

Supplementary information

Temperature-dependent soft wetting on amorphous, uncrosslinked polymer surfaces

*Krishnaroop Chaudhuri and Jonathan T. Pham**

Department of Chemical and Materials Engineering, University of Kentucky, Lexington,
KY 40506, USA

E-mail: Jonathan.Pham@uky.edu

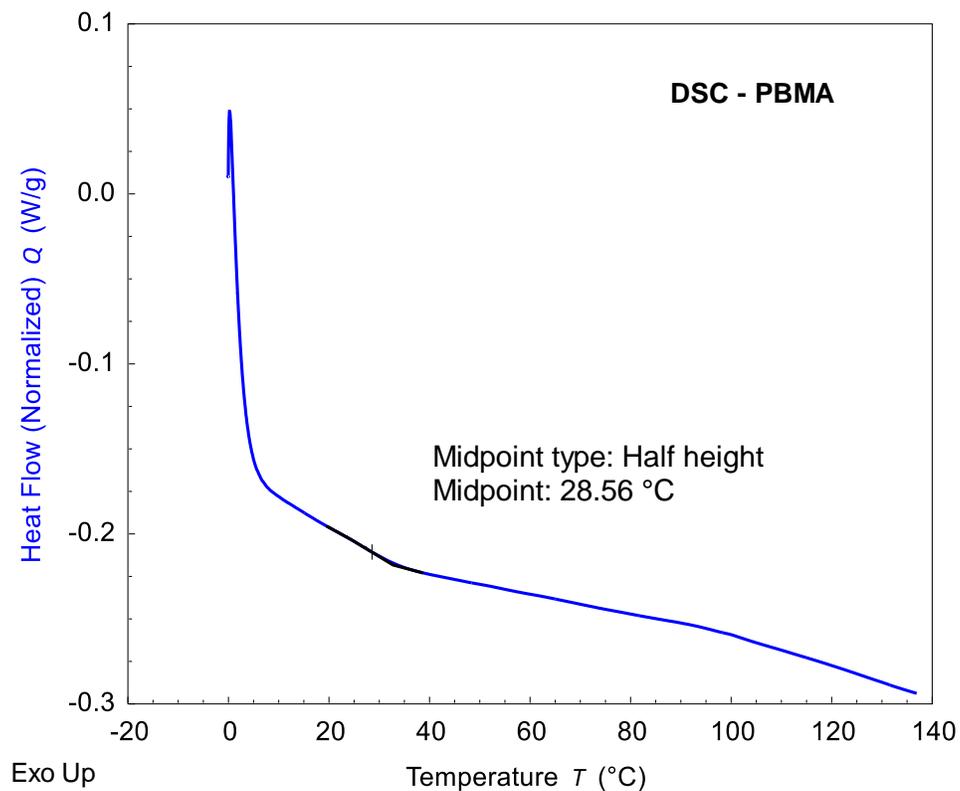


Figure S1: Differential scanning calorimetry (DSC Q200, TA Instruments) measurements of the PBMA powder (Sigma Aldrich). The sample was used as-received in a hermetic aluminum pan. Heating and cooling cycles were run from 0°C to 140°C at a rate of 10°C/min. The glass-transition temperature was determined to be $T_g \approx 28^\circ\text{C}$ using Trios software and the midpoint in the transition region.

Comparison of methods used to measure wetting ridge profiles

We made a comparison of different techniques to measure the peak height: optical profilometry, atomic force microscopy (AFM), and stylus profilometry. The wetting ridge sample used for this comparison was formed at $T=95^{\circ}\text{C}$ for 5 min. The details of the methods and the corresponding results are elucidated below:

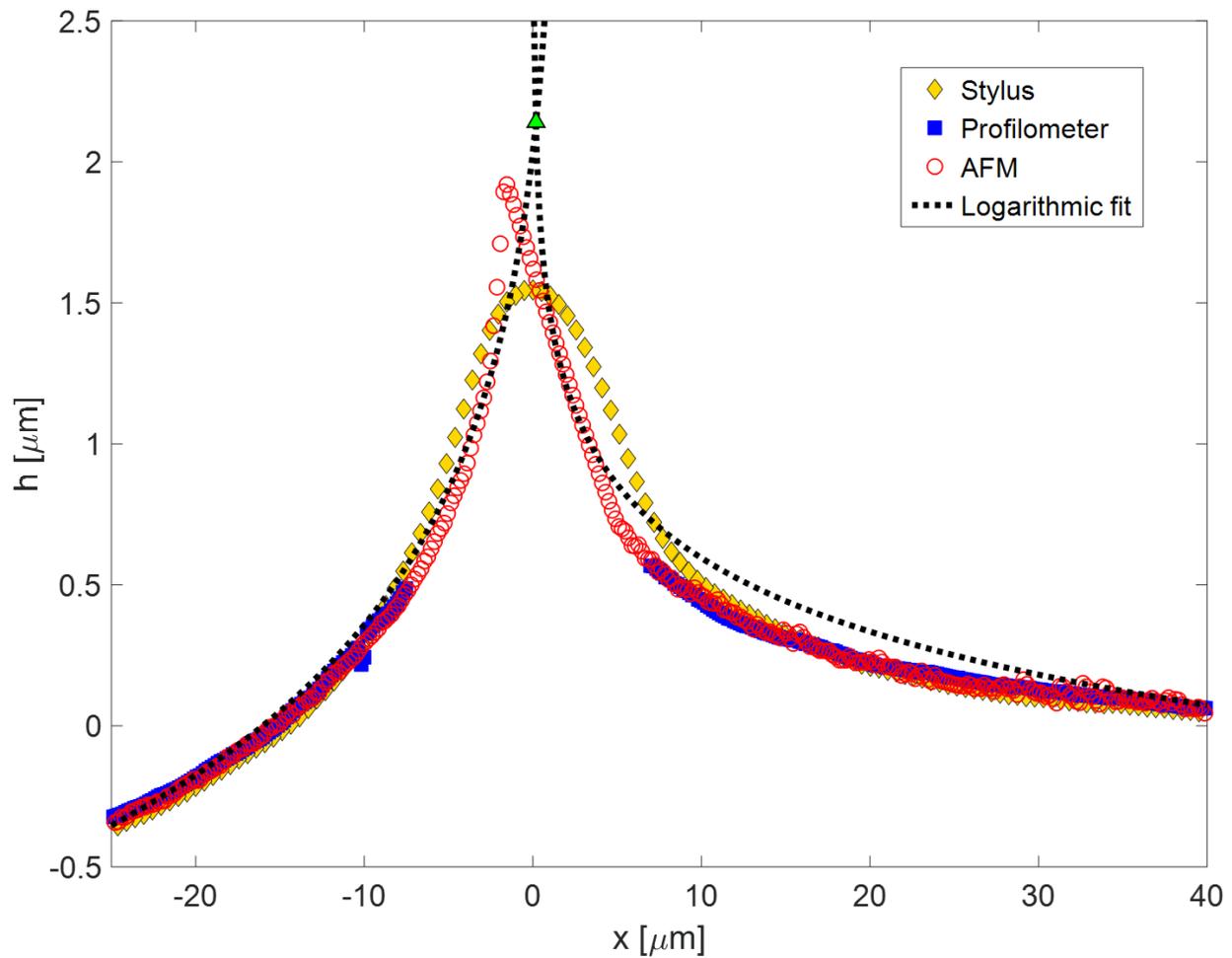


Figure S2: An overlay of wetting ridge profiles obtained using different measurement techniques. This particular sample is from an experiment at $T=95^{\circ}\text{C}$ with a wetting time of $t_d = 5$ min. The green triangle is the point of intersection of the logarithmic fits (black dotted lines), indicating the predicted peak height of the wetting ridge.

Optical Profilometry: The wetting ridge was scanned using a white light profilometer (Profilom3D, Filmetrics) equipped with a 50x objective (Nikon Corp.). The 3D data was processed using the built-in software (ProfilomOnline) and the 2D wetting ridge profile was extracted. It can be seen from Fig. S2 (blue squares) that although a uniform profile can be obtained for regions away from the three-phase contact line (TPCL), the instrument is unable to capture any usable data at a distance of $\pm 8 \mu\text{m}$ from the TPCL, which includes the ridge peak. This is due to the inherent shortcoming of reflective microscopes where the steep surface reflects the incident light away from the detector. For surfaces steeper than 35° , proper visualization is not possible by this method [1,2]. Hence, we used the stylus profilometer for wetting ridge peaks higher than $0.25 \mu\text{m}$, and optical profilometry for only peaks less than $0.25 \mu\text{m}$ (up to the first few minutes at 65°C).

