

Shifting Dynamics of Polymer Thin Films

David Durden

Literature Seminar

October 31, 2021

Polymer thin films have become integral to our manufacturing process for many industries, from electronics to pharmaceuticals, and look to only become more prominent in the future.^{1,2} Despite this, the dynamics of films with thicknesses lower than ~ 100 nm are not well understood compared to their bulk counterparts. It is known that the behavior of these films, specifically its glass transition temperature T_g , varies significantly from the bulk material at low thicknesses; there appear to be many factors influencing the change but the details of each remain unclear. Recently, these dynamics have been probed by a large variety of different experimental techniques in an attempt to deduce the dynamics and, in so doing, explain the behavior of these unique systems.

The oldest, and still one of the most common, techniques for determining T_g of polymer films is ellipsometry.³ The refractive index and thickness of a film changes as a function of temperature, however the slope of this change is dependent upon whether the film is in its amorphous or glassy state. By looking at where the slope of the response changes, the glass transition temperature of the polymer can be identified. It was found early into the investigation of these properties that T_g varied significantly from the bulk, often decreasing on the order of 10 K for many types of polymers. As the field progressed, other methods including broadband dielectric spectroscopy (BDS) and differential scanning calorimetry (DSC) were used to analyze T_g , however this initially led to further confusion rather than clarification because different techniques often gave different results for the same polymer. A clear showcase of this is figure 1 from a review paper by Kremer et al. of different polystyrene T_g analysis papers.⁴ In it, one can see that even the same technique often gives different results for T_g dependent on experimental conditions and film thickness. In recent years, the focus has changed from a pursuit of determining a single physical quantity, T_g , to determining the nature of the dynamics which ultimately lead to the changing T_g .

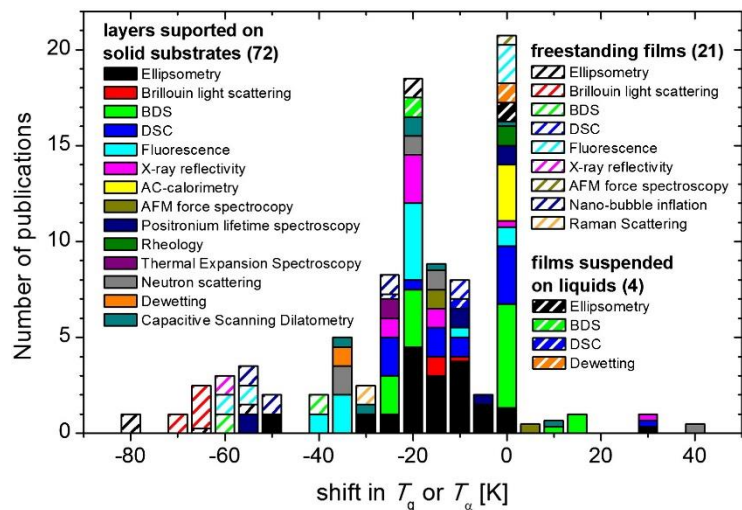


Figure 1. Different reported T_g values for polystyrene films. Each increment represents one published paper. Total of 92 papers represented, published between 1993 and 2014.⁴

One of the most interesting findings was the discovery that the polymer dynamics was very dependent on proximity to film interfaces as well as the composition of those interfaces. It is currently believed that the dynamics slow down near substrate interfaces

but speed up near the free surface. One demonstration of this was performed by Glor et al. in a 2017 study in which an ultra-thin film (<16 nm) was found to have two separate T_g 's.⁵ In this experiment, a thin film of poly (2-vinyl pyridine) on a silicon substrate was heated above its glass transition then cooled at a rate of 1K/min. During this, ellipsometric measurements were taken and it was found that there was not one, but two different changes in the coefficient of thermal expansion suggesting that there

were two separate T_g 's for representing two different layers of the film, as seen in figure 2. Other measurements made at faster cooling rates showed a broadening of T_g as the cooling rate decreased. It was hypothesized that the break in the two T_g 's was due to a complete decoupling of the dynamics between the surface and substrate layers. The changing T_g behavior due to proximity to different interfaces supports a simulated molecular dynamics model made by Mangalara et al. that proposes a dynamics gradient for each interface.⁶

The dynamics of polymer films are also dependent on the type of substrate that is present. For polystyrene, Zuo et al. found that increasing the phenyl group content of the surface of the substrate increased the viscosity of the film in its glassy state.⁷ This effect was more pronounced for thinner films and higher M_w polystyrene molecules; above a certain thickness threshold, it was found that the viscosity of the polymer returned to the bulk value for polystyrene. By performing this kind of measurement for other polymer/substrate pairs, it is possible to get deeper insight into the distance over which film dynamics are affected by the substrate.

