMA/silicon and 40% modulus increase for PMMA/alumina can still be observed.

4. Conclusion

We have presented a technique, including sample preparation method, and AFM indentation, to quantitatively measure mechanical properties of interphase polymer near confining surfaces. Results demonstrate the gradient of mechanical properties change of polymers near chemically and geometrically confining surfaces. Both magnitude and dimension of interphase polymers are provided. The similar increase of modulus observed for PMMA on two chemically different substrates indicates that the geometric confinement constraint may play a larger role than surface chemical interaction for mechanical properties. Therefore, the approach provides a new experimental method to characterized interphase mechanical properties to expand our fundamental understanding of
polymer physics near interfaces as well as for the design of nanocomposites.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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