

**THE INFLUENCE OF SHEARING PARAMETERS
ON THE FRICTIONAL FORCES MEASURED
BETWEEN POLYMER BRUSHES**

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Introduction

Polymer brushes are formed when polymer chains are tethered by their ends to a surface or interface at distances less than the radius-of-gyration of the chain. The crowded nature of this tethering restricts the motion of a chain such that it must extend normal to the surface in order to minimize its free energy. The barrier layer formed by brushes has been shown to dramatically reduce friction between two surfaces when immersed in a good solvent [1]. A complete picture of how the structure of the chains within the layer is related to their ability to dissipate frictional interactions has not been realized. The research described herein is focused on investigating the role of solvent quality and shearing parameters on the frictional forces measured between opposing, sliding brush layers [2]. In these experiments solvent quality is not only changed by switching solvents, but also by increasing the temperature.

Experimental

We have used a modified surface force apparatus (SFA) [3] to make normal and frictional force measurements on opposing polymer brushes. The polystyrene brushes were formed from the preferential adsorption of polystyrene-polyvinylpyridine (PS-PVP) diblock copolymers onto mica surfaces from toluene. The formation of the brush in toluene drives the adsorption of the PVP block (anchor block) to the surface while allowing the PS block (buoy block) to form the brush. A distinct advantage of this adsorption strategy is that the PVP anchor layer will prevent the adsorption of PS to the surface during a later switch to a theta solvent (cyclohexane at 32 °C) [4]. The three different diblock copolymers studied were PS/PVP [103/114] k, [70/30] k, and [255/24] k, where the numbers in brackets represent the relative molecular mass, in thousands, of the PS and PVP blocks; respectively. The normal and frictional forces between the brush layers were measured in toluene at 32 °C and in cyclohexane at 32 °C, 40 °C, and 50 °C ($\pm 1^\circ\text{C}$). The shearing experiments were performed using amplitude and frequency pairs between 0.5 to 6.0 Volts peak-to-peak and 0.01 Hz to 0.2 Hz, and a triangular ramp input signal was used to induce steady sliding of one surface relative to the other. The product of these two quantities defines a shear velocity of one layer with respect to the other. Therefore, sliding velocities ranging from 1.0 nm/s to 600 nm/s were probed. Frictional forces were measured in each solvent for different degrees of compression and different combinations of sliding velocity and frequency. After each set of shearing experiments the normal forces were measured again to verify that the brush layers remained intact.

Results and Discussion

In a normal force experiment, opposing brush layers are brought together in a series of equilibrium steps to measure the forces of interaction normal to the surfaces. As the distance between the layers decreases and the brushes begin to interact, the polymer segment concentration within the gap increases. This increases the osmotic pressure for each layer, which causes the layers to repel each other. The repulsive force is measured as a function of the distance between the layers. This force profile is a monotonically increasing curve and, due to the symmetric nature of the system, one-half of the distance at which repulsive forces are seen is indicative of the equilibrium height of one brush layer. In a good solvent (toluene), the polymer-solvent interaction is favorable and the brush height is greater than in a theta solvent (cyclohexane at 32 °C). We have previously shown that for the [103/114] k

and [70/30] k brush the height of the layer, as measured through SFA experiments, is not strongly dependent upon cyclohexane temperature [5]. Table 1 details the equilibrium heights of the different brush layers as a

Table 1. The equilibrium heights of each brush layer investigated in different solvent qualities. The SFA-measured heights are insensitive to solvent temperature, except for the [255/24] k brush. The standard uncertainty within the height is estimated to be $\pm 10 \text{ \AA}$.

Brush	L_{eq} Toluene \AA	Leq, Cyclohexane (\AA)		
		32 °C	40 °C	50 °C
[PS/PVP]				
[103/114] k	450	250	250	250
[70/30] k	475	225	225	212
[255/24] k	1050	525	375	425

function of solvent quality. The height of the [255/24] k brush does decrease with increasing temperature, though the cause of this height change is unknown at this time. It is possible that there is some surface rearrangement or desorption of the chains, however the force profiles properly coalesce to a “universal profile” [6] with the [103/114] k and [70/30] k brushes when scaled by the Alexander-de Gennes model [7,8].

Table 2. The ability of the brush layer to dissipate friction is represented as a percent of the equilibrium brush height where frictional forces are first measured. This percentage is calculated as the distance at which the onset of frictional forces is measured (d) divided by the equilibrium height of the layer (L_{eq}) multiplied by 100. The standard uncertainty within the onset of frictional forces is estimated to be $\pm 10 \text{ \AA}$.

