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Pressure Dependence of Surface Tension of Polymer Melts under High Vacuum

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Abstract

The surface tension of polymers under ambient or high-pressure conditions has been extensively studied but is less explored under high vacuum. Here, the effect of air pressure on the surface tension of polymer melts is studied by using a home-built apparatus. While previous studies showed that the surface tension of most polymers decreases linearly when the temperature or pressure is increased, we show that the surface tension of polymer is found to exhibit an anomalous behavior: The surface tension remains a decreasing function of the temperature, but increases with increasing air pressure. The measured surface tension of several polymer samples is well described by the Hill equation in the pressure range of 10^{-4} to 10^{5} $\mathrm{N/m^2}$. The implication of this behavior on the air-polymer interaction is discussed within the context of air adsorption

Keywords: polymer melt, surface tension, pressure dependence, high vacuum

Introduction

The surface tension (γ) of polymer melts is an important property of polymeric materials and plays a key role in numerous engineering processes, such as polymer blending[1], polymer foaming[2], wetting[3], and particles or fiber dispersion in polymers[4]. Naturally, the surface tension of polymers depends on the thermodynamic conditions, commonly specified by the temperature (T) and pressure (P). It is well-established that the surface tension of most polymer melts decreases slightly with the temperature, following approximately a linear relationship, at ambient pressure of the order of 10^5 Pa[5-10]. Similarly, the pressure dependence of γ, determined under high-pressure conditions, was observed to decrease linearly when the pressure is increased at a constant temperature[11-18]. The decrease of γ with increasing P is attributed to either increased gas dissolution or the reduction of density difference between the two phases across the interface[11-18]. However, the pressure dependence of γ under high vacuum conditions has not been studied prior to the current work.

In contrast to the abundant studies under ambient or high-pressure, the phase behaviors of polymers and their surface tension under high vacuum conditions have attracted much less attention, largely due to the difficulty of precisely controlling pressure to reach high vacuum conditions. Recently, it has been discovered that placing diblock copolymers under high vacuum conditions could lead to a drastic orientation change from parallel to perpendicular for the self-assembled cylindrical nanostructure[19]. The origin of this interesting discovery could be attributed to a much-reduced surface tension difference between the different blocks, *i.e.* polystyrene (PS) and polydimethylsiloxane (PDMS) or poly(L-lactide) (PLLA), under high vacuum[20,21]. While it is natural to suggest that the surface tensions of the polymers depend on the pressure, a systematic study, quantitatively or even qualitatively, of the effect of air pressure on the surface tension of

polymers has been lacking. Here, we fill this gap by carrying out a systematic study of the effect of air pressure on the surface tension of polymer melts under high vacuum. Specifically, we designed and constructed a homemade vacuum oven (Supplementary Figure. 1) that enabled us to achieve a high vacuum and measured the surface tension of polymer melts by the pre-coated capillary height method. It is noted that several techniques, such as pendant, sessile, spinning drop, *etc*. could be used to obtain the surface tension. These methods have the advantage of requiring a minimum amount of sample and are applicable to various cases[22-24]. However, their performance and sensitivity significantly decrease when the drop shape becomes nearly spherical[25,26]. In the current study, the pre-coated capillary technique was chosen due to its simplicity and reliability[20]. We carried out surface tension measurements on several representative polymer samples, including polyethylene glycol (PEG), polyisoprene (PI), polypropylene (PP), PS, and PDMS, with a wide range of surface tension values under ambient conditions. A very surprising observation from our study is that, in contrast to the pressure effect on the surface tension under ambient or high-pressure, the surface tension of all the polymers exhibits a significant decrease when the pressure drops below 10^3 N/m^2. This anomalous behavior of the polymer surface tension must be related to the polymer-air interactions. This new finding reveals interesting physics at the air-polymer interfaces and, furthermore, sheds light on potential applications of designing polymeric materials for nanopatterning technologies within nano-microelectronic manufacturing systems (MEMS).

Results

Temperature Dependence of Surface Tension

To explore the temperature dependence of surface tension for polymeric melts, systematic measurements were carried out using a homemade vacuum oven apparatus. As a validation of our

experimental method, the surface tension of the polymer samples (shown in Fig. 1) was obtained as a function of temperature in the range from 170 to 220°C, under ambient pressure (~10^5 N/m^2). It is noted that the surface tension data for PS and PDMS were reported in our previous work[20]. The data for PI was not available for temperatures over 200°C due to thermal degradation of the sample. In agreement with the literature[5-10], the measured surface tension shown in Fig. 1 for the five polymers (PEG, PS, PI, PP, and PDMS) exhibits a slight linear decrease when the temperature is increased, with a slope in the range of -0.08 to -0.12. The agreement between the results from the current study and the literature validates our experimental methods.

