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Capillary Rise Infiltration (cari) Of Polymer In Nanoparticle Packings

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Capillary Rise Infiltration (cari) Of Polymer In Nanoparticle Packings

Abstract
Capillary rise infiltration (CaRI) enables the fabrication of polymer nanocomposite films (PNCFs) with high nanoparticle loading (> 50 vol%). The process involves generating a bilayer of nanoparticle and polymer film, and thermally annealing the film above the glass transition temperature (Tg) of the polymer to induce polymer imbibition into the voids in the nanoparticle packing. Upon CaRI, polymer experiences strong physical confinement within the nanoparticle packing, which may lead to changes in the polymer properties and the infiltration dynamics, subsequently affecting the macroscopic PNCF structure and properties. As such, understanding polymer behavior under confinement is crucial to enable optimal process and nanocomposite design.

In this work, we study the effect of physical confinement, polymer-nanoparticle interactions, and undersaturation on the polymer CaRI dynamics. We utilize in situ spectroscopic ellipsometry to determine the effective polymer viscosity based on the Lucas-Washburn analysis, and to determine the polymer Tg when confined in the nanoparticle packing. We observe increased polymer viscosity and Tg with confinement, until a threshold confinement ratio is reached. Furthermore, under extreme nanoconfinement, the polymer-nanoparticle interaction is negligible relative to the confinement effect. In undersaturated CaRI (UCaRI), such that a bilayer film with insufficient polymer to completely fill the void space in the nanoparticle packing is annealed, there is a two-stage filling process – a rapid capillary rise with a clear invading front, and a gradual polymer spreading likely via surface diffusion. As such, the UCaRI process enables the fabrication of nanoporous polymer-infiltrated nanoparticle films with uniform or gradient composition, depending on the annealing time and polymer volume fraction. These UCaRI films also have tunable optical and mechanical properties with polymer composition. Finally, we characterize the fracture toughness of UCaRI films based on a nanoindentation-based pillar splitting method. We show that confinement-induced polymer capillary bridges and chain bridging of nanoparticles to drastically toughen the UCaRI film, even upon infiltrating small amounts of polymer. Thus, this work provides insights to the processing-structure-property relationships of the CaRI process to generate functional nanocomposite films with high nanoparticle loadings.

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CAPILLARY RISE INFILTRATION (CARI) OF POLYMER IN NANOPARTICLE PACKINGS

Jyo Lyn Hor

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2018

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ABSTRACT

CAPILLARY RISE INFILTRATION (CARI) OF POLYMER IN NANOPARTICLE PACKINGS

Jyo Lyn Hor
Daeyeon Lee

Capillary rise infiltration (CaRI) enables the fabrication of polymer nanocomposite films (PNCFs) with high nanoparticle loading (> 50 vol%). The process involves generating a bilayer of nanoparticle and polymer film, and thermally annealing the film above the glass transition temperature ($T_g$) of the polymer to induce polymer imbibition into the voids in the nanoparticle packing. Upon CaRI, polymer experiences strong physical confinement within the nanoparticle packing, which may lead to changes in the polymer properties and the infiltration dynamics, subsequently affecting the macroscopic PNCF structure and properties. As such, understanding polymer behavior under confinement is crucial to enable optimal process and nanocomposite design.

In this work, we study the effect of physical confinement, polymer-nanoparticle interactions, and undersaturation on the polymer CaRI dynamics. We utilize in situ spectroscopic ellipsometry to determine the effective polymer viscosity based on the Lucas-Washburn analysis, and to determine the polymer $T_g$ when confined in the nanoparticle packing. We observe increased polymer viscosity and $T_g$ with confinement, until a threshold confinement ratio is reached. Furthermore, under extreme nanoconfinement, the polymer-nanoparticle interaction is negligible relative to the
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Chapter 1. Introduction

1.1 Background: Polymer Nanocomposite Films

Polymers are molecules composed of many basic building units, called monomers. Nanoparticles (NPs) are microscopic particles with at least one spatial dimension of 100nm or less. Polymer nanocomposite films (PNCFs) are films composed of a mixture of NPs and polymer, such that it derives the functionality and processability from either phase, which leads to synergistic mechanical, transport, catalytic, and optical properties. Since the early focus of developing PNCs for tires by the addition of carbon black to rubber polymers, PNCs today have expanded to a wide range of NPs and polymers for tailored applications. For instance, carbon nanotubes and graphene sheets have been used to enhance electrical properties of PNCs; whereas nanosheets, nanorods, and other anisotropic nanoparticles have been found to mechanically reinforce PNCs.

By incorporating NPs into a polymer matrix, whereby the NPs are on the order of the polymer size, often described by the polymer radius of gyration ($R_g$), the NPs can perturb the polymer chain conformation in the polymer-NP interface. This structural perturbation of polymer in the interface, in turn, can lead to dramatic deviation of the polymer properties in the interface from the bulk, which may dominate in the PNCFs macroscopic properties due to the large interfacial area to volume ratio in PNCFs.
1.2 Polymer Nanocomposite Films with High Nanoparticle Loading

Present applications of polymer nanocomposites (PNCs) include car tires, packaging materials, and automotive parts, which typically incorporate small loadings of NPs; that is, the NPs form the minority phase of the composite (< 50 vol%). As such, highly loaded PNCs, with NPs constituting the majority phase (> 50 vol%), are still relatively unexploited in the PNC design parameter space. Interestingly, highly loaded PNCs exist abundantly in nature, such as nacre, tortoise shell, and dactyl club of a mantis shrimp, which exhibit superb mechanical properties. Bioinspired PNCs with high NP loading are therefore increasingly attractive to derive enhanced mechanical performance for applications in structural coatings. Besides, highly loaded PNCFs also show promising applications in separation systems and energy storage and conversion. For example, perovskite solar cells incorporating polymer scaffold with high concentrations of perovskite crystals show high energy conversion efficiency, and the thermal conductivity of thermal energy storage device increases with NP loading. Separation membranes with high concentrations of NPs also show enhanced permeability and selectivity, overcoming the traditional trade-off between these two separation properties.

The fabrication of PNCFs with high loading of NPs is however, challenging. The most common technique to prepare PNCFs is by melt- or solution-compounding, whereby NPs are added or mixed into a melt or solution of polymer. However, these compounding approaches are challenging for high concentrations of NPs due to the high viscosity of the mixture, as well as the NPs’ tendency to aggregate. This limitation is exacerbated when
using anisotropic NPs. *In situ* polymerization involves mixing the NPs into monomer solution, followed by polymerization of the monomers,\(^{33}\) thereby achieving mixtures with lower viscosity and higher processability. However, this technique is limited to only certain polymers and the polymerization step may not be well controlled, which leads to incomplete polymerization and polydisperse polymers.\(^{34}\) Layer-by-Layer (LbL) assembly enables generation of highly loaded PNCFs by depositing oppositely charged polymer and NPs alternatingly and in a sequential manner,\(^{35-38}\) but the process tends to be time-intensive and limited to water-soluble charged species.\(^{39}\) As such, a simple yet robust processing technique that enables to the fabrication of PNCFs with high loading of NPs is desirable for various potential applications.

### 1.3 Capillary Rise Infiltration (CaRI)

To address this issue, a simple thermally-induced, capillarity-based process to generate PNCFs with uniform distribution of nanoparticles at extremely high NP fraction (> 50 vol\%) is recently developed. As shown in Figure 1.1, this process involves first generating a bilayer film composed of a NP layer and a polymer layer, followed by thermally annealing the bilayer above the glass transition temperature \(T_g\) of the polymer to induce polymer wicking into the voids in the NP packing. We termed the process capillary rise infiltration (CaRI) to reflect the similarity of the polymer infiltration to ubiquitous capillarity processes, such as water wicking into porous media and drawing of water into a straw.\(^{40}\) Accordingly, our preceding work confirmed that the CaRI obeys the Lucas-Washburn model, which relates the rate of liquid infiltration into a porous medium to the geometry of the medium and the liquid properties.\(^{41}\) In fact, polymer infiltration into
anodized aluminum oxide (AAO) templates,\textsuperscript{42,43} nanotubes,\textsuperscript{44–46} NP packing,\textsuperscript{47} and other cylindrical pores\textsuperscript{48–51} show similar Lucas-Washburn behavior. We validated that CaRI of polymer is applicable to NP packings of various aspect ratios, and in all cases tested we reported enhanced hardness, modulus, scratch, and wear resistance of CaRI PNCFs than those of their individual constituents.\textsuperscript{40} We regard CaRI PNCFs as a new class of NCFs with NP as the majority phase and will henceforth refer to them as polymer-infiltrated nanoparticle films (PINFs), which more accurately reflects the morphology of our model systems.

Figure 1.1 Schematic illustration of the capillary rise infiltration (CaRI) process of a polymer into voids of a densely packed nanoparticle packing to generate a PINF.

1.4 Nanoconfinement of Polymer in NP Packings

Because we generate the NP packing via spin-coating of aqueous suspension of NPs, the NP packing is random and disordered, with a porosity of \(\sim 35 – 45\ vol\%\) depending on the NP shape and size polydispersity.\textsuperscript{40,52–55} The characteristic pore size of a random closed packing of sphere is \(\sim 30\%\) of the NP size.\textsuperscript{56} Polymer chain size is characterized by the radius of gyration \((R_g)\), whereby \(R_g\) squared is defined as the average square distance between monomers in a given conformation to the center of mass of the polymer chain,\textsuperscript{1} lies on the order of \(1 – 35\) nm depending on the polymer chain length. As such, polymer undergoing CaRI into disordered NP packings are confined in the extremely narrow pores,
comparable to the polymer $R_g$. As such, this situation presents an entirely unexplored domain of capillarity, unlike conventional capillary rise of simple liquids in porous solids where confinement effects are often negligible. For large polymers to transport through the interstices of the NP packings, they have to drastically change their conformations, as demonstrated in Figure 1.2. While this polymer conformational change is entropically unfavorable, sufficiently high capillary force driven by enthalpic interactions between the NP and polymer could force polymer to undergo CaRI.

![Figure 1.2. A simplified depiction of polymer chain in the equilibrium (bulk) state, and when confined in a densely packed NP packing after undergoing CaRI.](image)

Polymer under confinement occurs when a hard wall imposes physical constraint on a polymer phase.\textsuperscript{57} The topic of polymer under confinement has been extensively researched and there is a general acceptance that confinement leads to significant deviation of the polymer behavior from the bulk.\textsuperscript{11,58} However, there are still conflicting evidences of enhanced and suppressed polymer dynamics under confinement,\textsuperscript{59} depending on the materials, extent and geometry of confinement, and the polymer-NP interaction.
Common geometries of confinement are thin films, nanopores, and PNCs, as depicted in Figure 1.3. In polymer thin films, generally prepared through spin-coating a polymer solution onto a substrate, the thickness (i.e. the confinement length scale) can be readily controlled by the spin-coating rate and polymer solution concentration. In nanopores, polymer is infiltrated into a cylindrical porous template, such as anodic aluminum oxide (AAO)\textsuperscript{42,43,60,61} and pore glasses.\textsuperscript{57} The confinement length scale in nanopores is the pore size, which is depends on the material constituting the template. In PNCs, NPs can induce confinement, and the confinement length scale, the interparticle distance, can be controlled by varying the NP loading as well as the NP size.\textsuperscript{62} One principle challenge in studying confinement behaviors involve decoupling the physical nanoconfinement from the interfacial effect stemming from the polymer-NP and the polymer-air interfaces.\textsuperscript{59,63–67} This challenge is especially prevalent in polymer thin films, where free surface effects may dominate the overall dynamics.\textsuperscript{68} Whereas in nanopores and PNCs, the large polymer-NP interfacial area typically renders the surface effects negligible. Sandwiched thin films have also been studied as model nanocomposites to unify polymer dynamics across different confinement geometries.\textsuperscript{66,69} On the polymer-solid interface, interaction strengths are typically categorized into attractive or repulsive interaction, depending on the presence (or absence thereof) of hydrogen bonding or other bonding types.
In literature, both polymer segmental and chain dynamics under confinement have been reported. The polymer segmental motion is determined either through relaxation time measurements, or glass transition temperature (T_g), which is typically attributed to the arresting of segmental modes of motion in bulk polymers. These two parameters are correlated by way of the dynamical T_g being the temperature at which the segmental relaxation time equals 100 seconds, which has been validated using differential scanning calorimetry (DSC) and spectroscopic ellipsometry upon cooling at 10K/min. In polymer thin films, the T_g is often influenced by both substrate and free surface. It is generally reported that systems with strong and weak polymer-substrate interaction experience increasing and decreasing T_g with decreasing film thickness, respectively. In PNCs and nanopores, there have been reports of increase, no change, and decrease in segmental relaxation time. There have also been reports in increase, no change, and decrease of polymer T_g under confinement. Some systems also display multiple T_g’s owing to competing interfacial effects.

Polymer chain dynamics are typically quantified by the diffusion coefficient or viscosity. Under confinement, polymer diffusion has been reported to slow down near attractive
substrate\textsuperscript{14} and nanoparticles,\textsuperscript{89,90} as well as non-attractive nanoparticles.\textsuperscript{91–93} On the contrary, there have also been reports of increased chain mobility under confinement, which are often attributed to chain disentanglement effects under nanoconfinement.\textsuperscript{42,85,94} Other interesting polymer behaviors have also been reported in PNCs with anisotropic NPs, whereby polymer diffusion slows down at low NP concentration and recovers to bulk above the NP percolation threshold.\textsuperscript{95} Viscosity of PNCs have also been reported to increase\textsuperscript{96–98} and decrease\textsuperscript{99–103} relative to the bulk polymer.

Polymer behavior under confinement remains a question of tremendous interest because such understanding is crucial for optimizing processing parameters for fabrication of PNCFs. In our CaRI PINFs, the extremely high NP loading of > 50 vol\% creates strong confinement environment not otherwise easily achievable in conventional PNCFs and nanopores. The degree of confinement can be tuned in a straightforward manner by varying the NP size and polymer size. Furthermore, the effect of polymer-NP interaction under nanoconfinement can be explored because the CaRI process is robust across a wide range of polymer and NPs.\textsuperscript{52}

1.5 Polymer Wetting Behavior under Nanoconfinement

An emerging challenge in the field of interface science is to understand the effect of nanoconfinement on the dynamics of soft matter systems such as colloids and polymers.\textsuperscript{104} For instance, increasing the NP volume fraction in PNCFs increasingly perturb the polymer chains, which may lead to significant deviation of the polymer properties relative to its bulk counterpart. The notion of describing these interaction strengths using macroscopic contact angles may not be inadequate in the nanoscale, whereby interfacial effects may be
amplified and contribute to disjoining pressure, a phenomenon that has been attributed to the formation of prewetting films in spreading liquid thin films. Furthermore, functional PNCFs are often generated with solid NPs and polymer, with relatively high interfacial tension relative to polymer surface tension, which may drive the spreading of polymer, especially under nanoconfinement. In prior studies, microscopic precursor films of polymer have been observed in spreading polymer melt and ahead of a polymer melt meniscus undergoing capillary rise. As such, we propose to explore and utilize this polymer spreading, alongside CaRI, to generate nanoporous PINFs and study their corresponding processing-structure-property relationship.

1.6 Thesis Outline

To develop and subsequently scale up the production of CaRI PINFs, it is essential to understand the polymer CaRI dynamics to optimize processing parameters, such as annealing time and temperature. Besides, it is also crucial to recognize the applicability and limitations of the CaRI process by exploring the PINF design parameter space, as well as identifying the how these factors influence the PINF’s macroscopic properties. Therefore, the goal of this thesis is to develop a more in-depth understanding of the fundamental principles governing the polymer CaRI process into a NP packing, and to develop the processing-structure-property relationship of the CaRI nanocomposites. This thesis will aim to tackle the following fundamental questions:

- How does physical nanoconfinement affect the polymer CaRI dynamics?
- How does polymer-nanoparticle interaction affect the polymer CaRI dynamics?
• What happens when an undersaturated NP/polymer bilayer film \( (i.e. \text{ insufficient polymer to fill the interstitial void volume in the NP packing}) \) undergoes CaRI?
• Following the previous question, what is the processing-structure-property relationship of these corresponding undersaturated CaRI PINFs?

In Chapter 2, we study the effect of physical nanoconfinement on the viscosity and glass transition temperature \( (T_g) \) of unentangled polymer during CaRI. We systematically tune the confinement ratio \( (CR) \) in our model systems, defined as the ratio of the polymer \( R_g \) to the average pore radius \( R_{pore} \), by varying the polymer molecular weight and the NP size. We found that under nanoconfinement, the polymer exhibits higher-than-bulk viscosity and \( T_g \). Furthermore, we observe that viscosity and \( T_g \) of the confined polymer increases with \( CR \) and plateaus above a threshold of \( CR \sim 1 \). As the increase in viscosity highly correlates with the increase in \( T_g \), we believe that the slowdown in chain dynamics may be a direct consequence of the slowdown in segmental motion of the polymer under physical nanoconfinement.