In addition to cooling rate, film thickness, and polymer and substrate composition, there are many other parameters which can affect the dynamics of polymer films; a more complete analysis of these parameters was performed by Li et al. in their excellent review paper on the topic.⁸ One particularly notable parameter is the geometry of the film and its

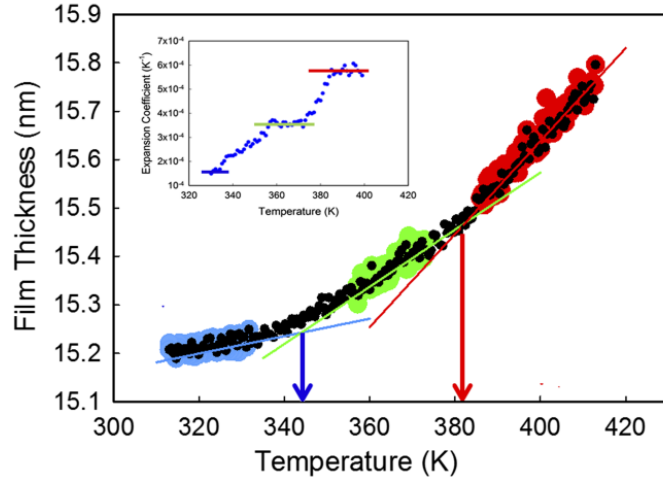


Figure 2. Three different regions of thermal expansion. The two transitions correspond to two different glass transition temperatures⁵

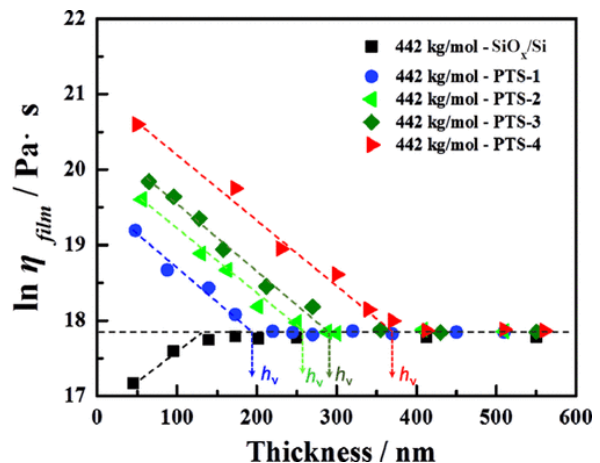


Figure 3. Viscosity vs film thickness at varying phenyl content. PTS-1 is lowest phenyl content with the lowest viscosity and PTS-4 is the highest phenyl content with the highest viscosity

interfaces. For example, Unni et al. found that increasing the surface roughness caused an increase in the T_g of a poly(4-chloro styrene) film; they hypothesized this increase was due to increasing substrate-polymer interactions.⁹ Additionally, freestanding films and capped films, films sandwiched between two substrates, can have significantly different dynamics than films with one substrate and one free interface.¹⁰ Capped films are particularly notable as they are often cited as analogues to polymer nanocomposites, which are a relatively new material type in which nanoparticles are dispersed in a polymer matrix.¹¹

Currently, causes for the shift in the dynamics of polymer thin films are being investigated but are as of yet not fully understood. What is known, however, is that for very thin films, the behavior of the polymer differs greatly from what is expected of the bulk and can differ within the film itself depending on its proximity to various interfaces. It also appears to vary with many other parameters such as film confinement and substrate composition. As this new field matures, further exploration into the nature of the interaction between the film and its interfaces will be key to understanding the behavior of this prominent material.

References

1. Felton, L. A.; Porter, S. C. An update on pharmaceutical film coating for drug delivery. *Expert Opinion on Drug Delivery*. **2013**, 10 (4), 421-435
2. Stingelin-Stutzmann, N.; Smits, E.; Wondergem, H.; Tanase, C.; Blom, P.; Smith, P.; de Leeuw, D. Organic thin-film electronics from vitreous solution-processed rubrene hypereutectics. **2005**, 4, 601-606
3. Beaucage, G.; Composto, R.; Stein, R. S. Ellipsometric study of the glass transition and thermal expansion coefficients of thin polymer films. *J. Polym. Sci. B. Polym. Phys.* **1993**, 31 (3), 319-326.
4. Kremer, F.; Tress, M.; Mapesa, E. U. Glassy dynamics and glass transition in nanometric layers and films: A silver lining on the horizon. *Journal of Non-Crystalline Solids*. **2015**, 407, 277-283
5. Glor, E. C.; Angrand, G. V.; Fakhraia, Z. Exploring the broadening and the existence of two glass transitions due to competing interfacial effects in thin, supported polymer films. *J. Chem. Phys.* **2017**, 146, 203330.
6. Mangalara, J. H.; Mackura, M. E.; Marvin, M. D.; Simmons, D. S. The relationship between dynamic and pseudo-thermodynamic measures of the glass transition temperature in nanostructured materials. *J. Chem. Phys.* **2017**, 146, 203316
7. Zuo, B.; Wang, F.; Hao, Z.; He, H.; Zhang, S.; Priestley, R. D.; Wang, X. Influence of the Interfacial Effect on Polymer Thin-Film Dynamics Scaled by the Distance of Chain Mobility Suppression by the Substrate. *Macromolecules*. **2019**, 52 (10), 3753-3762
8. Li, B.; Zhang, S.; Andre, J. S.; Chen, Z. Relaxation behavior of polymer thin films: Effects of free surface, buried interface, and geometrical confinement. *Progress in Polymer Science*. **2021**, 120, 101431
9. Cheng, S.; Carroll, B.; Bocharova, V.; Carrillo, J.; Sumpter, B. G.; Sokolov, A. P. Focus: Structure and dynamics of the interfacial layer in polymer nanocomposites with attractive interactions. *J. Chem. Phys.* **2017**, 146, 203201
10. Forrest, J. A.; Dalnoki-Veress, K.; Dutcher, J. R. Interface and chain confinement effects on the glass transition temperature of thin polymer films. *Physical Review E*, **1997** 56 (5) 5705
11. Unni, A. B.; Chat, K.; Duarte, D. M.; Wojtyniak, M.; Geppert-Rybczyńska, M.; Kuback, J. Experimental evidence on the effect of substrate roughness on segmental dynamics of confined polymer films. *Polymer*. **2020**, 199, 122501