Pressure Dependence of Surface Tension

Several previous studies have demonstrated a small reduction in surface tension at high pressure and temperature. However, there has been less focus on the low-pressure region. To fill this gap, we carried out measurements of polymer surface tension under low-pressure conditions. The homemade oven allowed us to access low-pressure conditions, thus enabling the measurement of the surface tension under high vacuum conditions. Specifically, surface tension of several sample polymers was obtained in the pressure range from atmospheric pressure (10^5 N/m^2) to 10^{-4} N/m^2. The measured surface tension of the samples at a temperature of 200°C are presented in Table 1, revealing a clear decrease in surface tension with decreasing air pressure. Interestingly, a drastic reduction in surface tension is observed as the pressure drops below atmospheric levels (10^5 N/m^2). Since the pressure change was over 8 orders of magnitude, a linear plot of our data compresses most of the points to a vertical line. Instead, it is the best to use log-linear plot to demonstrate the change of the measured surface tension. The data points and their best fitting by Hill equation as shown in Fig. 2. It is important to mention that the trend of the surface tension change is qualitatively different from the pressure effect under high-pressure conditions, where a

slight decrease of γ is observed when the pressure is increased[11-18]. Note that the low- and high-pressure regimes involve distinct mechanisms. At low pressure, surface tension changes are primarily governed by modifications in polymer–air interactions, as captured by the lattice model. At high-pressure, the decrease in surface tension arises from gas dissolution or the reduced density difference across the interface.

To examine the generality of the observed behaviour, we measured the surface tension of two polymers, PEG and PDMS, with different molecular weights under high vacuum conditions. These two polymers were chosen because they possess the highest (PEG) and the lowest (PDMS) surface tension under ambient conditions. Note that the PEG with a molecular weight (MW) of 20000 g/mol is referred to as PEG HMW and PEG with MW of 10000 g/mol molecular weight is referred to as PEG LMW. Also, low MW (21,000 g/mol) PDMS is referred to as PDMS LMW and high MW (38,000 g/mol) PDMS is referred to as PDMS HMW. As shown in Fig. 3, the molecular weight of the polymers has a negligible effect on the surface tension. The observed pressure dependence of surface tension is consistent across polymers of different molecular weights, indicating that polymer chain length or PDI does not play a dominant role. Instead, the trend primarily reflects intrinsic polymer-air interfacial interactions, suggesting that the pressure dependence should be universal to polymers. It is plausible that the observed pressure dependence of surface tension is not polymer-specific. Rather, it is the result of surface-air adsorption. In what follows, we construct a theoretical model to understand and explain the observed temperature and pressure dependence of the surface tension.

Theoretical Model

To understand and explain the experimental observations, a theoretical model of the surface tension of a condensed sample, such as a polymer melt, surrounded by air molecules is desirable.

For a system composed of a substrate and a gas, the surface tension could be divided into two components, the surface tension of the neat material γ_0 and the contribution from interaction with the air molecules, $\Delta\gamma$. The reduction of the surface tension in high vacuum (low pressure) region is due to air-polymer interaction and that could be estimated by using a lattice gas model. We assume that half of the lattice is occupied by polymeric species (P), while the other half of the lattice is occupied by gas (air) molecules (A) or empty (vacuum) (B). We use a simple cubic lattice in the following discussion, although any type of lattice would be equally valid. We assume nearest-neighbour interactions between the different species. For a surface in the *xy* plane, the surface area is $S = Na^2$ where N is the number of lattice sites on the *xy* plane and a is the lattice constant. The total energy between the polymeric species and the lattice gas is given by,

$$E = N_{PA}\varepsilon_{PA} + N_{PB}\varepsilon_{PB}, \quad (1)$$

where N_{PA} and N_{PB} are the number of nearest-neighbor polymer-air and polymer-vacuum bonds, respectively, and ε_{PA} and ε_{PB} are the corresponding interaction energies. We use a mean-field approximation to estimate the number of nearest-neighbor bonds. Specifically, we assume that the air concentration is given by ϕ, then the average number of nearest-neighbor bonds are given by, $N_{PA} = \phi N$ and $N_{PB} = (1-\phi)N$. Therefore, the total surface energy becomes,

$$E = N\phi\varepsilon_{PA} + N(1-\phi)\varepsilon_{PB} = N[\varepsilon_{PB} + \phi(\varepsilon_{PA} - \varepsilon_{PB})] \quad (2)$$