In Chapter 3, we study the effect polymer-nanoparticle interaction on the viscosity and \( T_g \) of unentangled polymer during CaRI.\(^{55}\) We use two polymers which interact strongly and weakly, respectively, with silica NPs. We find that both polymers exhibit higher-than-bulk viscosity and \( T_g \) values. Furthermore, the increase in viscosity and \( T_g \) relative to the bulk is comparable across the polymers, which suggests that under strong nanoconfinement, the confinement effect dominates the polymer-NP interaction effect.
In Chapter 4, we explore undersaturated CaRI (UCaRI) of polymer, such that there is insufficient polymer to completely fill the voids in the NP packing. We determine the polymer UCaRI dynamics and characterize the processing-structure-property relationship of the UCaRI PINFs. We observe polymer infiltration occurring in two steps: first via a capillarity-induced infiltration, followed by a spreading process likely due to surface diffusion. We can vary the annealing time and consequently extent of polymer spreading, which enables us to generate either uniform or graded nanoporous UCaRI PINFs. We can tune the optical and mechanical properties by varying the extent of undersaturation or polymer volume fraction in the NP packing.

In Chapter 5, we study the fracture properties of UCaRI films. We observe that the fracture toughness of the UCaRI PINFs increases with polymer volume fraction. Even at very low polymer volume fraction, there is substantial toughening of the NP packings, which we attribute to the confinement-induced formation of polymer capillary bridges. Increasing polymer molecular weight further toughens the nanoparticle packing at low polymer volume fraction, which suggests the role of multiple nanoparticle bridging by the stretched polymer chains under nanoconfinement.

Finally, Chapter 6 summarizes this thesis and proposes future directions to further our understanding in polymer CaRI dynamics and apply CaRI for fabrication of biomimetic functional coatings.
Chapter 2. Effect of Weakly Interacting Physical Nanoconfinement on the Viscosity of Unentangled Polymers during Capillary Rise Infiltration

This chapter is adapted from work that is under preparation for publication, and this work is performed in collaboration with Haonan Wang and Zahra Fakhraai from the Department of Chemistry at the University of Pennsylvania.

2.1 Introduction

Physical confinement of polymers occurs in a wide range of applications including nanostructured polymers in solar cells,\textsuperscript{28,109} electronic components,\textsuperscript{110} protective coatings,\textsuperscript{33,53} energy storage devices\textsuperscript{111} and separation systems.\textsuperscript{25} Confinement of polymers to nanoscopic dimensions\textsuperscript{57} can induce drastic changes in their properties and dynamics.\textsuperscript{11} In some cases, confinement-induced changes can be deleterious for the final applications of confined polymers due to their poor structural integrity relative to the bulk. For instance, polymers intercalated in between graphene oxide sheets have lower decomposition temperature than their bulk counterparts.\textsuperscript{112} Polymer chains confined in thin films show reduced elastic modulus and fracture strength with decreasing thickness.\textsuperscript{113–115} Thus, to enable new applications and to circumvent potential pitfalls that may result from unexpected changes in the properties of confined polymers, it is extremely important to understand the effect of physical confinement on the properties of polymers.

Nanocomposites made of mixtures of polymers and nanoparticles represent one common system whereby nanoparticles can intrinsically impose physical confinement onto polymer chains. In particular, when there is a high volume fraction of nanoparticles and the nanoparticles are small, a large volume fraction of polymers present in the composite
is within the interfacial region of the nanoparticles; that is, polymers are in the vicinity of solid surfaces and their properties may be affected.\textsuperscript{62,89,92,93,116} When the volume fraction of the nanoparticles is above certain limits (for example, 50 vol\%), the interparticle distance can become comparable or smaller than the characteristic size of polymer chains,\textsuperscript{62,89,92,93,116} inducing significant confinement on the polymer chains, which results in changes in the dynamics and mechanical properties of polymers.\textsuperscript{11} Interestingly, several naturally-occurring nanocomposites have emergent properties that stem from the presence of extremely large volume fractions of nanoparticles and small fractions of highly confined polymer phase. Nacre, known for its ultrahigh strength and toughness, is made of more than 90 vol\% rigid nanoplatelets and less than 10\% of proteinaceous polymers.\textsuperscript{18}

Capillary rise infiltration (CaRI) relies on the infiltration of polymers into dense nanoparticle packings via capillarity and thus enables manufacturing of nanocomposite films with extremely high volume fractions of nanoparticles (> 50 vol\%) with a relatively simple procedure.\textsuperscript{40,47,52–55} The CaRI method circumvents processing challenges associated with the fabrication of highly filled nanocomposites using conventional methods such as compounding and layer-by-layer assembly.\textsuperscript{117,118} Moreover, CaRI represents a powerful method to induce extreme nanoconfinement of polymers because the characteristic pore size in the disordered packings of spherical nanoparticles is approximately 30\% of the nanoparticle size\textsuperscript{56}, which can be comparable to or smaller than the dimension of unperturbed polymer chains. In other words, CaRI enables a simple approach of confining polymers in extremely small pores (< 10 nm), comparable to the polymer’s radius of gyration (R\textsubscript{g}) and tuning of average pore radius (R\textsubscript{pore}) based on nanoparticle sizes, \textit{i.e.}
smaller nanoparticles confine the polymer more strongly. To enable efficient production of CaRI nanocomposites, it is critical to understand the effect of extreme nanoconfinement on the capillarity-based transport phenomena.

In this work, we study the effect of physical nanoconfinement on the unentangled polymer viscosity during capillary rise infiltration (CaRI). We focus on unentangled polymers to rule out the effect of polymer disentanglement, which has been attributed to enhanced mobility of confined polymer in prior studies.\textsuperscript{42,94,119} Unentangled polymer networks with reversible bonds have shown to exhibit self-healing properties,\textsuperscript{120} hence could potentially be useful for the generation of bioinspired nanocomposites. For our experimental systems, we use polystyrene (PS) and silica nanoparticles (SiO$_2$ NPs), which have weak polymer-nanoparticle interaction. In our prior work, we showed that physical confinement effects dominate over polymer-nanoparticle interactions in affecting the polymer infiltration dynamics.\textsuperscript{55} We have also shown that confinement effects dominate over free surface effects in determining the glass transition temperature of weakly interacting polymers in undersaturated CaRI composite films.\textsuperscript{121} Thus, this weakly-interacting PS-SiO$_2$ NP pair represents an ideal model system to study the effect of physical confinement on the CaRI dynamics and glass transition temperature of polymers by systematically varying the relative sizes of pores and polymers. We tune the confinement ratio (CR), defined as the ratio of the bulk polymer $R_g$ to the $R_{pore}$, by using combinations of unentangled PS with various molecular weights and SiO$_2$ NPs of varying diameters. We show that under extreme nanoconfinement, unentangled PS exhibits higher-than-bulk viscosity and glass transition temperature ($T_g$). Specifically, we observe increasing confined polymer viscosity
and $T_g$ with CR until CR $\sim$ 1, i.e. when $R_g$ is comparable to $R_{pore}$, above which the confined polymer viscosity and $T_g$ values plateau. The similar trends observed in the viscosity and $T_g$ of unentangled PS suggest that the slowdown in the chain dynamics is strongly correlated to the slowdown in the segmental dynamics.

2.2 Experimental Section

2.2.1 Materials

Polystyrene (PS) (8k PS, $M_n = 8,000 \text{ g mol}^{-1}$, PDI = 1.10; 21k PS, $M_n = 21,000 \text{ g mol}^{-1}$, PDI = 1.04) are purchased from Polymer Source Inc. 13k PS ($M_w = 13,000 \text{ g mol}^{-1}$, PDI = 1.06) is purchased from Pressure Chemical Company, whereas 19k PS ($M_w = 18,700 \text{ g mol}^{-1}$) is purchased from Aldrich Chemical Company. Aqueous suspensions of silica nanoparticles (SiO$_2$ NP) with diameters of 9 nm (LUDOX SM-30, 30 wt% suspension in water) and 27 nm (LUDOX TM-50, 50 wt% suspension in water) are purchased from Sigma Aldrich, those with diameters 56 nm (SNOWTEX ST-OL Silica, 29.6 wt% suspension in water) and 77 nm (SNOWTEX ST-YL Silica, 40.4 wt% suspension in water) are obtained from Nissan Chemical America Corp. 130 nm and 200 nm SiO$_2$ NPs are synthesized using a modified Stöber method.$^{122,123}$ The NP size distribution is determined from literature$^{124}$ and using scanning electron microscopy (SEM) image analysis, as shown in Figure 2.1.

2.2.2 Preparation and characterization of bilayer and trilayer films

Silicon wafers are cut into approximately 1 cm x 1 cm squares. The wafers are rinsed with acetone, isopropanol, and deionized water, and dried with air, before further cleaned by oxygen plasma treatment for $\sim$5 mins. 6 wt% PS solution is prepared by dissolving PS in
toluene. The SiO$_2$ NP suspension is diluted to 10 – 15 wt% using water. All solutions are bath-sonicated for at least 2 hours and filtered prior to use. The 200 nm thick PS layer is deposited by spin-coating the 6 wt% PS solution at 3000 rpm for 30 s onto the cleaned silicon wafer using a WS-400BZ-6NPP/Lite spin-coater from Laurell Technologies Corporation. Then, the polymer film is oxygen plasma-treated for ~2 s to render the film surface hydrophilic, on which the SiO$_2$ NP suspension is deposited is spin-coated at 3000 rpm for 30s to generate a ~200 nm SiO$_2$ NP.

Figure 2.1. SiO$_2$ nanoparticle size distribution for nanoparticles with diameters (a) 27 nm (measured 27.1 ± 4.3 nm (count = 115)), (b) 56 nm (measured 56.1 ± 11.5 nm (count = 314)), (c) 77 nm (measured 77.4 ± 14.0 nm (count = 108)). The size distribution is determined from SEM images.

To generate trilayer samples consisting of two sequentially deposited SiO$_2$ NP packings with different sizes atop ~200 nm thick 8k PS layer, 5 wt% suspensions of 9 nm and 27 nm
SiO$_2$ NPs are prepared. ~100 nm layer of each SiO$_2$ NP packing is generated by spin-coating the NP suspension at 3000 rpm on the polymer film and allowed to dry at ambient conditions for at least an hour prior to depositing the next layer.

Scanning electron microscopy (SEM) images of the samples before and after CaRI are taken using a JEOL 7500F HRSEM. The sample is sputtered with a thin gold/palladium layer using a Cressington Sputter Coater 107 prior to imaging to prevent charging. Cross-section images are taken by cleaving across the sample using a diamond scribe and mounting the sample vertically on a stub with the sample cross section facing up toward the beam. The samples are imaged at an accelerating voltage of 5 kV, emission current 20 μA, at a working distance of ~8 mm.

2.2.3 Characterization of polymer capillary rise infiltration (CaRI) process

The polymer infiltration into the voids of the NP packing is monitored in situ using a J. A. Woollam Alpha-SE spectroscopic ellipsometer, while the bilayer sample is annealed above the glass transition temperature ($T_g$) of the polymer using a Linkam THMS350V heating stage, under constant pressure (ambient conditions). The heating stage is 22 mm in diameter, open to ambient air, and has a temperature resolution of ~1 K. The Linksys software displays the temperature and allows user to set the desired setpoint temperature, heating rate, and hold time for the setpoint temperature. To ensure good thermal contact, the sample is adhered to the heating stage using a thermal paste (Arctic Silver Ceramic polysynthetic thermal compound). The ellipsometry data is collected in the wavelength ($\lambda$) range of 380 – 900 nm at an incident angle of 70°. The CompleteEASE software package provided by J. A. Woolam enables the analysis of the raw psi ($\psi$) and delta ($\Delta$)
data by fitting to a 3-layer Cauchy model (NP packing, composite, polymer) on a silicon substrate with native oxide layer.\textsuperscript{52,55,126} The Cauchy model for each layer is expressed as 
\[ n(\lambda) = A + B/\lambda^2 + C/\lambda^4 \]
and 
\[ k(\lambda) = 0 \]
whereby A, B, and C are the optical constants, \( \lambda \) is the wavelength [\( \mu m \)], and n and k are the real and imaginary components of the index of refraction, respectively. The model fitting enables translation of the raw data into physical parameters describing the thickness and refractive index of each layer in the sample.\textsuperscript{127} The temperature at which the sample is annealed is chosen to be above the \( T_g \) of the polymer, in the range of \( T = 383 \) K to 433 K, such that the infiltration rate is still resolvable within the time resolution of the ellipsometry data.

### 2.2.4 Glass transition temperature measurements

The glass transition temperature (\( T_g \)) of the polymer confined in the NP packing is measured using a J. A. Woollam M-2000V spectroscopic ellipsometer. A polymer-infiltrated film is mounted onto a Linkam THMS 600 temperature-controlled stage attached to the ellipsometer. The \textit{in situ} ellipsometry sampling rate is 1 s with high accuracy zone-averaging. Three heating and cooling cycles between 303 K and 423 K under dry nitrogen flow are performed for each sample, with heating rate of 30 K/min and cooling rate of 10 K/min, respectively. \( T_g \) data is only reported upon cooling. The thickness and refractive index of the sample is determined by fitting the cooling ramp raw data to the Cauchy model. The \( T_g \) of the confined polymer for each film is determined \textit{via} the intersection of the linear fits to the supercooled and glassy regimes in the plots of nanocomposite refractive index versus temperature, as shown in Figure 2.2. The error is determined as the 95\% confidence range of the distance between the intersection of fitting lines. Since the NP packing is not
perturbed by the polymer infiltration process, the thickness of the composite layer is held constant during the dynamic data fit. The bulk polymer $T_g$ is determined using the same protocol on the residual polymer layer’s refractive index versus temperature. The $T_g$ of the bulk polymer samples are also determined using the TA Instruments Q2000 differential scanning calorimetry (DSC). For each PS, 6 mg of PS sample is placed in a non-hermetically sealed pan, and the sample is initially cooled to 293K, before subjecting it to two heating and cooling cycles from $T = 293$ K to $T = 423$ K at 10 K/min. The $T_g$ is defined as the midpoint of the step transition of the heat capacity and expressed as the average from the two cooling cycle measurements. The $T_g$ values measured are in good agreement with those reported previously.$^{128,129}$

![Figure 2.2](image_url)

Figure 2.2. The glass transition temperatures ($T_g$) of (a) 8k PS and (b) 21k PS confined in 77 nm SiO$_2$ NP packing are measured using spectroscopic ellipsometry, by determining the inflection point in the composite layer refractive index ($n$) with temperature at a cooling rate of 10 K/min. The confined polymer $T_g$ is determined from the composite layer, whereby polymer has fully filled the voids in the NP packing. The error is determined as the 95% confidence range of the distance between the intersection of the fitting lines.
2.3 Results

2.3.1 Polymer capillary rise infiltration (CaRI) dynamics

We generate bilayer films composed of a disordered dense packing of SiO₂ NPs atop a polystyrene (PS) film. We use unentangled polystyrene with molecular weights ~8,000 g mol\(^{-1}\) (8k) and ~21,000 g mol\(^{-1}\) (21k), with radii of gyration (\(R_g\)) of ~2.5 nm and ~4.0 nm, respectively, calculated based on the Kuhn segment length of each polymer.\(^1\) We use SiO₂ NP with various diameters as shown in Figure 2.3, to generate different average pore radius (\(R_{pore}\)) in which polymer is confined. The average pore size, \(R_{pore}\), is estimated based on \(R_{pore} = 0.29 \times R_{NP}\),\(^5\) where \(R_{NP}\) refers to the NP radius. The confinement ratio (CR) of polymer in the SiO₂ NP packing is defined as \(CR = R_g / R_{pore}\), as listed in Table 2.1. The polymers and NPs used in this work form CR in the range from 0.2 to 3.1. Since PS interacts weakly with SiO₂ NP, we can rule out the role of polymer-NP interaction and focus on the effect of physical confinement. Moreover, under extreme nanoconfinement of CaRI, the effect of physical confinement has been shown to affect the overall polymer chain and segmental dynamics more significantly than polymer-NP interactions.\(^{55}\) The bilayer film consisting of SiO₂ NP packing and PS is annealed above the polymer glass transition temperature (\(T_g\)) to induce polymer wicking into the void spaces in the NP packing.
Figure 2.3. SEM images of SiO$_2$ nanoparticle with diameters – (a) 9 nm (measured 8.6 ± 1.3 nm), (b) 27 nm (measured 27.1 ± 4.3 nm), (c) 56 nm (measured 56.1 ± 11.5 nm), and (d) 77 nm (measured 77.4 ± 14.0 nm). The NP size distribution for NPs in (b – d) is determined from SEM images, as shown in Figure 2.1. All scale bars are 500 nm.