Atomic Force Microscopy: AFM imaging was conducted using a JPK Nanowizard 4A equipped with a Mikromasch HQ NSC15/ Al BS cantilever tip. An area of $4 \mu\text{m} \times 100 \mu\text{m}$ was scanned in tapping mode at a scan rate of 0.1 Hz. As is seen in Fig. S2 (red circles), the AFM data closely matches the available optical profilometry data, and also converges to a point near the expected TPCL. Hence, the wetting ridge peak can be mapped with greater clarity than optical profilometry. However, while the AFM provides a complete image of the peak in this case, it cannot be used for the total scanning of ridges where the curved region exceeds $\pm 50 \mu\text{m}$ on either side of the TPCL. Additionally, the instrument has a z-axis scan limit of $15 \mu\text{m}$. This causes issues for measuring the complete profile of wetting ridges whose peak heights were greater than $\sim 10 \mu\text{m}$ and the curved surface extends beyond $40 \mu\text{m}$, the latter of which accounted for over 75% of our samples. Furthermore, each AFM scan is a much slower process than profilometry, and the tips are subject to erosion, which can lead to erroneous results. Thus, for our system, the AFM was only used to compare the results obtained using optical profilometry for peaks of sub-micron heights.

Stylus profilometry: The 2D profiles of the wetting ridges were measured using a Dektak 6M stylus profilometer (Veeco Instruments Inc.). The stylus tip has a radius of $12.5 \mu\text{m}$ and the applied force was set to 3 mg. The data was collected at a spatial resolution of $0.051 \mu\text{m}$ per point. Fig S2 (yellow

diamonds) show that stylus profilometry provides a complete and uninterrupted data set, and the spatial limits in all three dimensions of the instrument are all larger than all of the wetting ridges in our set of samples. Hence, stylus profilometry was chosen as the method to measure the wetting ridge profiles. However, due to the radius of the probe being larger than the smaller size scales of the actual tip, the profile appears “blunter” than it should be. To account for this discrepancy, we have used a curve fitting method to determine the expected peak height, as described in the main text.

Briefly, to locate the peak using the experimental data from the stylus, we follow a method previously used by van Gorcum et al. [3] where the curved ridge profiles are fitted using mathematical functions of the form $h = a + b \log(\pm(x - c))$ (Fig. S2, black dotted lines). These lines intersect at a point (Fig. S2, green triangle), which is considered to be the expected peak of the wetting ridge. Indeed, when compared to the peak obtained using AFM – which may be taken as the most accurate experimental data possible (Fig. S2, red circles) – it can be seen that there is a close agreement between these maxima. We have compared these theoretical peaks with the experimental peaks obtained via stylus profilometry in Fig. S4. For all time and temperature data points, the expected peak is consistently and proportionately higher than its stylus experimental data counterpart. This validates the use of fitting to determine the peak of the wetting ridge.