Using the expressions of the total surface energy and surface area, the surface tension that is the surface energy per unit area is obtained as,

$$\gamma = \frac{E}{S} = \frac{\varepsilon_{PB} + \phi(\varepsilon_{PA} - \varepsilon_{PB})}{a^2} \quad (3)$$

We now introduce the polymer-vacuum surface tension, $\gamma_0 = \frac{\varepsilon_{PB}}{a^2}$, and the differential interaction energy $\Delta\varepsilon = \varepsilon_{PA} - \varepsilon_{PB}$, the surface tension is now given by,

$$\gamma = \gamma_0 + \frac{\Delta\varepsilon}{l^2}\,\phi \tag{4}$$

where l is a length scale characterizing monomer-monomer distance, $\Delta\varepsilon$ quantifies the difference of air-polymer and vacuum-polymer interaction, and ϕ is the concentration of air molecules at the polymer surface that is the key property determining the pressure-dependence of the surface tension.

The simplest assumption is that there is no adsorption of air molecules. In this case, the air concentration is given by the ideal gas law, $\phi = \frac{Nv_0}{V} = \frac{v_0 P}{k_B T}$, where v_0 is the volume of one gas molecule. Using this expression obtained,

$$\gamma = \gamma_0 + \frac{v_0\Delta\varepsilon}{l^2}\,\frac{P}{k_B T} \tag{5}$$

This result predicts that the surface tension is an increasing function of the pressure, P, and a decreasing function of the temperature, T. This predicted behavior is in qualitative agreement with our experimental observations. However, this simple model does not provide an explanation of the observed relationship reported above. Therefore, a more sophisticated model for air adsorption is needed. When air adsorption to the polymer surface occurs, the surface concentration of air molecules becomes larger than that predicted by the ideal gas model. The reduction of surface tension in the high-pressure region is primarily due to the increase in the dissolution of the gas molecule (solubility) with the increase in pressure[12,14-18]. The drop in surface tension in high-pressure can also be explained in terms of density which is mostly attributed to the reduction in density difference between the gas molecule and polymer at the interface[11,13]. On the other hand,

the behaviour of the surface tension in the high vacuum region must be due to different mechanisms. Here, we propose that the reduction of surface tension with the decrease of pressure could be attributed to the adsorption of air molecules to the surface. We assume that the air adsorption is described by the Hill's function[32,33],

$$\phi = \frac{P^H}{P_0^H + P^H} \tag{6}$$

Here H is the Hill coefficient and P_0 represents a threshold pressure at which $\phi = 1/2$. The familiar Langmuir adsorption isothermal ($\phi = P/(P_0 + P)$) is recovered when $H = 1$. The Hill equation is used widely in biochemistry to describe the ligand binding, which is similar to the adsorption process. The Hill coefficient is commonly found to be larger than 1 in biologically systems, indicating positive corporative binding. The case with $H < 1$ corresponds to negative cooperative binding. Since the polymer and air molecules are not strongly interacting, a small Hill coefficient is not an unreasonable assumption. Using the Hill equation, we can write the surface tension as,

$$\gamma = \gamma_0 + (\gamma_\infty - \gamma_0)\frac{(P/P_0)^H}{1+(P/P_0)^H} \tag{7}$$

Here γ_0, γ_∞ and P_0 are fitting parameters for a fixed value of the Hill coefficient H. γ_0 is surface tension in vacuum (P=0) and γ_∞ represents the surface tension where air adsorption is effectively saturated. We have tested different values of H and found that a small $H < 1$ gives good fitting to all the data. After some exploration, we decided to use $H = 0.2$ that gives good fitting to all the data. The fitting was carried out by using the NonlinearModelFit function of Mathematica. It is found that all the data could be well described by this equation with $H = 0.2$ and the fitting parameters are given in Table 2. Such negative cooperative binding (H = 0.2) is generally observed in ligand-protein binding.[35] It is interesting to note that for finite value of P/P_0 and small H, the

Hill function can be approximated as $\phi \approx \frac{1}{2}(1 + \frac{H}{2}\ln P/P_0)$, therefore the observed surface tension data could be described by a linear function of $\ln P$.Note that the parameter P_0 in our model as shown in Equation 7 can be temperature-dependent. When the Hill function is used, the temperature-dependence of the surface tension is embedded in the parameter P_0 in our model. The temperature-dependence shown in Figure 1 could be explained by using the approximate expression $\phi \approx \frac{1}{2}(1 + \frac{H}{2}\ln P/P_0)$.