Table 2.1. Silica nanoparticles by label, measured average diameter, average pore radius when densely packed, and the confinement ratio $CR = R_g / R_{pore}$ for 8k PS ($R_g \sim 2.5$nm) and 21k PS ($R_g \sim 4$nm), respectively. The average diameter of the nanoparticles are determined from SEM images (Figure 2.1) and from literature.$^{124}$

<table>
<thead>
<tr>
<th>Silica nanoparticle label</th>
<th>Measured diameter (nm)</th>
<th>Average pore radius, $R_{pore}$ (nm)</th>
<th>$CR_{8k\ PS}$</th>
<th>$CR_{21k\ PS}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>9 nm</td>
<td>8.6 ± 1.3</td>
<td>1.3 ± 0.2</td>
<td>1.88 ± 0.27</td>
<td>3.05 ± 0.44</td>
</tr>
<tr>
<td>27 nm</td>
<td>27.1 ± 4.3</td>
<td>3.9 ± 0.6</td>
<td>0.63 ± 0.10</td>
<td>1.02 ± 0.16</td>
</tr>
<tr>
<td>56 nm</td>
<td>56.1 ± 11.5</td>
<td>8.1 ± 1.7</td>
<td>0.30 ± 0.06</td>
<td>0.49 ± 0.10</td>
</tr>
<tr>
<td>77 nm</td>
<td>77.4 ± 14.0</td>
<td>11.2 ± 2.0</td>
<td>0.22 ± 0.04</td>
<td>0.35 ± 0.06</td>
</tr>
</tbody>
</table>
Figure 2.4 shows the cross-sectional SEM images of bilayer films representing the extreme cases where polymer is least confined (77 nm SiO$_2$ NP/8k PS, CR = 0.22) and most confined (9 nm SiO$_2$ NP/21k PS, CR = 3.05), before and after CaRI. After CaRI, we observe that the polymer layer becomes thinner, after the polymer infiltrates the voids in the disordered NP packing. The outline of the SiO$_2$ NP also appears less defined as polymer now covers the NPs, confirming the polymer infiltration process. The packing density of the NP packing is not altered by the CaRI process, as the average distance between the NPs remains constant following the polymer infiltration.$^{55}$

Figure 2.4. Cross-sectional SEM images of bilayer films of (a-b) 77 nm SiO$_2$ NPs atop 8k PS, (a) before and (b) after CaRI, respectively; (c-d) 9 nm SiO$_2$ NPs atop 21k PS (c) before and (d) after CaRI, respectively. These two systems represent the lowest (CR = 0.22) and highest confinement (CR = 3.05) tested in this work. All scale bars are 200 nm.
We study the dynamics of polymer CaRI using in situ spectroscopic ellipsometry, as previously described.\textsuperscript{40,52,55} During the annealing process, we monitor and collect the ellipsometry data on the bilayer sample. By analyzing the amplitude ratio ($\psi$) and phase difference ($\Delta$) to a three-layer Cauchy model, we track the changes in the thickness of the SiO$_2$ NP, composite (\textit{i.e.} PS-infiltrated SiO$_2$ NP packing), and PS layers. To reduce the degree of freedom and ensure solution uniqueness in the model, we determine and fix the refractive indices of the SiO$_2$ NP and PS layers from measurements at $\sim$383 K to account for polymer layer thermal expansion and the evaporation of condensed water in the interstices of the SiO$_2$ NP packing.

Figure 2.5(a) shows the thickness changes of the SiO$_2$ NP layer, composite layer, and the polymer layer with annealing time, in the 77 nm SiO$_2$ NP/8k PS system. During CaRI, polymer infiltrates into the voids of the NP packing, causing the thickness of the bottommost polymer layer to decrease, consistent to the SEM images in Figure 2.4. The ellipsometry model distinguishes between the unfilled and filled SiO$_2$ packing (\textit{i.e.} the composite layer) based on the refractive indices, and shows that upon thermal annealing the composite layer thickness increases as polymer invades the SiO$_2$ NP packing with a sharp front. Figure 2.5(b) shows representative composite layer thickness change for combinations of 77 nm SiO$_2$ NP, 9 nm SiO$_2$ NP, 8k PS, and 21k PS, where we observe varying rates of infiltration of polymer. Past work has shown that polymer CaRI can be modeled using the Lucas-Washburn model, which describes the infiltration dynamics of liquids into porous media.\textsuperscript{40,45,47,50–52,55}
\[ h^2 = \frac{\sigma R_{\text{pore}} \cos \theta}{4\tau^2 \mu} t \]

The parameters in the prefactor are physical parameters describing the macroscopic interaction between the polymer and NP surface (\(\sigma\) is the polymer surface tension, \(\theta\) is the contact angle of polymer on the NP surface), the pore geometry (\(R_{\text{pore}}\) is the average pore radius, \(\tau\) is the tortuosity of the infiltration path), and the polymer property (\(\mu\) is the polymer viscosity). Thus, plotting the thickness of the composite squared \((h^2)\) as a function of time \((t)\) enables us to infer the polymer viscosity undergoing CaRI,\(^{40,51,55}\) based on reported values of physical parameters from literature.\(^{42,56,130-132}\) Table 2.2 summarizes the parameters we use to determine the confined polymer viscosity \(\mu\) based on the Lucas-Washburn model. The average pore radius \(R_{\text{pore}}\) and tortuosity \(\tau\) are intrinsic to the SiO\(_2\) NP packing and are estimated based on the NP radius and the packing porosity, respectively.\(^{56,130}\) The porosity for packings of SiO\(_2\) NPs used in this study do not depend strongly on the nanoparticle size and is approximately 0.35. By measuring the initial and final thickness of the polymer layer upon infiltration, we can infer directly the amount of polymer in the interstices of the NP packing, thereby inferring the volume fraction of air before infiltration. Although this estimate may slightly overestimate the porosity due to cracks in NP films, we find that the estimated porosity is similar to that measured based on solution ellipsometry.\(^{55}\) The \(R_{\text{pore}}\) is estimated as 30% that of the NP radius, based on a modeling study of random packings of spheres and agglomerates of spheres.\(^{56}\) Although there are some differences in the size distribution of SiO\(_2\) NPs used in this study, the standard deviation of pore size is less than 2 nm and thus the four NPs used in this study provide four distinct pore sizes. The surface tension of PS (\(\sigma\)) is estimated based on the
molecular weight and temperature of the melt.\textsuperscript{131} The contact angle of PS is estimated as \(20^\circ\).\textsuperscript{42,132}

Figure 2.5. Thickness profile of the SiO\(_2\) NPs, composite, and polymer layer during CaRI in 8k PS/77 nm NP at 393 K. (b) Composite layer thickness profile during CaRI in 8k PS/77 nm NPs (393 K), 21k PS/77 nm NPs (393 K), 8k PS/9 nm NPs (403 K), and 21k PS/9 nm NPs (403 K).
Table 2.2. Parameters used in the Lucas-Washburn analysis to estimate polymer viscosity\textsuperscript{42,56,130–132}

<table>
<thead>
<tr>
<th>SiO\textsubscript{2} nanoparticle packing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanoparticle diameter (nm)</td>
</tr>
<tr>
<td>-------------------------------</td>
</tr>
<tr>
<td>9</td>
</tr>
<tr>
<td>27</td>
</tr>
<tr>
<td>56</td>
</tr>
<tr>
<td>77</td>
</tr>
</tbody>
</table>

Polymer

<table>
<thead>
<tr>
<th>PS molecular weight (g mol\textsuperscript{-1})</th>
<th>PS surface tension as function of temperature, $\sigma$ (mN m\textsuperscript{-1})</th>
<th>PS contact angle on SiO\textsubscript{2} surface, $\theta$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8,000 (8k)</td>
<td>40.5 - 0.068T</td>
<td>20</td>
</tr>
<tr>
<td>13,000 (13k)</td>
<td>42.1 - 0.068T</td>
<td>20</td>
</tr>
<tr>
<td>18,700 (19k)</td>
<td>42.1 - 0.068T</td>
<td>20</td>
</tr>
<tr>
<td>21,000 (21k)</td>
<td>42.1 - 0.068T</td>
<td>20</td>
</tr>
</tbody>
</table>

2.3.2 Effect of physical confinement on polymer dynamics

To assess the role of physical confinement, we compare the confined and bulk polymer viscosity as a function of temperature, as shown in Figure 2.6. For both 8k and 21k PS, we note a significant increase of the confined polymer viscosity relative to the bulk values which are obtained from literature\textsuperscript{133} As the size of the NP decreases, the increase in the viscosity becomes greater, indicating that increasing the degree of physical confinement by way of decreasing the pore size (decreasing the NP size), increases the polymer viscosity. This trend is true for all cases except at the highest degree of confinement in our system, whereby we see the viscosity values approximately overlap for 9 nm SiO\textsubscript{2} NP/21k PS and 27 nm SiO\textsubscript{2} NP/21k PS. This suggests that there may exist a CR threshold above which the polymer viscosity plateaus. We will revisit this point later in the discussion.
Figure 2.6. Bulk and confined polymer viscosity for (a) 8k PS and (b) 21k PS, as a function of temperature. The confined polymer data (filled markers) is labeled by the NP diameter constituting the NP packing. Each data point for the confined polymer viscosities is an average of at least two runs, and the error bar represents one standard deviation. The bulk viscosity values are obtained from literature.\textsuperscript{133}

To further demonstrate the role of confinement in slowing down polymer infiltration, we perform CaRI on a trilayer film, consisting of two distinct SiO\textsubscript{2} NP layers with different NP diameters atop the polymer layer, as shown in Figure 2.7. We denote 27 nm/9 nm or 9 nm/27 nm to indicate the top/bottom layer sequence of the SiO\textsubscript{2} NP double layers. These types of heterostructured NP packings (i.e., NP assemblies with distinct domains with different nanoparticle sizes and shapes) are important for creating multilayered Bragg reflectors\textsuperscript{126,134–136} and graded structures for enhanced damage tolerance in structural coatings.\textsuperscript{137,138} When 8k PS is induced to infiltrate these heterostructured NP packings the dynamics of CaRI through these films is distinguishable as seen in the amplitude ratio ($\psi$) and phase difference ($\Delta$) of ellipsometry data. As shown in Figure 2.8, it takes longer for the $\psi$ and $\Delta$ of 27 nm/9 nm SiO\textsubscript{2} NP/8k PS to stop changing under the same annealing
temperature (403K), indicating longer time needed for CaRI to complete as the thicknesses stop changing.

Figure 2.9 shows the refractive index profile of the films as a function of distance from substrate based on a four-layer Cauchy model, with each panel showing different stages of annealing. We see that the thickness of the pure PS layer decreases more rapidly in the 9 nm/27 nm SiO$_2$ NP/8k PS sample than in the 27 nm/9 nm SiO$_2$ NP/8k PS sample. Because the 9 nm SiO$_2$ NP packing has a smaller $R_{pore}$, it induces a higher degree of confinement, and thus polymer infiltration through this layer becomes the rate-limiting step. As polymer infiltrates the 27 nm/9 nm SiO$_2$ NP packing, the rate-limiting step occurs early in the process and subsequently limits the amount of polymer available to fill the voids in the next 27 nm SiO$_2$ NP layer. In contrast, in the case of 9 nm/27 nm SiO$_2$ NP packing, polymer infiltrates the bottom 27nm SiO$_2$ NP layer relatively quickly, and the rate-limiting infiltration only affects the top half of the film, thus leading to overall faster polymer infiltration throughout the film.
Figure 2.7. Top row: Cross-sectional SEM images of the 9 nm/27 nm SiO$_2$ NP on 8k PS (a) before and (b) after CaRI, (c) top view after CaRI. Bottom row: cross-sectional SEM images of 27 nm/9 nm SiO$_2$ NP on 8k PS (d) before and (e) after CaRI, (f) top view after CaRI. Dotted line in (a) and (d) outlines the interfaces between distinct SiO$_2$ NP layers, polymer layer, and the substrate. All scale bars are 500 nm.

Figure 2.8. Raw psi ($\psi$) and delta ($\Delta$) data obtained during capillary rise infiltration of 8k PS into a bilayer SiO$_2$ NP packing with diameters 9 nm and 27 nm using in situ spectroscopic ellipsometry. (a) and (c) show the data for 27 nm NPs atop 9 nm NPs (27 nm/9 nm), whereas (b) and (d) show the data for 8 nm NPs atop 27 nm NPs (9 nm/27 nm). The trilayer films are annealed at T = 403 K.
Polymer viscosity inferred from the Lucas-Washburn model represents the translational dynamics of the polymer as it undergoes CaRI in disordered NP packings. Our prior study showed that changes in the viscosity of polymers undergoing CaRI were correlated with their glass transition temperature ($T_g$), which provides information on their segmental relaxation under nanoconfinement. To test whether such a correlation is retained over a wide range of CRs that we test in this study, we determine the $T_g$ from fully annealed films – which now consist of a composite layer atop a residual polymer layer, via spectroscopic ellipsometry, a well-established technique to accurately determine $T_g$ of polymer in confined geometries.\textsuperscript{55,64,78,139,140} We use a two-layer Cauchy model describing the composite and polymer layers to analyze the ellipsometry data. Figure 2.10 shows the
confined polymer $T_g$ as a function of NP size, compared with the bulk polymer $T_g$ determined using DSC. For both polymers, we observe increased $T_g$ for confined polymer relative to the bulk. Moreover, the increase in $T_g$ ($\Delta T_g$) increases as the NP size is decreased (and hence higher CR). This trend indicates that the increase in polymer viscosity is highly correlated with decreased segmental mobility of polymer under nanoconfinement.

![Graph showing $T_g$ values for 8k and 21k PS in the bulk and in the confined state.](image)

Figure 2.10. The glass transition temperature ($T_g$) of 8k and 21k PS in the bulk and in the confined state, labeled by the NP diameter constituting the NP packing.

### 2.4 Discussion

Weakly interacting polymer/NP or polymer/substrate systems such as PS/SiO$_2$ have been widely used in nanocomposite, nanochannels, and thin film geometries to understand polymer behavior under confinement. Many thin film studies have reported decreasing $T_g$,$^{64,68,73,81}$ and decreased viscosity$^{141}$ with decreasing PS film thickness. These observations are attributed to the enhanced free surface ($i.e.$ polymer/air) dynamics which
dominates the overall chain dynamics of the system.\textsuperscript{64,68} In nanocomposite systems, there have been numerous reports of slowdown,\textsuperscript{89,91,92} and also some reports of bulk-like chain diffusivity\textsuperscript{61} and segmental motion\textsuperscript{58} (\textit{i.e.}, no changes due to confinement) near the NP surfaces. For highly entangled PS (typical MW > 10\textsuperscript{2} kg mol\textsuperscript{-1}) in anodic aluminum oxide (AAO) nanochannels, another interesting geometry with weak interaction, increased chain mobility (\textit{i.e.}, reduced viscosity) has been previously reported,\textsuperscript{42} which is in stark contrast to our observations. We attribute such discrepancy to the difference in confinement geometry and disentanglement effects. Instead of transporting through straight, cylindrical channels in the AAO templates, PS undergoing CaRI in disordered NP packings transports through tortuous pathways with variable pore sizes. The narrow regions within the packing may act as entropic barriers,\textsuperscript{92} whereby the polymers have to undergo substantial conformational changes to squeeze through. The enhanced mobility of highly entangled polymer in the cylindrical pores of the AAO membranes has been attributed to disentanglement effects, whereby confinement decreases the entanglement density, leading to facilitated transport.\textsuperscript{42,90,94,119} Since we use unentangled polymers, we do not expect this mechanism to play a significant role.