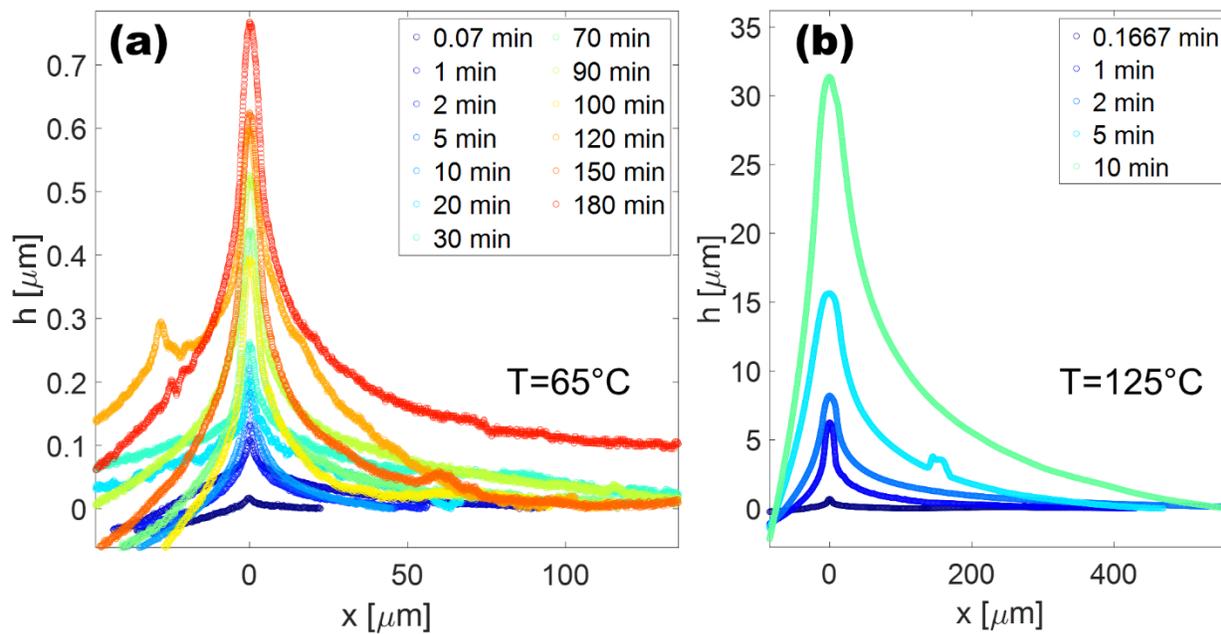


Figure S3: Growth of wetting ridges of PBMA substrates over time at (a) 65°C and (b) 125°C . The profiles have been plotted such that the y-axes for each line is zeroed at the x-axis point where the polymer film does not deviate from its initial height.

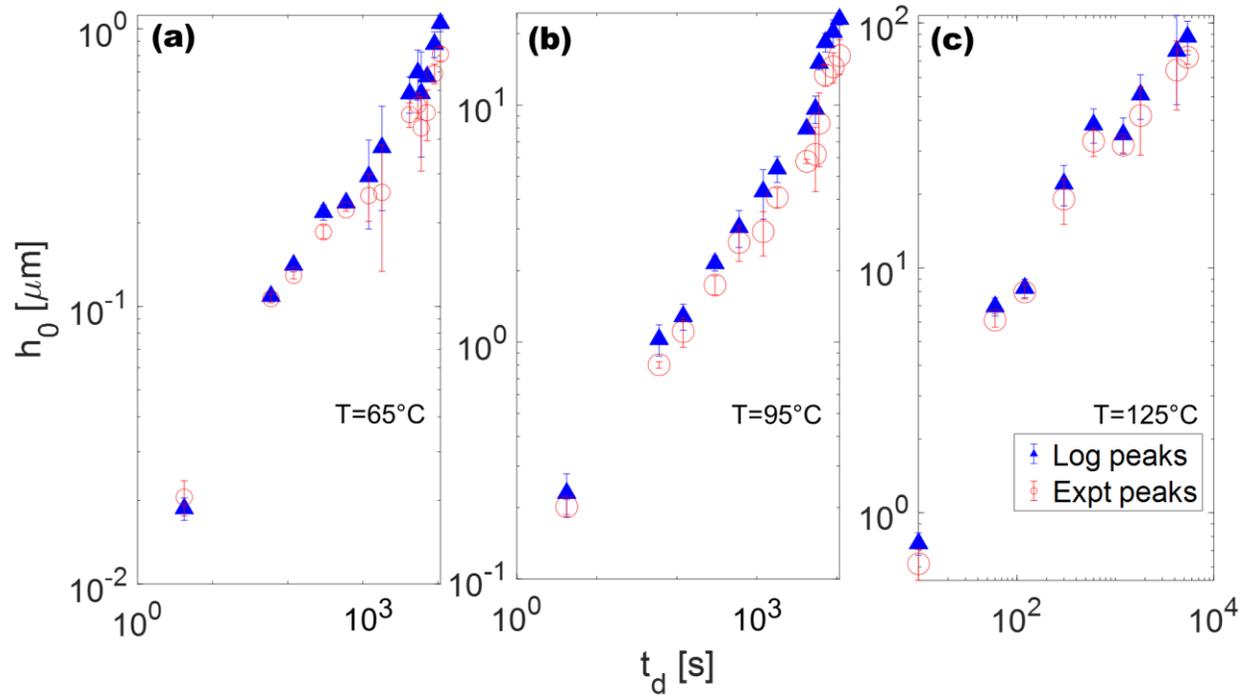


Figure S4: Wetting ridge growth of peak heights with respect to time, determined using two approaches: stylus profilometry data (red circles) and intersection of lines of logarithmic fits (blue triangles). For all three temperatures (a) 65°C , (b) 95°C , and (c) 125°C , stylus peaks are consistently lower than the logarithmic fitting peaks, indicating an obfuscation of the wetting ridge measurements due to instrument limitations. Error bars indicate standard deviation over 3 measurements.