As compared to other polymer systems, the PI sample shows a different behaviour in that the fitting parameter P_0 is much larger than that for all other samples. We speculate that this might be attributed to thermal degradation of PI since its degradable temperature is very close to the experimental temperature (~200 °C). The degradation could lead to subtle changes in surface composition or reactivity, thus resulting in a rather different fitting parameter. Overall, the quality of fitting is good for the data points over the range of the pressure.

The fitting formula allows us to display all the data on a universal plot, if we express the surface tension using the following scaled form,

$$\frac{\gamma-\gamma_0}{\gamma_\infty-\gamma_0} = \frac{(P/P_0)^H}{1+(P/P_0)^H} \quad (8)$$

The scaled data and the Hill function are shown in Fig. 3. It is very interesting to see that all the data points fall on a master curve. The fact that all the data is well described by one master curve indicates that the physics governing the behaviour of the surface tension as a function of air pressure at low pressure region should be universal, independent of the polymer samples. It is noted that air is a homogeneous mixture of N_2, O_2 and Ar. In our simple model, the contribution of different interactions of those gas molecules with polymer is represented by an averaged interaction parameter. Certainly, the model could be improved by performing control experiments to differentiate the interaction between individual molecule and polymer. However, the behaviors

with respect to the pressure dependence of surface tension for polymer melts under vacuum should be the same. We would like to mention that Herminghaus *et al.* observed that the pressure effect on polymer thin film rupture and shown that the effect is insensitive to the gas molecules[34]. When the experiments were carried out under vacuum conditions below roughly 1 mbar, no rupture occurred while the substrate was properly cleaned beforehand. In contrast, at pressures of 10 mbar or above, hole formation was consistently observed, independent of the gas type. Pressures at or below 1 mbar effectively inhibited rupture in all cases. Because thin film rupture is largely driven by the surface tension of the polymer, their observations imply a sharp decrease of polymer surface tension when the gas pressure is decreased to below 1 mbar, independent on the gas molecules. These observations are consistent with our results on the pressure-dependence of polymer surface tension. Although many details of the air-polymer interactions are ignored, the adsorption model with Hill function does provide an adequate description of the experiments.

Discussion

In conclusion, the surface tension of several polymeric melts has been measured by the pre-coated capillary technique, where the temperature and air pressure were controlled by using a homemade oven. At ambient conditions, the measured surface tension data exhibit a slight linear decrease when the temperature is increased, in agreement with the literature, validating our experimental protocol. Under high vacuum, it is discovered that the surface tension of polymers exhibits a drastic drop when the air pressure is decreased to below 10^3 N/m^2, which is opposite from the pressure effect at high-pressure region where the surface tension exhibits a slight decrease when the pressure is increased. In the air pressure range of 10^{-4} to 10^5 N/m^2, the measured surface tension follows the Hill equation, $\gamma = \gamma_0 + (\gamma_\infty - \gamma_0)\frac{(P/P_0)^H}{1+(P/P_0)^H}$ with $H = 0.2$. A key limitation of our results is the limited number of data points at high vacuum condition, which is

mainly attributed to the difficulties in maintaining precise control over intermediate vacuum pressures and achieving ultra-high vacuum levels. The dataset can be expanded to include a broader range of polymer systems and enhancing the precision of vacuum control representing important directions for future investigation. Also, this discovery of the dramatic variation of surface tension in regular polymeric melts gives rise to new ideas for the fabrication of BCP thin films in a variety of applications such as nanopatterning. Furthermore, the observed pressure effect should not be specific to polymers and should be universally applicable to any physiochemical systems.

Methods

Materials.

The polyethylene glycol (Mw = 20,000 g/mol, catalogue no. A17925.30) from Thermo Scientific and polyethylene glycol (Mw = 10,000 g/mol, product no. P6667) from Sigma-Aldrich used in this study were commercially available products. Polystyrene (Mw = 20,000 g/mol, PDI = 1.06), polyisoprene (Mw = 19,000 g/mol, PDI = 1.03), and polydimethylsiloxane (Mw = 21,000 and 38,000 g/mol, PDI = 1.09) were synthesized in the laboratory. Polypropylene (Mw = 12,000 g/mol, product no. 428116) used was a commercially available product and obtained from Sigma-Aldrich.

The polymer samples, whether commercially obtained or prepared in the laboratory, were used without additional processing such as solution casting or heat pressing. The samples were

either in powder form (*e.g.* PEG, PS, PP) or in viscous liquid-like form (*e.g.* PI and PDMS), and were placed directly into clean glass vials. Each sample was placed in a clean glass vial along with the suspended capillary tube and kept in a homemade vacuum oven. The rotary and diffusion pump were operated overnight to achieve a high degree of vacuum in the chamber. Following this, the oven was heated to the desired temperature while maintaining vacuum conditions. This process enabled thermal annealing under high vacuum prior to testing.