Although we have successfully infiltrated long chain, entangled polymer into NP packings,\textsuperscript{40,121} the infiltration behavior of these highly entangled polymers appears distinct from the capillary rise behavior in this current study. Thus, we focus our current study on unentangled polymers, with 21k PS being close to the entanglement molecular weight.\textsuperscript{142} Our ongoing work focuses on understanding the infiltration behavior of high molecular weight, entangled polymer in nanoparticle packings.
There are also contradictory reports of increased\textsuperscript{55,60} and decreased $T_g$\textsuperscript{31,86} in nanocomposites. $T_g$ of PS in AAO templates with 55-250 nm pores has been observed to increased (up to 379 K), which has been attributed to the geometric curvature of the wall decreasing the interchain proximity.\textsuperscript{60} Our previous work, which is currently under review for publication at the time of this writing, also shows increased $T_g$ of PS in undersaturated CaRI (UCaRI) nanocomposites, \textit{i.e.} NP packing that is partially filled with polymer.\textsuperscript{121} Despite the presence of polymer-air free surface in these UCaRI nanocomposites, the increased $T_g$ has been attributed to the formation of polymer capillary bridges in the neck regions of the NP contact points and thus more amplified confinement effect.\textsuperscript{121} When infiltrating the NP packing, we expect the PS to be in contact with multiple NPs; this similar bridging effect may explain the similar increase in $T_g$ trends we see in our CaRI films and the undersaturated films.\textsuperscript{121}

While Figure 2.6 and Figure 2.10 show qualitatively similar trend across 8k and 21k PS, each polymer exhibits increased viscosity and $T_g$ with decreasing NP size, we can further generalize the role of physical confinement by assessing both the roles of the polymer and NP size by plotting the normalized polymer viscosity and the $\Delta T_g$ as a function of confinement ratio (CR), $CR = R_g R_{pore}$, as shown in Figure 2.11. Similar confinement parameters have been used previously to scale the effect of physical confinement on the translational mobility of polymers in nanocomposites.\textsuperscript{62,89,92,93} To test the validity of the trends, we perform additional CaRI and $T_g$ measurements using 13k and 19k PS.

We observe that for both normalized viscosity (Figure 2.11a) and $\Delta T_g$ (Figure 2.11b), both quantities show an increasing trend with CR, approximately linearly, before plateauing at
CR ~ 1, *i.e.* when the $R_g$ equals the $R_{pore}$. From the initial slope of Figure 2.11(b), we estimate and predict the recovery of the bulk viscosity and glass transition at CR ~ 0.1, which suggests that the selection of a NP with radius ~30 times the size of $R_g$ would remove the physical confinement effect (*i.e.* increased viscosity and increased $T_g$). This CR would correspond to ~150 nm and ~240 nm diameter SiO$_2$ NPs, for 8k and 21k PS, respectively. This prediction agrees qualitatively with the previously reported universal scaling of polymer diffusion in polymer nanocomposite, where polymer diffusion is slowed down when the interparticle spacing is approximately 20 times the polymer $R_g$. Another study of PS thin film near oxide-covered silicon reports decreased diffusion which persist up to 10 $R_g$ from the interface.

To test the recovery of bulk-like viscosity, we perform CaRI on 196 nm SiO$_2$ NPs/21k PS (CR ~ 0.14) and 130 nm SiO$_2$ NPs/8k PS (CR ~ 0.13) bilayer films and compare the infiltration heights of PS obtained experimentally with the calculated height, assuming bulk polymer viscosity at the annealing temperature. As shown in Figure 2.12, We find qualitatively good agreement between our predictions and the experiments, whereby annealing the 196 nm SiO$_2$ NP/21k PS and 130 nm SiO$_2$ NP/8k PS bilayer films at 383 K for 3.5 hours and 19 minutes, respectively, led to infiltration height of ~210 nm, similar to the infiltration height of 200nm predicted by the Lucas-Washburn analysis assuming bulk polymer viscosity.
Figure 2.11. The (a) normalized viscosity ($\mu_{\text{confined}}/\mu_{\text{bulk}}$) obtained for PS undergoing CaRI at $T = 403$ K, and the (b) $\Delta T_g (T_g - T_{g,\text{bulk}})$ as a function of confinement ratio (CR). The lines are to guide the eye.
Figure 2.12. Cross-sectional SEM image of a bilayer film composed of (a-b) 196 nm SiO$_2$ nanoparticles and 21k PS (CR ~ 0.14) (a) before CaRI, and (b) after CaRI at 383 K for 3.5 hours, whereby ~210 nm of 21k PS infiltrates the NP packing. (c) The SiO$_2$ nanoparticle size distribution with diameter 196 nm, measured 196.2 ± 13.9 nm (count = 106). Cross-sectional SEM image of a bilayer film composed of (d-e) 130 nm SiO$_2$ nanoparticles and 8k PS (CR ~ 0.13) (d) before CaRI, and (e) after CaRI at 383 K for 19 mins, whereby ~230 nm of 8k PS infiltrates the NP packing. (f) The SiO$_2$ nanoparticle size distribution with diameter 130 nm, measured 129.7 ± 16.5 nm (count = 114). All scale bars in (a), (b), (d), and (e) are 500 nm.

Below CR of 1 (CR < 1), the increasing trend in the normalized polymer viscosity with CR suggests that physical confinement strongly and systematically affects the
translational motion of the chains. This slowdown may be associated with the entropic barrier, whereby chain loses entropy when stretching to squeeze through the narrow neck regions in the NP packing.\textsuperscript{92} In the 9 nm SiO\textsubscript{2} NP packing, we see 8k and 21k PS having comparable viscosity, suggesting that the physical confinement imposed by the NPs plays a more significant role than the polymer size or molecular weight. Furthermore, from Figure 4(b), we see that in 21k PS, the viscosity is comparable in 9 nm and 27 nm SiO\textsubscript{2} NP packings, consistent with the trends in Figure 2.11. These observations suggest that when the size of the polymer is similar to or larger than the pore size, the bottleneck process is the same, and may be related to the slowest segmental motion. To further understand this intriguing observation, our ongoing work focuses on developing a theoretical framework of CaRI to account for the conformational entropy loss of chain due to confinement and gain in free energy due to wetting of polymer on the pore surface.

2.5 Conclusion

In this work, we study the role of physical confinement on the polymer viscosity and glass transition temperature in composites prepared \textit{via} capillary rise infiltration (CaRI) of unentangled polymers in random packing of weakly interacting nanoparticles. The confinement ratio (CR), defined as the ratio of the polymer radius of gyration (R\textsubscript{g}) to the average pore radius in the disordered nanoparticle packing (R\textsubscript{pore}), is tuned by using four polystyrenes with distinct molecular weights, and SiO\textsubscript{2} NPs of four different diameters. We observe increased viscosity and T\textsubscript{g} of polymer relative to the bulk under nanoconfinement. Both extents of deviation of viscosity and T\textsubscript{g} relative to the bulk values
increase with CR until an upper threshold of CR ~ 1 is reached. Overall, the correlation between the viscosity and $T_g$ increase suggests the slowdown of translational motion of polymers is strongly influenced by the slowdown of the segmental motion. Furthermore, we show that the physical confinement effect saturates when the polymer $R_g$ is equal to or greater than the $R_{pore}$, such that the viscosity and $T_g$ no longer increases. Our work provides a fundamental framework to optimize processing parameters such as temperature and annealing time for scalable manufacturing of polymer-infiltrated nanoparticle films using CaRI. Our results also provide important guidelines in tailoring the processing conditions when heterostructured or hierarchically structured porous materials are infiltrated with polymers.
Chapter 3. Effect of Polymer-Nanoparticle Interactions on the Viscosity of Unentangled Polymers under Extreme Nanoconfinement during Capillary Rise Infiltration


3.1 Introduction

Incorporating extremely high concentrations (> 50 vol%) of nanoparticles (NPs) into nanocomposite films (NCFs) can drastically enhance their properties and functionality. For example, protective coatings with ultrahigh strength and toughness can be fabricated by emulating the structure of nacre, a natural NCF with an extremely high loading (> 90 vol%) of stiff nanoplatelets.\textsuperscript{22,144} Perovskite solar cells incorporating polymer scaffold supporting high concentrations of perovskite crystals show high energy conversion efficiency, excellent resistance to humidity and self-healing functionality.\textsuperscript{23} Separation membranes based on high concentrations of nanoparticles show enhanced permeability and selectivity, overcoming the traditional trade-off between the two separations properties.\textsuperscript{25} In addition, thermal energy storage device exhibits increasing thermal conductivity with nanoparticle loading.\textsuperscript{24} Despite the useful properties and functionality that can derive from high concentrations of NPs in NCFs, methods to produce such NCFs require multiple steps and thus tend to be energy-intensive and time-consuming. Solution- or melt-based processes, for example, are challenging to implement for mixtures with high concentrations of NPs because of high viscosity and elasticity, as well as NP’s tendency to aggregate during processing.\textsuperscript{15,145}
A new class of NCFs that circumvent many of the challenges associated with fabricating highly filled NCFs is the polymer-infiltrated nanoparticle films (PINFs). By infiltrating polymers into densely packed NP films, it is possible to create NCFs with extremely high concentrations of NPs.\textsuperscript{40,52-54} In previous work, we developed a thermally-induced, capillarity-based approach – capillary rise infiltration (CaRI), to achieve PINFs with > 50 vol\% NP loading.\textsuperscript{40,52} This technique involves first generating a bilayer film of NPs and polymer, followed by thermally annealing the bilayer above the glass transition temperature ($T_g$) of the polymer to induce polymer wicking into the voids of the dense NP packing via capillarity. PINFs prepared via CaRI have very high modulus and hardness as well as scratch and wear resistance owing to their high filler fractions.\textsuperscript{40} We have demonstrated that the CaRI process is robust across systems with different polymer-NP interaction as well as polymer molecular weights and morphology.\textsuperscript{40,52}

In addition to being a powerful and potentially scalable method of producing PINFs, CaRI provides a unique platform to study the viscosity and glass transition of polymers under extreme nanoconfinement. Despite general acceptance that physical confinement leads to significant deviation of polymer behavior from its bulk,\textsuperscript{11,58} a wide range of confinement-induced changes have been reported in literature, depending on the extent and geometry of confinement, and the polymer-nanoparticle interactions. For instance, some reports have shown that non-attractive nanoparticles significantly slow down the diffusion of polymers in polymer nanocomposites.\textsuperscript{85,89,91,92} In contrast, other studies based on molecular dynamics simulations have reported enhanced chain motion under repulsive polymer-nanoparticle interaction.\textsuperscript{146} One of the key challenges in deciphering the effect of confinement is that
effects of confinement and interfacial effects are often convoluted and thus are difficult to
decouple, especially in thin film geometries where free surface effects may play a
significant role in glass transition, such that it may mask substrate effects.59,63,65,67,73,86

In the CaRI system, the characteristic pore size of random close packings of spheres is
approximately 20 – 30% of the NP size.56 It is thus straightforward to confine polymers in
extremely small pores (< 10 nm) by using disordered packings of NPs. Polymer chains
infiltrating the dense NP packings are very close to the NP surface and could be in contact
with multiple nanoparticles, with negligible effect of free polymer surface.61,147,148 By
analyzing the wicking process of polymer into a NP packing based on the Lucas-Washburn
model, we recently estimated several orders of magnitude increase in the melt viscosity of
unentangled polymer.40 This increased viscosity relative to the bulk value suggests that
confinement significantly affects the polymer infiltration dynamics in the tight pore
network of the NP packing. Therefore, the CaRI of polymer into NP packing enables us to
systematically explore the effect of polymer-NP interaction under extreme
nanoconfinement by varying the type of polymer used in CaRI.89,92

In this work, we study the effect of polymer-NP interaction on the viscosity of unentangled
polymer in CaRI. We focus our analyses on unentangled polymer chains to exclude the
potential contribution of polymer chain (dis)entanglement, which has been attributed to
enhanced mobility of confined polymer chains of high molecular weights.42,94 We monitor
the infiltration process of unentangled poly(styrene) (PS) and poly(2-vinylpyridine)
(P2VP) into densely packed silica NP packings. The P2VP-SiO₂ NP and PS-SiO₂ NP pairs
represent strongly and weakly interacting systems, respectively; the nitrogen atom in P2VP
interacts strongly with the hydroxyl groups on the SiO$_2$ NP surface via hydrogen bonding, whereas PS interacts with the SiO$_2$ NP via van der Waals forces. We choose two unentangled polymer molecular weights for each polymer to vary the extent of confinement. This approach enables us to decouple the confinement and interaction effects on the polymer CaRI dynamics. We show that during CaRI, the polymers exhibit higher-than-bulk viscosity, regardless of polymer-NP interactions. We also show that the glass transition temperature ($T_g$) of these polymers increase significantly in the NP packings, again regardless of polymer-NP interactions. We find that in both systems, the increase in the viscosity is strongly correlated with the increased $T_g$, and the ratio of viscosity to bulk viscosity does not show strong dependence on the temperature. These observations suggest that confinement has a more significant impact on the CaRI dynamics than on the extent of polymer-NP interactions.

### 3.2 Experimental Section

#### 3.2.1 Materials

Poly(styrene) (PS) (PS-8k, Mn = 8,000 g mol$^{-1}$, PDI = 1.10; PS-21k, Mn = 21,000 g mol$^{-1}$, PDI = 1.04) and Poly(2-vinylpyridine) (P2VP) (P2VP-8k, Mn = 7,800 g mol$^{-1}$, PDI = 1.08; P2VP-22k, Mn = 22,000 g mol$^{-1}$, PDI = 1.06) are purchased from Polymer Source Inc. The silica NP suspension (Ludox TM-50, 25.0 ± 3.5 nm in diameter) is purchased from Sigma Aldrich.

#### 3.2.2 Preparation and characterization of bilayers

Silicon wafers are cut into approximately 1 cm x 1 cm squares. The wafers are rinsed with acetone, isopropanol, and water, and then dried with nitrogen. The wafers are then further
cleansed by oxygen plasma treatment for approximately 5 minutes. 5 wt% PS-8k and 6 wt% PS-21k solutions are prepared by dissolving PS in toluene. 8 wt% P2VP-8k and 8 wt% P2VP-22k are prepared by dissolving P2VP in 1-butanol. SiO₂ NP suspension is prepared by diluting the as-purchased suspension in DI water to 10 wt%, and the pH of the suspension is adjusted to ~11 using 1 M potassium hydroxide (KOH) solution. All solutions are bath-sonicated for at least an hour and filtered prior to use. To generate the bilayer films, the polymer layer is first spin-coated onto the silicon substrate using a WS-400BZ-6NPP/Lite spin-coater from Laurell Technologies Corporation. The polymer film is annealed at 393 K under vacuum condition for 12 h to remove residual solvent. Then, the polymer film is oxygen plasma-treated for ~2 s to render the film surface hydrophilic, on which the SiO₂ NP layer is spin-coated. This short plasma treatment facilitates the deposition of uniform nanoparticle layers atop polymer films. Our control experiments show that it is possible to create bilayers without plasma treatment by using isopropanol suspensions of silica nanoparticles and that there is little difference in the properties of CaRI composite films made using the two methods. Details will be reported elsewhere.¹²¹ The thickness of the polymer and NP layer is approximately ~200 nm to ensure that there is sufficient polymer to fill the interstices of the NP packing, which has average porosity of ~ 0.35. To generate ~200 nm polymer film, 5 wt% PS-8k and 6 wt% PS-21k solutions are spin-coated at 2000 rpm and 5000 rpm, respectively, whereas 8 wt% P2VP-8k and 8 wt% P2VP-22k are spin-coated at 4000 rpm and 5000 rpm, respectively. The 10 wt% SiO₂ NP suspension is spin-coated at 3000 rpm. The bilayer samples are subjected to vacuum for 12 hr to remove residual solvents. The vacuum treatment, however, does not
significantly change the CaRI behavior likely indicating that the influence of residual solvent on polymer infiltration dynamics is negligible.

Scanning electron microscopy (SEM) images of the bilayer films before and after the polymer infiltration process are taken using a JEOL 7500F HRSEM. Each sample is sputtered with a thin gold/palladium layer using a Cressington Sputter Coater 107 prior to imaging to prevent charging. The samples are imaged at an accelerating voltage of 5 kV, emission current 20 μA, and at a working distance of approximately 8 mm.