Brush	Toluene	Cyclohexane		
		32 °C	40 °C	50 °C
[PS/PVP]				
[103/114] k	23 %	58 %	42 %	36 %
[70/30] k	N/A	68 %	51 %	52 %
[255/24] k	28 %	68 %	54 %	44 %

The data in Table 2 capture the ability of the brushes to dissipate frictional forces with changes in solvent quality. These data show that increasing the cyclohexane temperature is effective in shifting the onset of frictional forces between the brush layers to smaller separation distances. For example, the [103/114] k brush in toluene was compressed to $\approx 23 \%$ of its toluene equilibrium height before measurable frictional forces were detected. Although frictional forces were not measured, the system was not “frictionless”. The magnitudes of forces were below our smallest force resolution, $\approx 20 \mu\text{N}$. In cyclohexane at 32 °C, the onset of measurable frictional forces occurred when this layer was compressed to $\approx 58 \%$ of its equilibrium height. As the temperature was increased above the theta point (34 °C for PS in cyclohexane) to 50 °C, the onset of frictional forces decreased to $\approx 36 \%$ of its equilibrium height at 32 °C. The normal force profiles and the changes in the onset of frictional forces for each of the different molecular weight brushes was repeatable between experiments. Another important aspect of brush shearing experiments is the role shearing parameters play in the magnitude of the frictional force measured.

Figure 1 is an example of how shearing at constant frequency and increasing amplitude can shift the dependence of frictional force with shear velocity for the [103/114] k brush in toluene. As the brushes are sheared at higher frequencies, the rate-of-rise or slope of frictional force with shear velocity decreases and the transition from a linear to less-than-linear dependence of frictional force on shearing velocity shifts to a higher shear velocity. While caution is taken not to irreversibly disturb the brush layers during shearing and the normal force profiles are confirmed after the brushes have been sheared, the trends presented in Figure 1 are not as clear when the brush molecular weight, solvent, or system temperature are changed. The lack of reproducible trends in terms of velocity and frequency dependence may ultimately lie in the complexity of the system. Brushes formed from adsorbed diblock copolymers have been shown to rearrange on the tethering surface in response to changes in solvent quality [9]. It is likely that inhomogeneities across the tethering surface, which yield regions of high

Research was conducted from 1997-2002, while Aaron M. Forster was a graduate student at Clemson University.

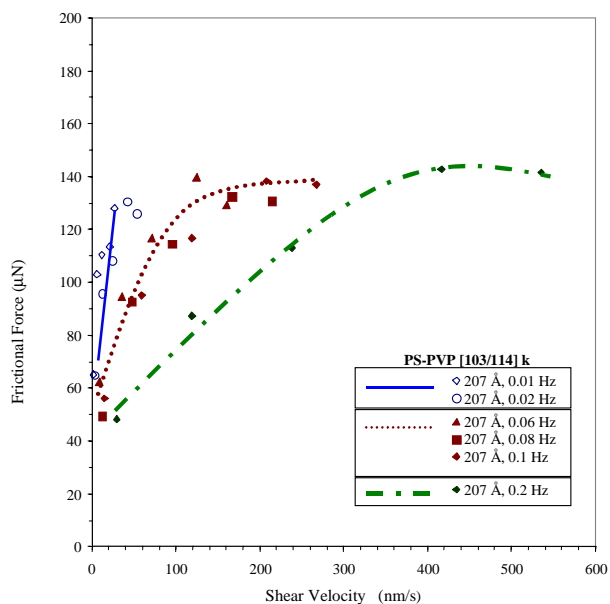


Figure 1. The frictional force versus shear velocity for the [103/114] k brush in toluene at 32 °C. The lines are a guide for the eye. The graph legend lists the separation between the brush-coated surfaces in Angstroms and the sliding frequency. The frictional force increases with increasing shear velocity at constant frequency and the rise in frictional force with shear velocity decreases with increasing shearing frequency. The standard uncertainty within the frictional force is estimated to be $\pm 5 \mu\text{N}$.

chain density and low chain density, lead to a varied response when the brush layers are sheared across each other. This is not to say that there are not similarities between shearing experiments. It will be shown that at low shearing velocities (within the linear regime), the trends in frictional force versus shear velocity data for different brushes at different degrees of compression and in different solvent qualities overlap. At this point it is clear that the strength of the solvent-segment interaction is the controlling feature, although the dependence of frictional force on shear velocity requires further investigation.

Conclusions

We have shown that brushes immersed in a good solvent are extended greater than their radius-of-gyration from the surface and these extended layers must be compressed well below their equilibrium height before frictional forces are measured. When immersed in a near-theta solvent, the brush layer contracts and the onset of frictional forces is measured soon after the brushes begin to interact. These results were consistent with normal force [10, 11] and frictional force [12, 13] experiments on brushes in toluene and cyclohexane at one temperature. Except for the [255/24] k brush, the height of the brush layer is relatively insensitive to increases in solvent temperature. The onset of frictional forces between the layers was found to decrease as the temperature was increased above the theta point. This indicates the brush layers are able to better dissipate friction with improved solvent quality. The method by which sliding is induced between the layers (manipulating frequency or amplitude) affects the dependence of frictional force on shear velocity. These trends are clear for some brush experiments and not as clear for others. It is possible to discern common trends between the different brush layers in similar shearing environments, but the exact reason for the differences is unknown. Further work is required to elucidate the reasons for the variability in the trends and how these trends are indicative of the specific interaction between the brush chains.

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