Measurement of surface tension for polymeric melt

The surface tension measurements of representative polymeric systems were carried out using the capillary rise method under zero-contact-angle conditions (See Supplementary information, Pre-coated Capillary Height Method section for details). The dependence of surface tension on thermodynamic variables like temperature and pressure was studied through experiments conducted using a homemade vacuum oven apparatus, which was designed to precisely control temperature and pressure conditions (See Supplementary Figure 1. for details). Five commonly used polymers, including PDMS, PP, PI, PS, and PEG, ranging from low cohesive density to high cohesive energy density, were employed in this study, and the values of surface tension at ambient conditions are shown in Supplementary Table 1.

Data availability. The data that support the findings of this study are provided with this paper and in the supplementary information. All additional data are available from the corresponding author upon request.

References

1. Virgilio, N., Desjardins, P., L'Espérance, G.& Favis, B. D. In situ measure of interfacial tensions in ternary and quaternary immiscible polymer blends demonstrating partial wetting. *Macromolecules* **42**, 7518-7529 (2009).

2. Liao, X., Li, Y. G., Park, C. B. & Chen, P. Interfacial tension of linear and branched PP in supercritical carbon dioxide. *J. Supercrit. Fluids* **55**, 386-394 (2010).

3. Sugiura, S., Nakajima, M., Oda, T., Satake, M. & Seki, M. Effect of interfacial tension on the dynamic behavior of droplet formation during microchannel emulsification. *J. Colloid Interface Sci.* **269**, 178-185 (2004).

4. Khoshkava, V. & Kamal, M. Effect of surface energy on dispersion and mechanical properties of polymer/nanocrystalline cellulose nanocomposites. *Biomacromolecules* **14**, 3155-3163 (2013).

5. Roe, R.-J. Surface tension of polymer liquids. *J. Phys. Chem.* **72**, 2013-2017 (1968).

6. Wu, S. Surface and interfacial tensions of polymer melts: I. Polyethylene, polyisobutylene, and polyvinyl acetate. *J. Colloid Interface Sci.* **31**, 153-161 (1969).

7. Wu, S. Surface and interfacial tensions of polymer melts. II. Poly (methyl methacrylate), poly (n-butyl methacrylate), and polystyrene. *J. Phys. Chem.* **74**, 632-638 (1970).

8. Moreira, J. C. & Demarquette, N. R. Influence of temperature, molecular weight, and molecular weight dispersity on the surface tension of PS, PP, and PE. I. Experimental. *J. Appl. Polym. Sci.* **82**, 1907-1920 (2001).

9. Demarquette, N. R., Moreira, J. C., Shimizu, R. N., Samara, M., Kamal, M. R. Influence of temperature, molecular weight, and molecular weight dispersity on the surface tension of polystyrene, polypropylene, and polyethylene. II. Theoretical. *J. Appl. Polym. Sci.* **83**, 2201-2212 (2002).

10. D. Yang, Z. Xu, Liu, C. & Wang, L. Experimental study on the surface characteristics of polymer melts. *Colloids Surf., A Physicochem. Eng. Asp.* **367**, 174-180 (2010).

11. Li, H., Lee, L. J. & Tomasko, D. L. Effect of carbon dioxide on the interfacial tension of polymer melts. *Ind. Eng. Chem. Res.* **43**, 509-514 (2004).

12. Park, H., Park, C., Tzoganakis, C., Tan, K. & Chen, P. Surface tension measurement of polystyrene melts in supercritical carbon dioxide. *Ind. Eng. Chem. Res.* **45**, 1650-1658 (2006).

13. Park, H., Thompson, R., Lanson, N., Tzoganakis, C., Park, C. & Chen, P. Effect of temperature and pressure on surface tension of polystyrene in supercritical carbon dioxide. J. *Phys. Chem. B* **111**, 3859-3868 (2007).

14. Wei, H., Thompson, R., Park, C. & Chen, P. Surface tension of high density polyethylene (HDPE) in supercritical nitrogen: Effect of polymer crystallization. *Colloids Surf. A: Physicochem. Eng. Asp.* **354**, 347-352 (2010).

15. Liao, X., Li, Y. G., Park, C. B. & Chen, P. Interfacial tension of linear and branched PP in supercritical carbon dioxide. *J. Supercrit. Fluids* **55**, 386-394 (2010).