3.2.3 Characterization of polymer infiltration process

The polymer infiltration process into the voids of the NP packing is monitored in situ using a J.A. Woollam Alpha-SE spectroscopic ellipsometer while the bilayer film sample is annealed above the glass transition temperature (T_g) of the polymer using a Linkam THMS350V heating stage, under constant pressure (ambient conditions). The heating stage has a temperature resolution of ~ 1 K. The stage on which the sample is placed is 22 mm in diameter and is open to ambient air. The Linksys software displays the stage temperature and allows the user to input the desired set-point temperature, heating rate, and hold time for the set-point temperature. The ellipsometry data is collected between λ = 380 nm and 900 nm at an incident angle of 70° and is analyzed using the CompleteEASE software package provided by J.A. Woollam. The psi (Ψ) and delta (Δ) data are fitted using a three-layer (nanoparticle/composite/polymer) Cauchy model on a Si substrate with a native oxide layer. The Cauchy model is expressed as: n(λ) = A + Bλ^2 + Cλ^4; k(λ) = 0, where A, B and C are optical constants, λ is the wavelength, n and k are the real and imaginary components of the index of refraction. The model fitting interprets the raw data into
physical parameters describing each layer in the sample, namely the thickness and the refractive index.\textsuperscript{127}

### 3.2.4 Glass transition temperature measurement

The glass transition temperatures (T\textsubscript{g}) of bulk polymer samples are determined using the TA Instruments Q2000 differential scanning calorimetry (DSC). PS samples are measured in a hermetically sealed pan, whereas P2VP samples are measured in a non-hermetically sealed pan. Each polymer sample (~ 6 mg) is initially cooled to 293 K, before subjecting it to two heating and cooling cycles in the range of 293 K – 423 K at 10 K/min. The T\textsubscript{g} is defined as the midpoint of the step transition of the heat flow/capacity and expressed as the average from the two cooling cycle measurements. The T\textsubscript{g} values measured using DSC are in good agreement with those reported previously.\textsuperscript{128,129} The T\textsubscript{g} of the confined polymers in the CaRI nanocomposite films are measured using a J. A. Woollam M-2000V spectroscopic ellipsometer. The PINF is mounted onto a Linkam THMS 600 temperature-controlled stage attached to the ellipsometer. The \textit{in situ} ellipsometry sampling rate is 1 s with high accuracy zone-averaging. Three heating and cooling cycles between 303 K and 423 K under dry nitrogen flow are performed for each sample, with heating rate of 30 K/min and cooling rate of 10 K/min, respectively. T\textsubscript{g} data is reported upon cooling. The thickness and refractive index of the sample is determined by fitting the cooling ramp raw data to the Cauchy model, as described earlier. The T\textsubscript{g} of the residual polymer layer and confined polymer for each film is determined \textit{via} the intersection of the linear fits to the supercooled and glassy regimes in the plots of nanocomposite and polymer layer refractive
indices versus temperature, as shown in Figure 3.1. The thickness of the composite layer is held constant for the dynamic data fits.

Figure 3.1. The glass transition temperatures ($T_g$) of bulk and confined (a)PS-8k, (b) P2VP-8k, (c) PS-21k, and (d) P2VP-22k are measured using spectroscopic ellipsometry, by determining the inflection point in the layer refractive indices with temperature at a cooling rate of 10K/min. The confined polymer $T_g$ is determined from the composite layer, where polymer has fully filled the voids in the NP packing; whereas the bulk polymer $T_g$ is determined from the residual polymer layer at the bottom.

3.3 Results and Discussion

3.3.1 Polymer infiltration dynamics

To study polymer capillary rise infiltration (CaRI) under confinement, we generate a bilayer composed of a dense disordered packing of 25nm SiO$_2$ nanoparticles (NPs) atop a polymer layer. We use poly(styrene) (PS) and poly(2-vinylpyridine) (P2VP) as the weakly and strongly interacting polymers. P2VP is known to interact with SiO$_2$ NP via hydrogen bonding interactions, whereas PS interacts with SiO$_2$ NP is primarily through van der
Waals interactions. We also use PS and P2VP with two different molecular weights: ~8000 (8k) and ~21,000 (21k) g/mol. The radii of gyration of 8k and 21k PS and P2VP, calculated based on the Kuhn segment length of each polymer, are approximately ~2.5 nm and ~4 nm, respectively, which are comparable to or slightly larger than the characteristic pore radius of the SiO$_2$ NP packing (~3.5 nm). The bilayer film is annealed above the glass transition temperature ($T_g$) of the polymer to induce the infiltration of polymer into the interstices of the NP packing. The changes that take place in the film during the CaRI process are schematically illustrated in Figure 3.2.

Figure 3.2. Schematic illustration of the capillary rise infiltration (CaRI) process of a polymer into voids of a densely packed nanoparticle film. Upon the initiation of the infiltration, the bilayer becomes a three-layer system composed of pure polymer, infiltrated nanoparticles (i.e., composite), and unfilled nanoparticle layers. Upon the completion of CaRI, the system has two layers: the composite (i.e., the nanoparticle layer is completely filled with the polymer) and the pure polymer layers.

We perform in situ spectroscopic ellipsometry to monitor polymer infiltration into the disordered SiO$_2$ NP packing. The infiltration of polymers in CaRI has been shown to follow the Lucas-Washburn model, which has been successfully used in prior experimental and computational studies to describe polymer wicking under confinement: $^{40,42,45,47,48,50,104}$

$$h^2 = \frac{\sigma R \cos \theta}{4\pi^2 \mu} t$$

where $h$ is the height of the NP packing infiltrated by the polymer, $\sigma$ is the surface tension of polymer melt, $R$ is the mean pore radius in the NP packing, $\theta$ is the contact angle of the
polymer melt on the NP surface, $\tau$ is the tortuosity of the disordered NP packing, $\mu$ is the viscosity of the polymer melt, and $\tau$ is the annealing time.$^{40,47}$ A three-layer Cauchy model, as shown in Figure 3.3, that accounts for the topmost neat SiO$_2$ NP layer, the middle composite layer, and the bottommost polymer layer, enables us to translate the amplitude ($\Psi$) and phase change ($\Delta$) data from spectroscopic ellipsometry to the index of refraction of each layer, in order to follow the structural evolution of the bilayer. To reduce the degrees of freedom and ensure solution uniqueness, we determine and set the refractive indices of the neat SiO$_2$ NP layer and the neat polymer layer from respective single-component film measurements at $\sim$383 K to account for thermal expansion of the polymer layer and the removal of condensed water from the neat SiO$_2$ NP packing.

Figure 3.3. (a) $\Psi$ and (b) $\Delta$ as a function of annealing time for P2VP-8k/SiO$_2$ NP bilayer film annealed at 403 K. (c) A time slice ($t = 6.005$ min) of a psi and delta data as a function of wavelength, where the dashed line indicates the (d) 3-layer Cauchy model fit to the data.
Figure 3.4(a) shows the thickness profile changes of the neat SiO$_2$ NP layer, the composite layer, and the polymer layer with annealing time for PS8k/SiO$_2$ NP film at 403 K. During CaRI, the polymer wicking into the SiO$_2$ NP causes the decrease in both the NP and polymer layer thicknesses, while the thickness of the composite layer – the portion of SiO$_2$ NP layer which has been filled with polymer, increases. This is also evident in Figure 3.4(b-e) which shows the polymer filling of the interstices of the SiO$_2$ NP packing and the decrease in polymer layer thickness after CaRI. The presence of polymer in the interstices of the NP packing following CaRI is also evident from the atomic force microscopy (AFM) topography and phase images in Figure 3.5. The interparticle distance between nanoparticles before (25.7 ± 2.9 nm) and after (26.1 ± 2.7 nm) CaRI, estimated from Figure 3.4(b and d) shows a negligible change, strongly indicating that the packing density of the nanoparticle layer does not change upon CaRI. Albeit having different infiltration rates, we observe that all polymers follow a similar infiltration behavior (See Figure 3.6, Figure 3.7, and Figure 3.8). At early times, the formation of the meniscus before the capillary rise and higher initial resistance causes the movement of polymer melt to be in an unsteady state.$^{51}$ Gradually, the infiltration stabilizes and approaches a steady state, where the slope of the composite growth remains uniform over the course of infiltration. We consider the steady state infiltration process in our analyses to infer the viscosity of the polymer melt based on the Lucas-Washburn model.
Figure 3.4. (a) Thickness profiles of the SiO$_2$ NP, composite, and neat polymer layer as a function of annealing time, obtained using \textit{in situ} spectroscopic ellipsometry while annealing ~200 nm SiO$_2$ NP/~200 nm PS-8k bilayer films at 403 K. The SEM images show the (b) top and (c) cross sectional views of the bilayer film before annealing, and the (d) top and (e) cross sectional views of the PINF atop a residual polymer layer after annealing. The scale bars are 100 nm.
Figure 3.5. Topography (a,c) of the PS-8k/SiO₂ NP bilayer film taken using tapping-mode AFM (a) before and (c) after CaRI; phase image (b,d) of the film (b) before and (d) after CaRI. The scale bars are 200 nm. The films are imaged using an Icon, Bruker AFM with a silicon tapping-mode probe.
Figure 3.6. Thickness profile evolutions of NP, composite, and polymer layers of (a) PS-8k/SiO₂ NP, (b) P2VP-22k/SiO₂ NP, (c) PS-21k/SiO₂ NP, and (d) P2VP-22k/SiO₂ NP bilayer films at (a-b) 403 K and (c-d) 423 K, respectively.
Figure 3.7. (a) The composite layer thickness squared, $h_{\text{comp}}^2$ of PS-8k and P2VP-8k NP versus annealing time, $t$, when the bilayer films are annealed at 403 K, shows a linear fit and agrees well with the Lucas-Washburn model. (b) The slope of $h_{\text{comp}}^2$ versus $t$ as a function of annealing temperature, $T$ for PS-8k, P2VP-8k, PS-21k, and P2VP-22k.
From the thickness profiles, we plot the composite layer thickness squared ($h_{\text{comp}}^2$), versus time ($t$) to confirm the Lucas-Washburn model. Figure 3.7(a) and Figure 3.8(a-b) show the linear dependences of $h_{\text{comp}}^2$ versus $t$ for the all polymer systems tested, consistent with the Lucas-Washburn model. We anneal each polymer-NP system in a range of temperature. For each run, we verify the validity of the Lucas-Washburn model as in Figure 3.7(a) and Figure 3.8(a-b), then extract the slope from $h_{\text{comp}}^2$ versus $t$ plot, which represents the prefactor in the Lucas-Washburn model ($\sigma \cos \theta / 4 \tau^2 \mu$). For each polymer system, the value of the slope, as shown in Figure 3.7(b), increases with temperature, indicating a more rapid infiltration process. This observation is consistent with the decreasing polymer melt viscosity as the temperature is increased.
Table 3.1. Parameters used for estimation of viscosity using the Lucas-Washburn model. 42,56,82,130-132,150-152

<table>
<thead>
<tr>
<th>Polymer/Nanoparticle</th>
<th>Average pore radius, R (nm)</th>
<th>Tortuosity, τ</th>
<th>Surface tension as function of temperature, σ (T [°C]) (mN/m)</th>
<th>Polymer contact angle on SiO₂ NP, θ</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-8k/SiO₂ NP</td>
<td>3.5</td>
<td>1.95</td>
<td>40.5 - 0.068T</td>
<td>20°</td>
</tr>
<tr>
<td>PS-21k/SiO₂ NP</td>
<td>3.5</td>
<td>1.95</td>
<td>42.1 - 0.068T</td>
<td>20°</td>
</tr>
<tr>
<td>P2VP-8k/SiO₂ NP</td>
<td>3.5</td>
<td>1.95</td>
<td>46.7 - 0.063T</td>
<td>0°</td>
</tr>
<tr>
<td>P2VP-22k/SiO₂ NP</td>
<td>3.5</td>
<td>1.95</td>
<td>46.7 - 0.063T</td>
<td>0°</td>
</tr>
</tbody>
</table>

Based on each slope, we infer the viscosity $\mu$ of the confined polymer by estimating the remaining parameters in the Lucas-Washburn prefactor, $\sigma R \cos \theta / 4 \tau^2 \mu$, from literature values.$^{51,153,154}$ Table 3.1 summarizes the parameters that are used to determine the viscosity $\mu$. The pore radius R and tortuosity $\tau$ values are intrinsic to the SiO₂ NP packing and are estimated based on the size of the NP and the porosity of the packing.$^{56,130}$ The surface tension of PS and P2VP are estimated based on the molecular weight and the temperature of the melt.$^{131,150}$ There are varying reports of PS contact angle on silicon oxide surfaces ranging from 7°- 23°;$^{42,132}$ we choose $\theta = 20°$ for this purpose, but the temperature-dependence of viscosity is independent of this choice. P2VP is reported to form strongly bound layer on SiO₂ NP surface due to favorable hydrogen bonding,$^{82,151,152,155}$ thus we estimate $\theta \approx 0°$ in the case of P2VP. We perform a sensitivity analysis by testing a range of contact angle values and considering other empirical relations in calculating the polymer surface tension, $\sigma(T)$. As shown in Figure 3.9 and Figure 3.10, this analysis confirms that the magnitude of the estimated viscosity of confined polymer is robust across a range of estimated $\sigma$ and $\sigma(T)$ parameters. To assess the effect of confinement and polymer-NP interaction, we compare the measured confined polymer viscosity with bulk values, which are obtained from literature values.$^{133,156}$
3.3.2 Role of confinement and polymer-nanoparticle interaction

To assess the role of confinement and polymer-NP interaction, we compare the confined and bulk polymer viscosity as a function of temperature, as shown in Figure 3.11. For both polymers, we note a significant increase in the viscosity of the confined polymer relative to the bulk values reported in literature,\textsuperscript{133,156} regardless of the polymer-NP interaction.
strength. The two graphs show remarkable similarities in the absolute values of viscosities for the confined PS and P2VP, and the extents of viscosity increases are also very similar.

![Graphs showing bulk and confined polymer viscosity](image)

Figure 3.11. Bulk and confined polymer viscosity for (a) P2VP-8k and P2VP-22k, and (b) PS-8k and PS-21k as a function of temperature. Each data point for the confined polymer viscosities are an average of at least 2 runs, and the error bar represents 1 standard deviation. The bulk viscosity values are obtained from literature.\(^{133,156}\)

The relative increases in the viscosity due to confinement (\(\mu_{\text{confined}}/\mu_{\text{bulk}}\)) also do not strongly depend on temperature, as shown in Figure 3.12. This is the opposite of what one would expect if the polymer-NP interactions significantly slowed the chain motion. In particular, the strength of hydrogen bonding is known to be strongly temperature dependent;\(^{160}\) thus one may have expected a strong temperature dependence of the normalized viscosity in the case of P2VP, which we do not observe. Furthermore, for a given polymer, there is no significant difference in \(\mu_{\text{confined}}/\mu_{\text{bulk}}\) for the two molecular weights (Figure 3.12). These observations imply that the increase in viscosity is not strongly influenced by the polymer-NP interactions.
Figure 3.12. The confined polymer viscosity normalized by the bulk viscosity \( \left( \frac{\mu_{\text{confined}}}{\mu_{\text{bulk}}} \right) \) for all polymer systems, as a function of temperature.

The significant increase in the polymer viscosity is reminiscent of an abrupt increase reported for the viscosity of simple liquids such as siloxane confined in a very narrow slit, although the phenomenon was attributed to a liquid-to-solidlike (i.e., first-order-like) transition in packing of the molecule.\(^{161}\) More relevant to our observation is the slowdown of chain diffusion observed in polymer nanocomposites, which was attributed to entropic barriers that are associated with chains passing through small constrictions between NPs. These studies showed that stronger interactions between NP and polymer do not necessarily lead to more significant reduction in diffusivity,\(^{89,160}\) consistent with our observations. Other measures of polymer dynamics have also described slowing down of chain relaxation\(^ {14,91}\) and diffusion\(^ {92,162}\) near strongly and weakly interacting solid surfaces. Another mechanism that could lead to the observed slowdown is the tortuous path and the high curvature in the NP packings which can increase the interchain packing proximity.\(^ {60}\) Such a change could in turn significantly strengthen polymer-NP interactions even in the case of the weak polymer-NP interacting system and lead to increased viscosity.
Interestingly, reports on the viscosity of polymer in thin films provide some conflicting
trends. The viscosity of polymer in thin films decrease for the weakly interacting polymer-
substrate system, which has been attributed to the enhanced free surface dynamics.\textsuperscript{60} The polymer viscosity in thin films has been reported to increase for strongly interacting polymer-substrate system above a threshold temperature.\textsuperscript{163} Increases in the viscosity of unentangled polymers during CaRI in dense nanoparticle packings (Figure 3.11 and Figure 3.12) are in stark contrast to the enhanced mobility observed in the capillary rise of highly entangled polymers in cylindrical pores of anodized aluminum oxide (AAO) membranes.\textsuperscript{42} We attribute this discrepancy to difference in confinement geometry and disentanglement effects. When infiltrating a dense nanoparticle packing, polymer chains transport through tortuous pathways with variable pore sizes (narrow necks and wide gaps), instead of straight, uniform, cylindrical nanochannels in AAO membranes with 55nm pores. The narrow regions may act as entropic barriers, where polymer chains have to sample multiple conformations to squeeze through the narrow pores for infiltration to occur. The enhanced mobility of high molecular weight polymers under confinement was attributed to a disentanglement effect,\textsuperscript{42,94} whereby increased confinement leads to decreased entanglement density. In our case, we do not expect such a phenomenon to play a role as both molecular weights studied here are below the entanglement limit.

Monitoring the infiltration dynamics in CaRI provides insights into the effects of confinement on translational (\textit{i.e.}, centre-of-mass) mobility of the polymers, whereas the determination of glass transition temperature of the polymers provides indirect information regarding their segmental relaxation under extreme confinement, as $T_g$ is typically
attributed to the arresting of segmental modes of motion in bulk polymers.\textsuperscript{71,72,164} We determine the $T_g$ of the fully annealed films, consisting of a composite layer atop a residual polymer layer, via spectroscopic ellipsometry, which is a well-established method for the accurate determination of $T_g$s of polymers under confined geometries.\textsuperscript{63,64,68,73,78,140} We use a 2-layer composite/polymer model to fit the spectroscopic ellipsometry data, as shown in Figure 3.1. We also measure the $T_g$ of the bulk polymer samples independently via differential scanning calorimetry (DSC) to validate our spectroscopic ellipsometry $T_g$ measurements (Table 3.2).