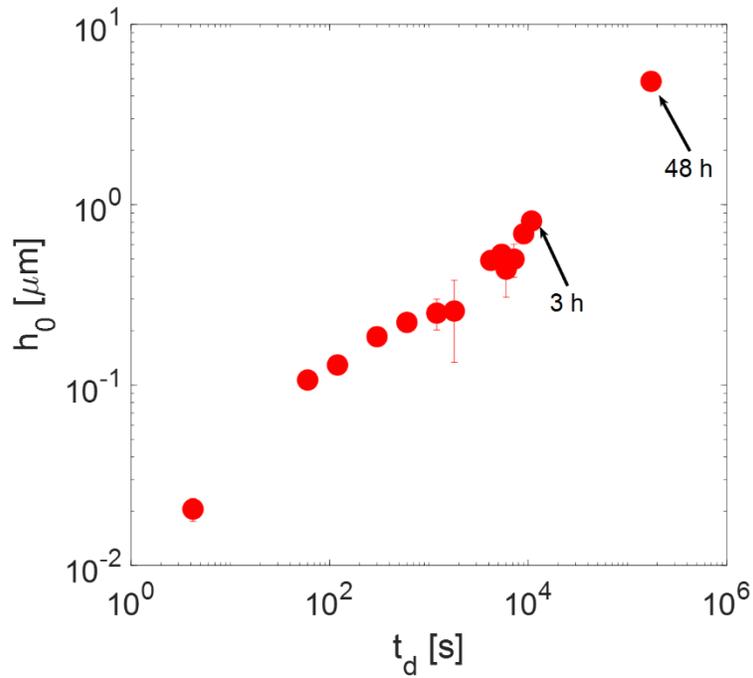


Figure S5: Wetting ridge peak height data over time for $T=65^\circ\text{C}$, with an additional data point at $t_d \approx 1.8 \times 10^5 \text{ s} \approx 48 \text{ h}$. It can be seen that, in the absence of significant glycerol evaporation, the ridge grows monotonously over time.

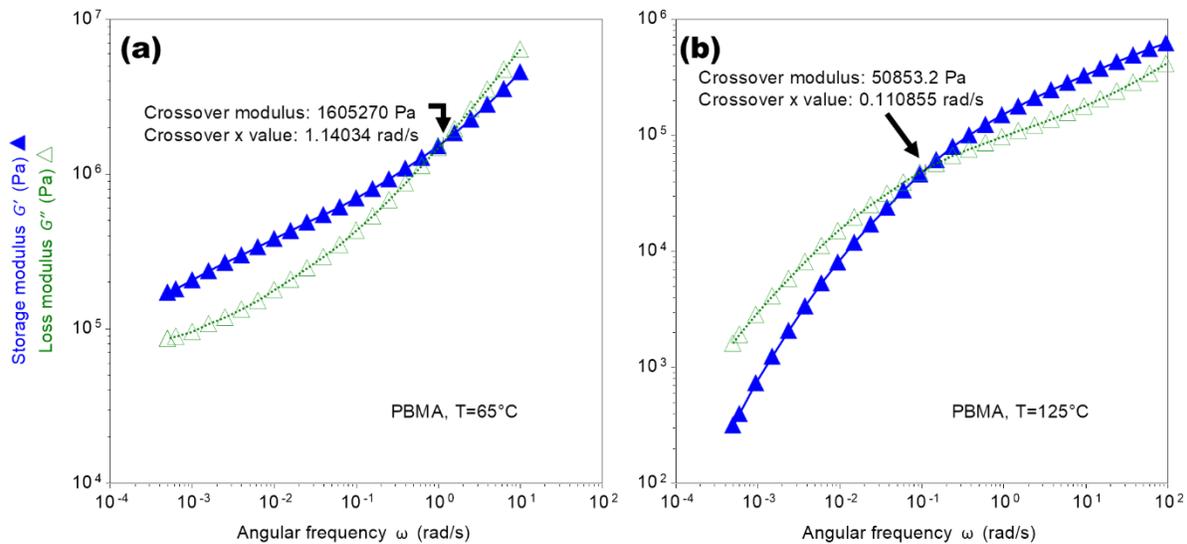


Figure S6: Dynamic oscillatory rheology of PBMA at (a) 65°C and (b) 125°C , and crossover points are observed at higher and lower ends of the spectrum, respectively.

References

- [1] R. Pericet-Cámara, A. Best, H.-J. Butt, and E. Bonaccorso, *Langmuir*, **24**, 10565–10568 (2008).
- [2] R. Pericet-Cámara, G.K. Auernhammer, K. Koynov, S. Lorenzoni, R. Raiteri, and E. Bonaccorso, *Soft Matter*, **5**, 3611–3617 (2009).
- [3] M. van Gorcum, S. Karpitschka, B. Andreotti, and J.H. Snoeijer, *Soft Matter*, **16**, 1306–1322 (2020).