16. Mahmood, S., Ameli, A., Hossieny, N. & Park, C. The interfacial tension of molten polylactide in supercritical carbon dioxide. *J. Chem. Thermodyn.* **75**, 69-76 (2014).

17. Sarikhani, K., Jeddi, K., Thompson, R., Park, C. B. & Chen, P. Effect of pressure and temperature on interfacial tension of poly lactic acid melt in supercritical carbon dioxide. *Thermochim. Acta* **609**, 1-6 (2015).

18. Kravanja, G., Hrnčič, M. K., Škerget M. & Knez, Ž. Interfacial tension and gas solubility of molten polymer polyethylene glycol in contact with supercritical carbon dioxide and argon. *J. supercrit. fluids* **108**, 45-55 (2016).

19. Hung, C.-J. *et al.* Direct Visualization of the Self-Alignment Process for Nanostructured Block Copolymer Thin Films by Transmission Electron Microscopy. *ACS Macro Lett.* **12**, 570-576 (2023).

20. Panda, A. S. *et al.* Vacuum-Driven Orientation of Nanostructured Diblock Copolymer Thin Films. *ACS nano* **16**, 12686-12694 (2022).

21. Liu, K.-P., Panda, A. S., Huang, W.-C. & Ho, R.-M. Vacuum-Driven Orientation of Nanostructured Polystyrene-block-Poly (L-lactide) Block Copolymer Thin Films for Nanopatterning. *Giant,* 100303 (2024).

22. Hoorfar, M. & Neumann, A. Recent progress in axisymmetric drop shape analysis (ADSA). *Adv. Colloid Interface Sci.* **121**, 25-49 (2006).

23. Zuo, Y. Y., Do, C. & Neumann, A. W. Automatic measurement of surface tension from noisy images using a component labeling method. *Colloids Surf., A: Physicochem. Eng. Asp.* **299**, 109-116 (2007).

24. Saad, S. M. & Neumann, A. W. Total Gaussian curvature, drop shapes and the range of applicability of drop shape techniques. *Adv. Colloid Interface Sci.* **204**, 1-14 (2014).

25. Saad, S. M., Policova, Z. & Neumann, A. W. Design and accuracy of pendant drop methods for surface tension measurement. *Colloids Surf., A: Physicochem. Eng. Asp.* **384**, 442-452 (2011).

26. Zuo, Y., Ding, M., Bateni, A., Hoorfar, M. & Neumann, A. Improvement of interfacial tension measurement using a captive bubble in conjunction with axisymmetric drop shape analysis (ADSA). *Colloids Surf., A: Physicochem. Eng. Asp.* **250**, 233-246 (2004).

27. Peliti, L. *Statistical mechanics in a nutshell*, (Princeton University Press, ed. 2, 2024) pp. 143-145.

28. Macleod, D. On a relation between surface tension and density. *Trans. Faraday Soc.* **19**, 38-41 (1923).

29. Ferguson, A. & Kennedy, S. Free and total surface energies and related quantities. *Trans. Faraday Soc.* **32**, 1474-1481 (1936).

30. Yurdakal, S., Garlisi, C., Özcan, L., Bellardita, M. & Palmisano, G. "(Photo) catalyst characterization techniques: adsorption isotherms and BET, SEM, FTIR, UV–Vis, photoluminescence, and electrochemical characterizations" in Heterogeneous photocatalysis (Elsevier, 2019), pp. 87-152.

31. Wu, S. *Polymer interface and adhesion*. (Routledge, 2017).

32. Hill, A.V., The possible effects of the aggregation of the molecules of hemoglobin on its dissociation curves. *J Physiol,* **40,** 4–7(1910).

33. Hill, A.V., The combinations of haemoglobin with oxygen and carbon monoxide. *Biochem J,* **7**, 471–480(1913).

34. Jacobs, K., Herminghaus, S. & Mecke, K.R. Thin liquid polymer films rupture via defects. *Langmuir*, **14,** 965-969 (1998).

35. H. Abeliovich. An Empirical Extremum Principle for the Hill Coefficient in Ligand-Protein Interactions showing Negative Cooperativity, *Biophysical Journal*, **89**, 76-79 (2005).

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Competing interests. Authors declare that they have no competing interests.

Tables

Table 1. Measured surface tensions of polymer samples at different pressures at 200°C.