Table 3.2. Glass transition temperature, $T_g$ (K) measured using differential scanning calorimetry (DSC) and spectroscopic ellipsometry (SE) in the bulk and confined state.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Glass transition temperature, $T_g$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bulk (DSC)</td>
</tr>
<tr>
<td>P2VP-8k</td>
<td>342</td>
</tr>
<tr>
<td>P2VP-22k</td>
<td>355</td>
</tr>
<tr>
<td>PS-8k</td>
<td>356</td>
</tr>
<tr>
<td>PS-21k</td>
<td>366</td>
</tr>
</tbody>
</table>

Figure 3.13 shows the confined and bulk $T_g$ values for each polymer-NP system. In all systems, we observe increased $T_g$ in the confined systems relative to the bulk, which is highly correlated with the increased viscosity we observe, even in the case of the weakly interacting system (PS-SiO\textsubscript{2}). Previous studies have shown that while strong interfacial interactions between SiO\textsubscript{2} and P2VP do not necessarily lead to increased $T_g$ in nanocomposites, confinement has shown to increase $T_g$ \textsuperscript{63,83}. Although most studies involving PS films on SiO\textsubscript{2} show decrease in $T_g$ due to the free surface effect,\textsuperscript{64,68} one study
has shown that the $T_g$ of PS confined in AAO membranes, in the absence of free surface, increases, consistent with our results.\textsuperscript{60}

Surprisingly, in our current study, the increase in $T_g$ for the two polymers of similar molecular weights are approximately the same. Also, similar increases in $\Delta T_g$’s are observed for the two polymers when the molecular weight of the polymers is increased. These observations point to the fact that physical confinement has a stronger impact on the glass transition of polymers than polymer-NP interactions under these extreme nanoconfinement conditions. This is in contrast to measurements in thin films where free surface (polymer-air interface) effects always dominate, resulting in decrease in average $T_g$ for PS as opposed to increased $T_g$ in P2VP.\textsuperscript{63,73} Overall, observed increases in $T_g$s’ are consistent with the increased viscosity for PS and P2VP, suggesting that the increased viscosity in CaRI under extreme nanoconfinement is likely correlated with impact of confinement on segmental motion of the chains as deduced from their $T_g$s’.
3.4 Conclusion

In this work, we perform capillary rise infiltration (CaRI) of unentangled polymer into a disordered, dense nanoparticle packing of SiO$_2$ to study the viscosity and glass transition of the polymers with different polymer-nanoparticle interactions under extreme nanoconfinement, where the polymer chain size is comparable or smaller than the average pore size. Using the Lucas-Washburn model, we measure the viscosity of the polymer during infiltration in disordered nanoparticle packings, and observe increased viscosity of unentangled polymers under such extreme nanoconfinement conditions relative to their respective bulk values, significantly different from the results obtained based on highly entangled polymers undergoing capillary rise in well-defined cylindrical pores. Surprisingly and somewhat unexpectedly, the extent of viscosity increase is not strongly dependent upon the polymer-NP interactions. We also observe comparable increase in $T_g$. 

Figure 3.13. The glass transition temperature $T_g$ of P2VP (black) and PS (red) in the bulk (striped bar) and the confined state (filled bar).
for both the strongly and the weakly interacting polymer-NP systems, which is different from prior studies on $T_g$ changes observed in supported polymer thin films.

Overall, our results demonstrate that confinement, rather than polymer-NP interaction, has more significant impact on the viscosity and glass transition of polymers in CaRII systems. The increases in $T_g$ are strongly correlated with the viscosity changes observed for the two polymers, suggesting that extreme nanoconfinement is affecting the transport phenomena of polymers by influencing the segmental motion. Our results provide fundamental frameworks for the optimization of process parameters such as temperature and annealing time to enable scalable manufacturing of polymer-infiltrated NP films using CaRI.

There are several outstanding questions that warrant future investigation. Our ongoing work, for instance, focuses on the infiltration dynamics of highly entangled polymers to test the validity of Lucas-Washburn model. The effect of molecular weight and polymer-nanoparticle interactions of polymers on the mechanical properties of CaRI composites is potentially of significant importance as high molecular weight polymers can lead to bridging of multiple NPs and in turn significant enhancement of the toughness of the composite.
Chapter 4. Nanoporous Polymer-Infiltrated Nanoparticle Films with Uniform or Graded Porosity via Undersaturated Capillary Rise Infiltration


4.1 Introduction

The structural and transport properties imparted by nanoporosity can be exploited to realize structural materials that have low density, desirable optical properties, and applications in separation and energy systems. Introducing uniform or graded nanoporosity to composites would offer significant advantages by combining the functionality of nanomaterials and processability of organic materials. For example, nanoporous ion-exchange membranes with nanoparticles have shown increased water uptake with porosity, which in turns increases the ion conductivity of the membrane. Likewise, porous nanocomposite electrodes provide a high surface area for ionic diffusion, which leads to increased cyclic stability in energy storage applications. Furthermore, nanoporous composites with graded structures can be extremely useful for optical waveguides, antireflective coatings, optical components for consumer electronics, and medical imaging devices. Graded structures are key features that impart superb mechanical properties to several biological composites such as dermal armors of a fossil fish.

Fabrication techniques have been developed to generate nanoporous composite films; however, few methods have demonstrated that composite films with spatially controlled...
porosity (i.e., uniform or graded) along with extremely high nanoparticle loadings\textsuperscript{10,180} can be generated using a simple and potentially scalable procedure. One common approach is to combine solution- or melt-based processing to generate composites and an additional postprocessing step to introduce pores.\textsuperscript{28,181} These methods, however, can be challenging to implement because mixtures with high concentrations of nanoparticles have high viscosity and nanoparticles tend to aggregate,\textsuperscript{40,145} thus a nanoparticle loading exceeding 10–20 vol\% cannot be readily achieved.\textsuperscript{169,182} Furthermore, it is not possible to create nanocomposites with graded porosity using this conventional method. Layer-by-layer assembly enables the generation of nanoporous composite films with graded composition;\textsuperscript{183} however, the process tends to be time-consuming and limited to water-soluble oppositely charged species.\textsuperscript{184} An alternative route is to infiltrate a porous nanoparticle packing with a polymer through the solution phase\textsuperscript{185–187} or a monomer through the vapor,\textsuperscript{188,189} which is subsequently polymerized \emph{in situ}. However, the extent of polymer infiltration depends on various factors such as the nanoparticle surface chemistry, nanoparticle size, and other operating parameters,\textsuperscript{189} complicating the precise control over the composition and structure. Also, these methods seldom allow for the fabrication of nanocomposites with graded porosity.

In this work, we demonstrate that compositionally uniform or graded nanoporous composite films with extremely high nanoparticle loadings can be prepared through undersaturated capillary rise infiltration (UCaRI) of a polymer into a nanoparticle film. We investigate the processing-structure-property relationship of the UCaRI nanoporous polymer-infiltrated nanoparticle films (PINFs). By tuning the amount of polymer relative
to the void volume in the nanoparticle film and the duration of thermal annealing, we are able to generate uniform PINFs with well-defined compositions and porosity, as well as those with compositional gradients. Using in situ spectroscopic ellipsometry and molecular dynamics (MD) simulations, we monitor the polymer infiltration during the formation of the nanoporous PINFs, which undergo two distinct polymer transport phenomena to generate PINFs with uniform or gradient porosity. Finally, we demonstrate that the optical and mechanical properties of these films can be tailored over a wide range simply by changing the saturation level by altering the thickness of the polymer layer relative to that of the nanoparticle layer. We show that UCaRI represents a versatile approach for preparing nanoporous PINFs with uniform or graded porosity with a variety of polymers, which could have broader impacts in the fabrication of nanoporous composites for energy conversion and storage, optical coatings, and separations and structural applications.

4.2 Experimental Section

4.2.1 Materials
TiO$_2$ nanoparticles (TiO$_2$ NPs) are synthesized using the hydrothermal method detailed by Sugimoto et al.$^{190}$ The major and minor axes of the NPs are $37.4 \pm 6.7$ nm and $28.8 \pm 4.1$ nm, respectively. Polystyrene (PS) (Mn = 8000 g mol$^{-1}$, PDI = 1.10) is purchased from Polymer Source, Inc.

4.2.2 Preparation of Bilayer Films
Prior to film deposition, the silicon wafers are cut to approximately 1 cm $\times$ 1 cm squares. The wafers are rinsed with acetone, 2-propanol, and deionized water and then dried with nitrogen. Then, the wafers are oxygen plasma treated for $\sim$5 min for further cleaning. The
PS solution is prepared by dissolving PS in toluene. TiO$_2$ NP is dispersed in water. The solutions are filtered prior to use. To generate the nanoporous PINFs, the PS layer is first deposited onto the silicon substrate via spin-coating, using a WS-400BZ-6NPP/Lite spin-coater from Laurell Technologies Corporation. Next, the PS film is annealed at 120 °C under vacuum conditions for 20 h to remove residual solvent. Then, the PS film is oxygen plasma treated for 2 s to render the film surface hydrophilic, on which the TiO$_2$ NP layer is spin-coated to form a bilayer film. The concentrations of the PS and TiO$_2$ NP solutions depend on the desired film thickness. For PS films less than 100 nm, a 1−3 wt% PS solution is prepared and spin-coated at 3000−6000 rpm. To generate a ~200 nm TiO$_2$ NP layer for polymer infiltration studies, we prepare a 20 wt% TiO$_2$ NP solution and spin-coat at 3000 rpm. For nanoindentation tests, thick PS films (>400 nm) require spin-coating a 10−15 wt% PS solution at 1000−3000 rpm, whereas the TiO$_2$ NP layer (>1.7 μm) requires spin-coating a 45 wt% TiO$_2$ NP solution at 1000 rpm.

4.2.3 Characterization
PS infiltration into the voids of the TiO$_2$ NP layer is monitored using an Alpha-SE spectroscopic ellipsometer, while the bilayer film sample is annealed using a Linkam THMS350 V heating stage. The heating stage has a temperature resolution of 0.1 °C. The stage on which the sample is placed is 22 mm in diameter and is open to ambient air. The Linksys software displays the stage temperature and allows the user to input the desired set-point temperature, heating rate, and hold time for the set-point temperature. The ellipsometry data are collected in the range of λ = 380 - 900 nm at an incident angle of 70° and are analyzed using the CompleteEASE software package provided by J.A. Woollam.
The contact angles of water on the film surfaces are determined using a Biolin Scientific Attension goniometer. Scanning electron microscopy images are taken using a JEOL 7500F HRSEM to observe the nanoporous PINF morphology and to measure the film thickness. Before imaging, each sample is coated with a thin gold/palladium layer using a Cressington sputter coater 108 to prevent charging. The samples are imaged at an accelerating voltage of 5 kV, emission current of 20 μA, and a working distance of approximately 8 mm.

The hardness and elastic modulus of the PS film, TiO$_2$ NP film, and the nanoporous PINFs (>1.7 μm thick) are measured using nanoindentation (Hysitron TI 950 Triboindenter). A diamond Berkovich tip is used for all nanoindentation measurements; the area function of the tip is calibrated using a fused quartz standard sample. The thermal drift of the indenter is stabilized to less than 0.3 nm s$^{-1}$ before performing the nanoindentation tests. For each sample, 49 indentation tests, with nine partial unloading cycles each, are performed on a 7 × 7 grid with a spacing of 20 μm between the indents. Each data point in Figure 4.15 represents the average of 441 measurements on a single sample. The maximum loads in the test ranged from 40 to 500 μN, resulting in indentation depths of 50 − 250 nm. The hardness and modulus are determined from the force displacement curves using the Oliver-Pharr method.$^{191}$

4.2.4 Spectroscopic Ellipsometry Data Fitting and Modeling
First, the optical constants (A, B, and C) of pure PS film and pure TiO$_2$ NP film are measured using spectroscopic ellipsometry under ambient conditions. The thickness of the
TiO$_2$ NP/PS bilayer film is determined using a two-layer Cauchy model, as shown in Figure 4.1.

![Diagram showing TiO$_2$ NPs layer: A, B, C known and PS layer: A, B, C known](image)

Figure 4.1. Measurement of thickness of bilayer film consisting of a TiO$_2$ NPs layer on a PS layer, using a two-layer Cauchy model.

We perform *in situ* spectroscopic ellipsometry to monitor the PS infiltration into the TiO$_2$ NPs packing. The bilayer sample is placed on the heating stage at ambient condition. The temperature is ramped from room temperature to the setpoint temperature $T = 150 \, ^\circ\text{C}$ at 30 $^\circ\text{C}$/min. At the same time the raw data is collected in the form of amplitude ratio $\psi$ and phase difference $\Delta$. When $\psi$ and $\Delta$ cease to change, the infiltration process is completed as there is no longer any optical (and structural) changes to the film sample.

To analyze the spectroscopic ellipsometry data, we first try fitting with the three-layer Cauchy model. Since the refractive index of the composite layer is not known beforehand, the optical constants are set as variables, whereas those of the PS and TiO$_2$ NP layers are fixed. The thicknesses of all three layers are also set as variables.

For each time step, in order to ensure solution uniqueness, we use the “parameter uniqueness” feature in the CompleteEASE software to determine the most physically feasible solution with the lowest mean squared error (MSE), as shown in Figure 4.2. Once
the solution is updated, we use the “use alternative model” panel, which shows a side-by-side comparison of model fits with gradient and roughness, as shown in Figure 4.3. We use a gradient model to describe the composite layer if there is a significant improvement in the MSE of the gradient model fit compared to the uniform layer model. Finally, we verify if the solution uniqueness still holds upon updating the model before proceeding to fit the next time step.

![Parameter Uniqueness Fit](image)

Figure 4.2. The parameter uniqueness feature maps the MSE of the model as a function of a variable.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Ideal</th>
<th>Roughness</th>
<th>Grading</th>
<th>Roughness &amp; Grading</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSE</td>
<td>21.099</td>
<td>19.439</td>
<td>8.595</td>
<td>7.823</td>
</tr>
<tr>
<td>Roughness</td>
<td>N/A</td>
<td>4.24 ± 0.649 nm</td>
<td>N/A</td>
<td>1.86 ± 0.281 nm</td>
</tr>
<tr>
<td>A</td>
<td>1.790 ± 0.0048</td>
<td>1.766 ± 0.0056</td>
<td>1.789 ± 0.0019</td>
<td>1.779 ± 0.0023</td>
</tr>
<tr>
<td>B</td>
<td>0.01546 ± 0.001755</td>
<td>0.02904 ± 0.002592</td>
<td>0.01753 ± 0.00072023</td>
<td>0.02399 ± 0.001043</td>
</tr>
<tr>
<td>C</td>
<td>0.00274 ± 0.00019581</td>
<td>0.00105 ± 0.00031028</td>
<td>0.00253 ± 0.0434E-05</td>
<td>0.00185 ± 0.00012555</td>
</tr>
<tr>
<td>% Inhomogeneity</td>
<td>N/A</td>
<td>N/A</td>
<td>-5.20 ± 0.159</td>
<td>-4.98 ± 0.150</td>
</tr>
<tr>
<td>Thickness # 2</td>
<td>221.38 ± 0.458 nm</td>
<td>221.32 ± 0.422 nm</td>
<td>220.56 ± 0.182 nm</td>
<td>221.01 ± 0.166 nm</td>
</tr>
<tr>
<td>n of Cauchy @ 632.8 nm</td>
<td>1.84519</td>
<td>1.84490</td>
<td>1.84917</td>
<td>1.84825</td>
</tr>
</tbody>
</table>

Figure 4.3. The ‘try alternative model’ panel summarizes the model output of an ideal model, model with roughness, modeling with grading, and model with both roughness and grading. The panel recommends a model which has a significant MSE improvement with the fewest number of variables relative to other models.
4.2.5 Refractive Index Calculation for Graded Cauchy Model

The Cauchy model with simple grading reports the optical gradient across a film with the variable % gradient, and an additional “number of slices” parameter to divide the film into slices of equal thickness with varying refractive index.\textsuperscript{127,192} The gradient index describes the gradient in dielectric constant or relative permittivity, $\epsilon$, which is related to the refractive index, $n$ by $\epsilon = n^2$.