Pressure (N/m^2)	Surface Tension γ, ($J/m^2 \times 10^3$)

Polydimethylsiloxane (PDMS) high molecular weight	100000	12.7
	316	11.4
	0.3	10.8
	4E-4	9.5
Polydimethylsiloxane (PDMS) low molecular weight	100000	13.5
	158.49	12.6
	1	12.1
	0.01	11.1
	1.00E-03	10.7
	1.00E-04	9.6
Polypropylene (PP)	100000	22.9
	17500	21.4
	316	19.4
	0.4	17.3
	3E-4	12.3
Polyisoprene (PI)	100000	24.9
	316	20.5
	1	17.8
	8E-4	14.3
Polystyrene (PS)	100000	27.4
	17500	24.6
	1000	23.2
	0.1	18.2
	1E-3	15.1
	1E-04	13.1
Polyethylene Glycol (PEG) high molecular weight	100000	34.1
	316	31.9
	0.2	26.4
	4E-4	20.9
Polyethylene Glycol (PEG) low molecular weight	100000	31.9
	17500	29.7
	316	28.6
	0.6	25.3

7E-4	19.4	

Table 2. Fitting parameters for the data points.

	γ_0 ($J/m^2 \times 10^3$)	γ_∞ ($J/m^2 \times 10^3$)	P_0 (N/m^2)
PEG	16.2	35.2	0.10
PEGLmw	13.5	31.9	0.03
PS	11.6	27.5	1.15
PI	13.5	28.1	226.2
PDMS	9.2	13.1	9.6
PDMSLmw	7.6	13.4	1.19E-3
PP	9.8	23.0	0.31

Figures

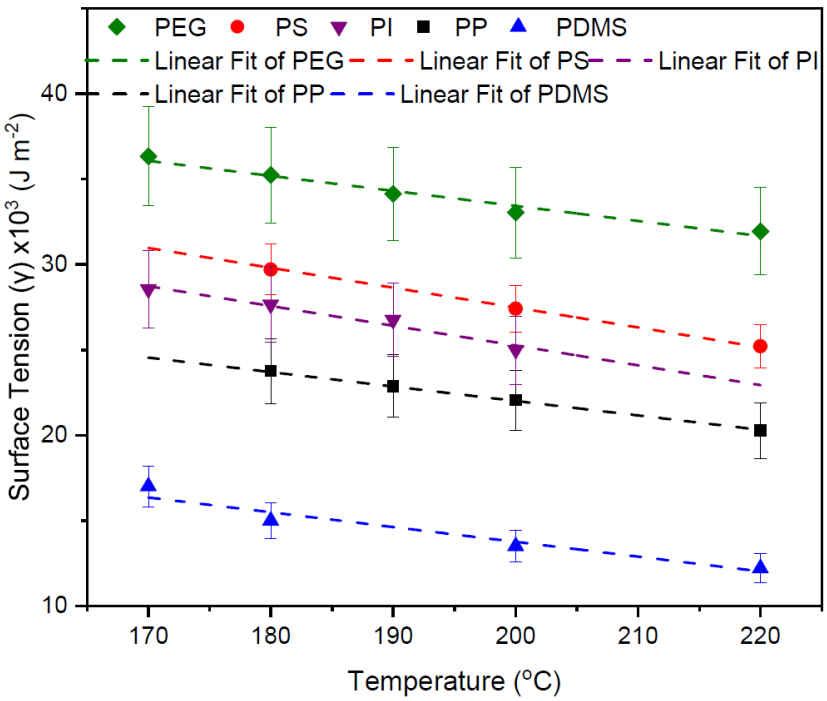

Fig. 1. Temperature dependence of surface tension of polymer melts. Surface tension (γ) as a function of temperature for different polymers (PEG (green filled circle), PS (red filled circle), PI (purple filled circle), PP (black filled circle), and PDMS (blue filled circle)) under ambient pressure (~10^5 N/m^2). In this study, symbols represent experimental data points, and dashed lines indicate linear fits to the experimental data. For all polymers, γ decreases monotonically with increasing temperature. Error bars represent the standard error of the mean from five independent measurements.

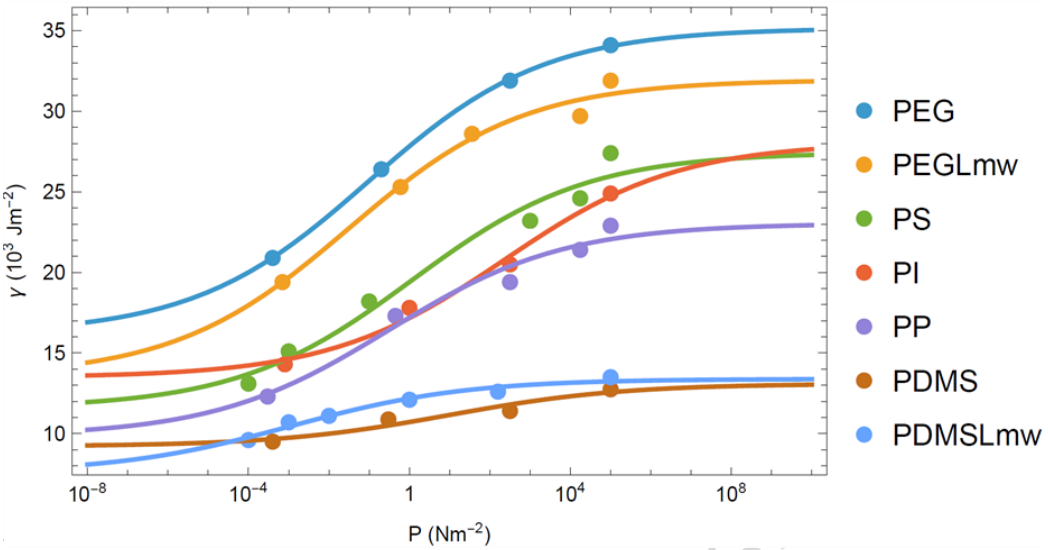

Fig. 2 Pressure dependence of surface tension of polymer melts. Log-linear plot of surface tension data for PEG (blue filled circle), low molecular weight PEG (PEGLmw) (orange filled circle), PS (green filled circle), PI (red filled circle), PP (purple filled circle), PDMS (red filled circle), and low molecular weight PDMS (PDMSLmw) (light blue filled circle) in the high vacuum range (~10^5 - 10^{-4} N/m^2) at 200 ^{o}C. The measured surface tension decreases systematically with decreasing air pressure, with the trend following the Hill equation. Symbols represent experimental data points, and solid lines show the corresponding best fits using the Hill equation.

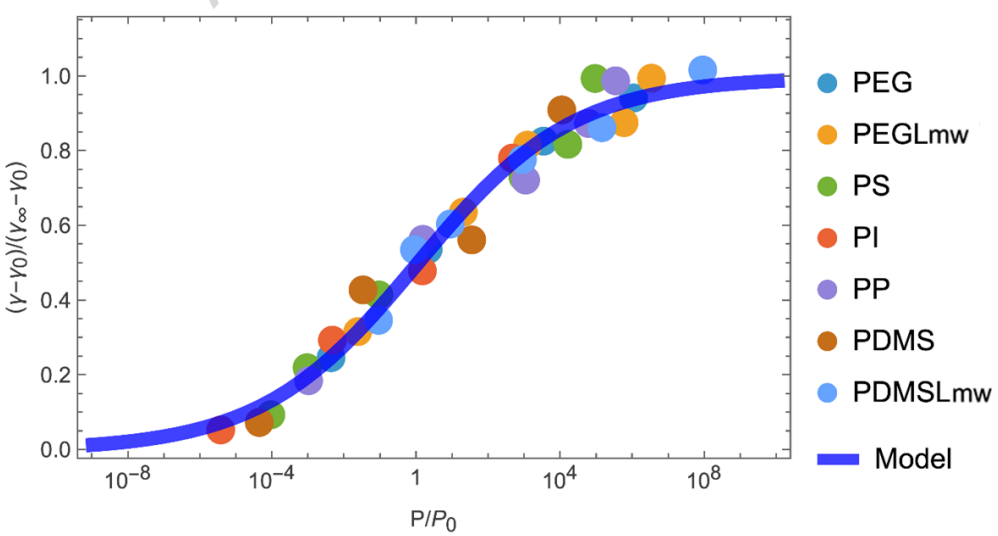

Fig. 3 Master curve of pressure dependence for polymer melts. Scaled surface tension $(\frac{\gamma-\gamma_0}{\gamma_\infty-\gamma_0})$ versus (P/P_0) for PEG (blue filled circle), low molecular weight PEG (PEGLmw) (orange filled circle), PS (green filled circle), PI (red filled circle), PP (purple filled circle), PDMS (red filled circle), and low molecular weight PDMS (PDMSLmw) (light blue filled circle). Symbols denote scaled experimental data, and the solid curve shows the model using the Hill equation, demonstrating that all the data points fall on a master curve (solid blue line).

Editorial Summary

The surface tension of polymers under ambient or high-pressure conditions has been extensively studied but it remains much less explored under high vacuum conditions. Here the authors study the effect of air pressure on the surface tension of polymer melts.

Peer review information: *Nature Communications* thanks the anonymous reviewers for their contribution to the peer review of this work. A peer review file is available.