Cauchy model is valid for non-absorbing films, where $k = 0$.\textsuperscript{192} If the number of slices is even, then the film refractive index is designated to the middle of the film. Otherwise, the slice at the center would adopt the film refractive index output by the model. A positive value in the % gradient indicates increasing refractive index toward the top surface of the layer, whereas a negative % gradient indicates increasing refractive index toward the bottom surface of the layer. Generally, the number of slices is selected such that the MSE stops improving significantly upon further increase of its value.

We show a worked example for gradient calculation to derive the refractive indices of a film from a graded Cauchy model.

$$n_{\text{air}} = 1$$

$$n_{\text{film}} = 2$$

![Diagram](image)

Figure 4.4. Example system of a film on a substrate, with $n = 2$ and 1% gradient obtained using a graded Cauchy model.
Figure 4.4. shows graded Cauchy film with 2 slices, with \( n_{\text{film}} = 2 \), and 1% gradient. Since there are only 2 slices, the refractive index value is assumed to be that of the middle of the film. The relative permittivity of the film would be \( \epsilon_{\text{film}} = 2^2 = 4 \). A 1% gradient across the film would translate to 0.005 variation in relative permittivity across the film, relative to that of air, \( \epsilon_{\text{air}} = 1 \). The difference in relative permittivity is then: \( \Delta \epsilon = 4 - 1 = 3 \). The variation in \( \epsilon \) of each slice is calculated by:

\[
\Delta \epsilon_{\text{slice}} = \frac{\% \text{ gradient} \times \Delta \epsilon}{\text{number of slices}}
\]

In this example, \( \Delta \epsilon_{\text{slice}} = \frac{1\% \times 3}{2} = 0.015 \). This enables us to assign the refractive indices for the individual slices in the layer, as shown in Figure 4.5.

In our work, the grading is an approximation to understand the structure of the composite qualitatively; the graded Cauchy acknowledges the presence of an optical gradient, but the gradient may be more ambiguous and less well-defined than the model suggests.

### 4.2.6 Molecular Dynamics Simulation

The simulations are performed using the molecular dynamics simulation package LAMMPS with a similar approach to that previously described. All quantities are calculated in reduced units specified by the Lennard-Jones parameter \( \epsilon \) and \( \sigma \), which denote...
the interaction strength and size, respectively, of a Lennard-Jones unit. The interactions between all nonbonded units are described by the standard 12-6 LJ potential with cutoff radius 1.75σ:

$$U_{\text{LJ}}(r_{ij}) = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] - 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{\text{cut}}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{\text{cut}}} \right)^{6} \right]$$

All $\epsilon_{ij}$ and $\sigma_{ij}$ values are unity to reflect neutral interactions between the NP, substrate, and the polymer monomers. The substrate is a flat surface of randomly packed LJ sites. Each polymer chain consists of 10 bonded LJ sites, where adjacent monomers interact through a harmonic bond potential $U_b(r) = k/2 (r - \sigma)^2$ with spring constant $k = 2000 \epsilon/\sigma^2$. Each ellipsoidal NP is treated as one rigid molecule composed of 4684 LJ sites arranged in a shell with dimensions 25σ by 50σ.

The NP packing is formed by annealing an array of 54 NPs at $T = 25 \epsilon/\sigma^2$ and then compressing it to an $xy$ cross-section of 100σ by 100σ to produce a dense packing of NPs with packing fraction $\sim 0.6$. Periodic boundaries are used in the $xy$-plane to simulate an infinitely extended packing. The packing is then placed on top of a film of the equilibrated polymers with half the number of LJ units necessary to fill the packing voids. The whole system is then annealed at $T = 0.7 \epsilon/\sigma^2$ to induce infiltration into the packing.

4.3 Results and Discussion

Recently, we introduced a technique that relies on capillary rise infiltration (CaRI) of a polymer to generate nonporous composite films with extremely high filler fraction (> 50 vol%).

This technique involves first generating a bilayer film of nanoparticle (NP) and
polymer, followed by annealing of the bilayer above the glass transition temperature ($T_g$) of the polymer to induce polymer infiltration into the interstices of the disordered NP packing.

A key fundamental question that we address in this work is how the polymer distributes spatially in a NP packing prepared via CaRI in an undersaturating condition, that is, when the amount of polymer is insufficient to completely fill the voids in the NP packings. There are two potential outcomes as illustrated in Figure 4.6. The resulting film may end up with two distinct layers: a pure NP layer atop a completely filled nanocomposite layer as a result of the CaRI process (Figure 4.6a) or a uniform PINF with porosity due to spreading of the polymer throughout the structure (Figure 4.6b).

Figure 4.6 The possible PINFs morphology upon annealing an undersaturated bilayer film of nanoparticle layer on a polymer layer. (a) The polymer infiltrates the voids via capillary rise infiltration (CaRI) and stops when it is depleted; (b) the polymer distributes throughout the nanoparticle packing to form a uniform nanoporous PINF.
To monitor the fate of the polymer and to determine the type of nanocomposites that would be obtained based on undersaturated CaRI, we generate a bilayer film of a disordered NP layer on a polymer layer, while keeping the amount of polymer below the void volume of the NP layer. We use polystyrene (PS, Mn = 8000 g mol$^{-1}$) and titanium dioxide nanoparticles (TiO$_2$ NPs, 37.4 ± 6.7 and 28.8 ± 4.1 nm in their long and short axes, respectively), synthesized using a previously reported hydrothermal method,$^{190,194}$ as the polymer and NP phases, respectively. Henceforth, we will refer to the volume fraction of PS in each film by $\phi_{PS} = h_{PS}/h_{TiO_2\,NP}$, where $h_{PS}$ and $h_{TiO_2\,NP}$ are the thicknesses of the PS layer and TiO$_2$ NP layer, respectively. The average porosity of the TiO$_2$ NP film ($p_{NP}$) is $\sim$0.45, measured using liquid cell ellipsometry.$^{195}$ We first spin-coat the PS layer from a toluene-based PS solution onto a silicon substrate, then the TiO$_2$ NP layer from an aqueous TiO$_2$ NP solution on the PS layer. Subsequently, we anneal the bilayer film above the $T_g$ of PS for 72 h to induce its infiltration into the NP packing.

Figure 4.7 shows the cross-sectional scanning electron microscopy (SEM) images of the samples before and after thermal annealing. The polymer layer is completely depleted after annealing, confirming polymer infiltration. PINFs with different degrees of undersaturation (i.e., polymer fill fraction, $\phi_{PS}$) show some qualitative differences in their morphologies, as shown in Figure 4.7b–d. Specifically, the PINF with lower polymer fraction in Figure 4.7b displays a clearer outline of the NPs, whereas Figure 4.7d shows NPs covered in PS. Each sample shows, albeit qualitative, uniform morphology throughout the thickness, suggesting that the PINFs have macroscopically (i.e., at a length scale larger
than the particle size) uniform structures; that is, the polymer seems to have spread throughout the PINF including the top surface.

![Figure 4.7](image)

Figure 4.7 The cross-sectional scanning electron microscopy (SEM) images of (a) bilayer film composed of TiO$_2$ NPs layer atop a PS (Mn = 8,000 g mol$^{-1}$) layer, prior to the annealing process; and (b-d) nanoporous PINFs after annealing the bilayer films with different PS volume fraction $\phi_{PS}$ at 150 °C for 48 hours. Insets in (b-d) show high magnification morphology of the UCaRI PINFs. All scale bars are 500 nm.

The presence of polymers near the top surface of the UCaRI PINFs can also be confirmed by measuring the water contact angle after annealing, as shown in Figure 4.8. The water contact angles on a neat PS film and a neat TiO$_2$ NP film are \(~90^\circ\) and \(~17^\circ\), respectively, consistent with prior reports.$^{196,197}$ The contact angle on a \(~200\) nm TiO$_2$ NP layer atop a
(~ 45 nm PS film is ~ 25°, close to that of the neat TiO₂ NP film, whereas the PINFs with full infiltration (i.e., ϕₚₛ ≈ ϕₚₙ) have a contact angle of ~ 86°.

Figure 4.8. Contact angle measurement of water on (a) pure TiO₂ NPs film, (b) pure PS film, (c) TiO₂ NP/PS bilayer film surface prior to annealing, and (d) a fully saturated TiO₂ NP/PS PINF.

The contact angle of water on the PINFs is greater than 60° for different extents of undersaturation, as shown in Figure 4.9, indicating the presence of polymer at or near the top surface of the film.
Figure 4.9. Contact angle of water on the UCaRI PINFs at various ϕ_{PS} are significantly larger (> 60°) than that on pure TiO_{2} film (17°).

To quantitatively understand the dynamics of polymer infiltration into the NP layer in real time and to characterize the structure of the fully annealed UCaRI PINFs, we perform in situ spectroscopic ellipsometry to monitor PS infiltration into the TiO_{2} NP packing. Data analysis with an appropriate model is necessary to translate the phase difference (Δ) and amplitude ratio (Ψ) data from the ellipsometry into physical parameters describing the sample, such as thickness and refractive index.\textsuperscript{127} We approximate our system as three distinctive layers on a substrate, from the top: the TiO_{2} NP layer, the PS/TiO_{2} NP composite layer, and the PS layer. The refractive index (n) of each layer is described by the Cauchy model as a function of wavelength (λ) following

\[ n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \]

where A, B, and C are optical constants. Previous work has shown that the dynamics of polymer infiltration into NP packing is consistent with capillary rise of liquid in porous media, as described by the Lucas-Washburn model,\textsuperscript{40,42,47} and could be described using the three-layer Cauchy model. The fundamental question that has yet to be addressed is the
fate of the infiltration liquid (in this case, PS) once the liquid reservoir is completely depleted. To our best knowledge, this question has not been addressed even for a simple liquid. As briefly mentioned above, the polymer can either only infiltrate via capillary rise into the base of NP packing, forming a dense nonporous composite layer beneath a pure NP layer (Figure 4.6a), or spread throughout the NP packing to form a nanoporous PINF (Figure 4.6b).

Figure 4.10. (a) Thickness profiles of the PS, composite, and TiO$_2$ NPs layers as a function of annealing time, obtained using in situ spectroscopic ellipsometry while annealing a 190 nm/45 nm TiO$_2$ NP/PS bilayer film ($\phi_{PS} = 0.24$) at 150 °C. (b) The calculated fraction of PS in the composite layer as a function of annealing time.

Figure 4.10a shows the evolution of the thickness profiles of each layer upon annealing a 190 nm TiO$_2$ NP/45 nm PS ($\phi_{PS} = 0.24$) bilayer film at 150 °C. The sample is heated from room temperature to the annealing temperature of 150 °C at a ramp rate of 30 °C/min. The time axis has been offset to demonstrate the thickness profile changes when the sample is above a $T_g$ of PS ($\sim$87 °C). In the initial stage of annealing during which there is still a residual polymer layer, we observe that the increase in the thickness of nanocomposite layer coincides with the reduction in the polymer layer thickness. Moreover, the increase in the nanocomposite layer at a given time is correlated with the loss of the polymer layer
by $h_{\text{comp}} = h_{\text{PS}}/h_{\text{NP}}$ as shown in Figure 4.10b, indicating that a solid front is moving through the NP packing during this initial stage of annealing. Despite the depletion of the PS layer around $T = 74$ sec, the sample continues to undergo changes in its optical properties, as observed by continued evolution of $\Delta$ and $\Psi$ with annealing time in Figure 4.11, suggesting morphological changes taking place within the UCaRI PINF. We monitor the onset of this transition in the polymer infiltration behavior using an iterative modeling process at each time step. The most reasonable solution is selected based on the best model fit and the solution uniqueness, as detailed in the Methods section.

![Figure 4.11](image)

Figure 4.11. The $\Delta$ and $\Psi$ as a function of time at $\lambda = 667.9$ nm obtained from annealing a bilayer film composed of ~190 nm of TiO$_2$ nanoparticles atop ~45 nm PS film at 150 °C.

From the thickness profiles, we calculate the fraction of infiltrated PS present in the composite layer as a function of time, as shown in Figure 4.10b. Initially, the calculated PS fraction within the composite layer is identical to the porosity of the TiO$_2$ NP packing, indicating the formation of a nonporous PS/TiO$_2$ NP composite consistent with the
observations from previous work.\textsuperscript{40} As soon as the PS layer depletes, however, there is an abrupt transition in the calculated PS fraction in the composite layer, which converges to the $\phi_{\text{PS}}$ value. A plausible explanation is that the polymer undergoes diffusion along the surface of NPs and spreads throughout the NP packing.

To test this hypothesis and to more accurately describe this spreading behavior during the polymer infiltration process, we consider a simple gradient in the composition of the composite layer. In addition to the thickness and optical constants, the graded Cauchy model assumes five layers within the Cauchy domain and provides an additional gradient parameter to approximate the refractive index gradient across the layer.\textsuperscript{127,192,198} A detailed description of the graded Cauchy model along with an example is provided in the Methods section. To reduce the number of variables in the model, the optical constants of the TiO$_2$ NP layer and the PS layer are predetermined from neat TiO$_2$ NP and PS films on silicon substrates.

To provide further insight into the morphological changes of the UCaRI PINF, we probe the spatiotemporal evolution of the refractive indices of the various layers in the film, as shown in Figure 4.12. Initially the sample is composed of the bilayer film of the TiO$_2$ NP layer ($n = 1.67$) atop a PS layer ($n = 1.58$). Upon annealing, the nonporous composite layer emerges between the TiO$_2$ NP and the PS layer, whereas the thicknesses of both NP and polymer layers decrease. When the PS layer disappears, the sample consists of a noninfiltrated TiO$_2$ NP layer atop a nonporous composite layer. Further annealing results in a gradient across the polymer-infiltrated NP layer with decreasing refractive index toward the top surface of the film, indicating the spreading of PS within the TiO$_2$ NP layer.
Finally, the PS redistributes throughout the NP packing and forms a macroscopically uniform nanoporous PS/TiO$_2$ NP PINF. These analyses confirm the transition in the PS infiltration behavior, from a capillarity-induced sharp invading front, to a spreading behavior that eventually redistributes the PS throughout the voids in the TiO$_2$ NP packing. We believe the latter transport phenomenon likely involves the surface diffusion of PS on the NP surface.

![Graph](image)

Figure 4.12. Refractive index of the film as a function of distance from substrate at various annealing intervals, with the schematic illustration representing the film morphology at each stage. The bilayer film composed of 190 nm TiO$_2$ NP layer ($n_{NP} = 1.67$) on a 45 nm PS layer ($n_{PS} = 1.58$), is annealed at 150 °C.
We also perform molecular dynamics simulations to investigate the transport processes that take place during UCaRI. Following our prior work examining CaRI, our simulations use coarse-grained models to mimic the experimental procedure: an equilibrium film of polymer is placed in contact with a disordered NP packing, and we allow capillary forces to wick the polymer into the NP packing as shown in the simulation images in Figure 4.13a. The polymer density profile $\phi_{\text{poly}}(z)$ at different times during the infiltration is shown in Figure 4.13b, which shows the depletion of the polymer film and near homogenization of the NP film; residual variations in the density along the $z$-axis are due to variations in the porosity of the packing due to the finite size of our simulation box.
Figure 4.13. (a) The polymer/NP bilayer film prior to annealing (left) and the PINF after annealing (right). (b) The local polymer density profile along the z-axis with annealing time shows that the polymer infiltrates and gradually distributes throughout the NP packing to form a uniform PINF. (c) The probability that a bead on the surface of the NPs is not in contact with a polymer monomer as a function of time. The bottom 30σ is closest to the polymer film, and the rapid decrease in the probability indicates that this layer of NPs quickly becomes covered with polymer, and the UCaRI film gradually homogenizes with equilibration. Homogenization is accelerated by increasing the temperature from 0.7 to 1.0 around $4 \times 10^5 \tau_{LJ}$. 
To demonstrate that UCaRI occurs in two stages, we calculate the probability that one of the NP surface sites is bare (i.e., not in contact with a polymer monomer) as a function of time, 1 - $P_{\text{contact}}$. From the results in Figure 4.13c, we observe that when we average over the entire packing, 1 - $P_{\text{contact}}$ monotonically approaches its equilibrium value. However, the top and the bottom of the packing exhibit distinct behaviors from each other. The top of the packing also monotonically approaches its equilibrium value, while the NPs near the bottom are quickly covered with polymer (1 - $P_{\text{contact}}$ tends to 0). As the polymer homogenizes through the film, 1 - $P_{\text{contact}}$ calculated in the bottom portion of the film then increases and approaches the value averaged over the whole film.

Both the experimental and computational results indicate that UCaRI provides a simple approach to create graded refractive index (GRIN) PINFs, which could be extremely useful for the generation of broadband antireflection coatings and biomimetic materials with superb mechanical properties. As shown above, after the first stage of infiltration during which the polymer layer is depleted, the polymer starts to spread from the nonporous NP packing at the base of the film. During this intermediate spreading stage, the PINF develops a gradient in its composition as indicated by the gradient in its refractive index. Figure 4.14a shows the evolution of a PINF refractive index as a function of depth of the film with time, where the gradient across the film gradually decreases as the annealing time increases, as shown in the inset of Figure 4.14a.
Figure 4.14. (a) The gradient of the composite refractive index gradually decreases and homogenizes with annealing time. The nanoporous PINF is initially composed of a 190 nm TiO$_2$ NP layer ($n_{NP} = 1.67$) on a 45 nm PS layer ($n_{PS} = 1.58$) and is annealed at 150 °C. The inset shows the decreasing gradient in the composite with increasing annealing time. (b) The fully annealed composite shows little gradient in the refractive indices across the film, indicating even polymer distribution throughout the TiO$_2$ NP packing. For the definition of % gradient, refer to the Methods section. The inset shows that the PINF refractive index increases linearly with the volume fraction of PS, $\phi_{PS}$.

In addition to PINFs with graded structures, it is also possible to generate macroscopically uniform nanoporous PINFs with a wide range of optical and mechanical properties. By varying the polymer composition $\phi_{PS}$ in the initial bilayer films and annealing them completely (i.e., until structural evolution no longer occurs and polymer distributes uniformly throughout the NP packing), nanoporous PINFs with a range of refractive indices of $\sim 1.75 - 2.00$ can be attained, as shown in the inset of Figure 4.14b. More importantly, fully annealed samples are compositionally uniform, as indicated by the low % gradient, which defines the extent of gradient in a film$^{127,196}$ (Figure 4.14b; see Methods section for a more detailed description). These composite refractive indices vary linearly with $\phi_{PS}$ and can be modeled using the volume fraction weighted mixing rule$^{199,200}$:

$$n_{comp} = \phi_{void} n_{void} + \phi_{PS} n_{PS} + \phi_{TiO_2} n_{TiO_2}$$

where $n_{comp}$, $n_{void}$, $n_{PS}$, and $n_{TiO_2}$ refer to the refractive indices of the nanoporous composite, void (air), PS, and TiO$_2$ respectively, whereas $\phi_{void}$, $\phi_{PS}$, and $\phi_{TiO_2} NP$ refer to the volume
fraction of each component. We perform liquid cell ellipsometry to obtain the porosity $p_{\text{NP}}$ and $n_{\text{TiO}_2}$.\(^{195}\) Then, $\phi_{\text{void}}$ can be calculated by subtracting the $\phi_{\text{PS}}$ from $p_{\text{NP}}$.

The mechanical properties, specifically the hardness and elastic modulus, of these nanoporous PINFs are enhanced relative to that of their individual constituents, consistent with findings from previous reports.\(^{40,182}\) We characterize the hardness and modulus of relatively thick UCaRI PINFs (>1.7 μm) via quasi-static nanoindentation with a Berkovich tip. Figure 4.15 shows the normalized hardness and elastic modulus of the nanoporous PINFs relative to that of a pure TiO$_2$ NP film, as a function of $\phi_{\text{PS}}$. Both properties increase with $\phi_{\text{PS}}$; the hardness and modulus of the UCaRI PINF can be tuned up to 3.5 and 2.5 times those of the pure TiO$_2$ NP film, respectively, and 3.3 and 4.6 times those of the neat PS film, respectively. While PS has comparable hardness and lower modulus than TiO$_2$ NP packing, the mechanical properties improve with increasing volume fraction of PS because the PS is filling void space and strengthening the interactions between the particles.

![Figure 4.15. Mechanical properties of the nanoporous PINFs measured using nanoindentation tests. (a) The normalized hardness and (b) the normalized modulus of the composite increase with the PS volume fraction ($\phi_{\text{PS}}$). Every data point is expressed as a statistical average of nine partial loading cycles with loads 40−500 μN at 49 random spots on the sample, with indent depths of 100−200 nm. The error bar represents the standard deviation of the mean. The TiO$_2$ NP film’s hardness and reduced modulus are 271.6 ± 21.4 MPa](image-url)
and 12.9 ± 0.5 GPa, respectively, whereas the PS film’s hardness and modulus are 292.2 ± 28.9 MPa and 6.9 ± 0.3 GPa, respectively.

Remarkably, at fairly low polymer fill fractions ($\phi_{PS} < 0.03$), there appears to be an almost 2-fold increase in the PINF’s hardness from that of a neat TiO$_2$ NP film. This result indicates that the mechanical stability of the nanoporous PINFs can be enhanced significantly, possibly due to increased interparticle bonding via the preferential accumulation of polymers at or around contacts between NPs via capillary bridging$^{201,202}$ without substantial reduction of the porosity. Our MD simulations support the idea that at low fill fractions the polymers accumulate at NP contacts. We calculate the probability that a single polymer chain bridges between two NPs, i.e., that a chain has its monomers in contact with two NPs. When the volume fraction of the polymer is only 0.013, we find that approximately 65% of the chains contact two particles, and this fraction decreases as the polymer fraction increases to 32% at 0.03 and 6% at 0.13, as shown in Figure 4.16. Thus, these PINFs with low fractions of polymer could potentially be extremely useful nanoporous materials in mechanically demanding situations.$^{185,203,204}$
Figure 4.16. The probability that a polymer chain is in contact with two nanoparticles ($P_{\text{bridging}}$) for three different polymer fractions ($\phi_{\text{polymer}} = 0.013, 0.03$ and 0.13). $P_{\text{bridging}}$ increases drastically with lower $\phi_{\text{polymer}}$, suggesting the accumulation of polymer chains near particle contacts. Visualizations of each trajectory show that in lower fraction PINFs, the polymers form rings around nanoparticle-nanoparticle contacts.

Figure 4.17. % Gradient of the PINFs for various polymer/nanoparticle systems as a function of polymer composition $\phi_{\text{polymer}}$. Polystyrene (Mn = 21,000 g mol$^{-1}$, PDI = 1.04; Mn = 173,000 g mol$^{-1}$, PDI = 1.06) and Poly(2-vinylpyrridine) (P2VP) (Mn = 7,800 g mol$^{-1}$, PDI = 1.08) are purchased from Polymer Source, Inc. Poly(methylmethacrylate) (PMMA) (approximate Mw = 75,000 g mol$^{-1}$) is purchased from Scientific Polymer Products Inc. Polyvinylidene fluoride (average Mn = 71,000 g mol$^{-1}$) and silica nanoparticle suspension (Ludox TM-50) are purchased from Sigma Aldrich.
4.4 Conclusions

In this work, we have studied the fundamental processing-structure-property relationship of nanoporous polymer-infiltrated nanoparticle films prepared based on undersaturated capillary rise infiltration. UCaRI is a simple and potentially scalable approach to fabricate nanoporous PINFs with either uniform or gradient porosity. The optical and mechanical properties of these UCaRI PINFs could be varied over a wide range by changing the thickness of the polymer layer undergoing infiltration or the time of thermal annealing. In addition, UCaRI presents an intriguing system to explore polymer transport under confinement. We observe two-stage transport phenomena: the polymer spreads throughout the NP packing following capillarity-induced infiltration, leading to formation of a homogeneous nanoporous PINF. We believe the spreading of the polymer in the second stage is likely due to the surface diffusion of polymer chains on the surface of the NPs. While this work focuses on the transport mechanism of PS in a disordered TiO$_2$ NP packing, we have successfully generated nanoporous PINFs using silica (SiO$_2$) nanoparticles with multiple polymers, such as poly(2-vinylpyridine) (P2VP), poly-(methyl methacrylate) (PMMA), poly(vinylidene fluoride) (PVDF), and PS, whereby we show the refractive indices of these uniform PINFs with different $\phi_{\text{polymer}}$ in Figure 4.17, suggesting that this method is applicable to a wide range of polymers. Our ongoing work aims to systematically study the effects of confinement and the NP-polymer interactions on the polymer dynamics and the mechanical properties of UCaRI composites by changing the molecular weight of the polymer and the interactions between the polymer and NPs. We believe these compositionally uniform or graded nanoporous PINFs with high NP loadings
prepared via UCaRI can have broad impacts in multiple areas including antireflective coatings, separation systems, and protective coating applications that require high mechanical durability and enhanced transport properties.
Chapter 5. Nanoconfinement-Induced Toughening of Nanoporous Polymer-Infiltrated Nanoparticle Films

This chapter is adapted from work that is under preparation for publication, and this work is performed in collaboration with Yijie Jiang and Kevin T. Turner from the Department of Mechanical Engineering and applied Mechanics at the University of Pennsylvania.

5.1 Introduction

Nanoparticle (NP) films have tremendous potential applications in energy, optics, catalysis, sensing, and electronics. However, their applications are currently limited by a lack of durability and poor damage tolerance. NP films tend to be brittle and mechanically weak due to the weak cohesive strength between NPs. As such, there is a need for strategies to mechanically reinforce NP films without compromising their original functionality. Atomic layer deposition (ALD), surface functionalization of NPs, and use of anisotropic particles have been explored as potential routes for reinforcing NP packings.

Natural composite materials, such as nacre and tortoise shells, are comprised of a high volume fraction (> 50 vol%) of hard and brittle material and a smaller amount of soft polymer. Owing to the length scales of the NPs and the polymer, the high volume fraction of hard NPs strongly confine the polymer phase. This unique composite structure and composition of these natural composites lead to enhanced mechanical performance relative to the individual constituents. Thus, bioinspired nanocomposite films (NCFs) mimicking these morphologies present a promising route to reinforcing NP packings. One such NCF is the polymer-infiltrated nanoparticle film (PINF), whereby the void space within dense packed NP films is filled by polymer.
approximately 30% that of the NP size, thus the NP packing inherently imposes significant physical nanoconfinement to the infiltrated polymer with a comparable equilibrium coil size. Nanoporous PINFs with either graded or uniform nanoporosity can be fabricated using undersaturated capillary rise infiltration (UCaRI). In this technique, a bilayer film composed of a NP packing and a polymer film is fabricated. Then the bilayer film is annealed above the glass transition temperature of the polymer to induce wicking of the polymer into the voids of the NP packing. Depending on the relative amount of polymer to void volume in the NP packing and the duration of the thermal annealing, the porosity and the compositional gradient of the nanoporous PINFs can be tuned, respectively, which in turn affects the morphology, optical, and mechanical properties of the PINFs. Specifically, previous study has demonstrated that the elastic modulus of the PINFs can be tuned up to ~4.7 times and ~2.5 times that of the pure polymer and neat NP films, respectively, whereas the hardness can be tuned up to ~3.5 times those of the pure constituent films.

While the hardness and strength of a material are more readily characterized and often reported in literature, fracture toughness, i.e. a material’s resistance to fracture by crack propagation, presents a more critical material property for structural applications. There is typically a tradeoff in strength and toughness in materials, and thus the design of a material that is both strong and tough is an ongoing challenge. Biological nanocomposites show impressive mechanical performance, possessing both high strength and toughness due to their complex architecture and structural composition that enables toughening mechanisms. As such, we hypothesize that UCaRI PINFs can
accommodate increased deformation and exhibit increased fracture toughness relative to pure NP films, by mimicking the structural composition of these biological nanocomposites, by incorporating a small amount of polymer into densely packed NP packing.

In this study, we characterize the fracture toughness of titanium dioxide nanoparticles (TiO$_2$ NPs)/polystyrene (PS) PINFs generated using UCaRI, via the pillar splitting technique. We demonstrate that the fracture toughness of the UCaRI PINFs is tunable by the saturation level or volume fraction of PS and can be increased to ~6 times that of the neat NP film. Furthermore, relative to pure NP films, we observe large enhancement of fracture toughness in the PINFs even at very low polymer saturation level (< 10 vol%), which may indicate the role of polymer capillary bridging as an effective toughening mechanism in these PINFs. In addition, this enhancement in fracture toughness at low polymer volume fraction is further increased with increasing polymer molecular weight, which indicates the role of chain bridging of NPs when the infiltrated polymer stretches under confinement and comes into contact with multiple NPs. Thus, small amount of infiltrated polymer toughens nanoporous PINFs substantially without compromising the nanoporosity, showing UCaRI as a viable approach of mechanically reinforcing nanoparticle packings for various applications.

5.2 Experimental Section

5.2.1 Materials
Polystyrene (PS) of various molecular weights including 8k PS (Mn = 8,000 g mol$^{-1}$, polydispersity index (PDI) = 1.10), 30k PS (Mn = 30,000 g mol$^{-1}$, PDI = 1.06), 173k PS...
(Mn = 173,000 g mol\(^{-1}\), PDI = 1.06), and 500k PS (Mn = 498,000 g mol\(^{-1}\), PDI = 1.08) are purchased from Polymer Source, Inc. TiO\(_2\) nanoparticles (TiO\(_2\) NP) are synthesized using a hydrothermal method\(^{190}\). The major and minor axes of the NPs are 37.4 ± 6.7 nm and 28.8 ± 4.1 nm, respectively.

5.2.2 Fabrication of nanoporous PINFs

The nanoporous PINFs are generated using UCaRI.\(^{52}\) TiO\(_2\) NP/PS bilayer films are first prepared, where the PS layer and the TiO\(_2\) NP layer are deposited sequentially from their respective solution via spin-coating onto clean 1 × 1 cm\(^2\) silicon wafers, using a WS-400BZ-6NPP/Lite spin-coater from Laurell Technologies Corporation. After depositing the PS layer, the PS film is oxygen plasma-treated for ~2 seconds to render the film surface hydrophilic, on which the TiO\(_2\) NPs layer is spin-coated. The PS solution is prepared by dissolving PS in toluene, whereas TiO\(_2\) NPs are dispersed in water. The concentration and spin-rate of the solutions depend on the desired film thickness. For PS films in the range of 50 nm – 500 nm, 1 – 11 wt% PS solution is spin-coated at 1000 – 5000 rpm; whereas PS films 700 nm – 900 nm thick, 15 wt% PS solution is spin-coated at 1500 – 4000 rpm. 45 wt% TiO\(_2\) NP suspension is spin-coated at 1000 – 1500 rpm to generate > 2 μm thick TiO\(_2\) NP layer. The thickness of each layer is determined using spectroscopic ellipsometry (J.A. Woollam Alpha-SE) and scanning electron microscopy (SEM) (JEOL 7500F HRSEM). The bilayer films are then annealed above the PS glass transition temperature to infiltrate PS into TiO\(_2\) NP layer and form uniform PINFs.\(^{52}\) Samples with 8k PS are annealed at 150°C for 170 hours; whereas samples generated with 30k, 173k, and 500k PS are annealed at 170°C for 340 hours to ensure complete polymer infiltration and uniform
polymer distribution, which is verified using SEM and contact angle measurement. The volume fraction of PS in the PINF is determined by the initial ratio of the polymer to NP layer thickness, i.e. \( \phi_{PS} = \frac{h_{PS}}{h_{NP}} \), where \( h_{PS} \) and \( h_{NP} \) are the thicknesses of the PS and TiO\(_2\) NP layer before UCaRI.

Neat TiO\(_2\) NP film and neat PS film are prepared by directly spin-coating 40 wt% TiO\(_2\) NP suspension at 1000 rpm and 17 wt% PS solution at 1000 rpm, respectively, onto clean silicon wafers.

### 5.2.3 Pillar splitting method

The pillar splitting method for measuring fracture toughness is first proposed by Sebastiani et al.\(^{222}\) In this method, a micropillar is first fabricated on the PINF using focused ion beam (FIB). Then, a force-controlled indentation test with a Berkovich indenter is performed on the micropillar. The load increases until a critical load, \( P_c \), is reached and an unstable crack propagates causing the pillar to split. The fracture toughness, \( K_{IC} \) is calculated from the nanoindentation data using:\(^{222,223}\)

\[
K_{IC} = \gamma \frac{P_c}{R^{3/2}} \quad [1]
\]

where \( P_c \) is the critical load, \( R \) is the radius of the micropillar, and \( \gamma \) is a dimensionless coefficient related to the elastic modulus and hardness of material (See equation 6). While this model does not account for possible influence of residual stress in the thin film, our finite element analysis in Figure 5.1 shows negligible residual stress in the micropillar, as the FIB milling creates large free surfaces and enables stress relaxation.
The coefficient of $\gamma$ can be determined from finite element analysis.\textsuperscript{222,223} However, a perfectly sharp Berkovich indenter and an assumed cohesive zone model are needed in the simulations. Here, we use the following method to calculate $\gamma$. In a semi-infinite solid, the stress intensity factor, $K_I$, at the crack tip is:

$$K_I = \alpha \sqrt{\frac{E}{H}} \frac{P}{c^{3/2}}$$ \hspace{1cm} [2]

where $\alpha = 0.016$ for Berkovich indenter,\textsuperscript{194,224,225} $P$ is the applied load and $c$ is the crack length. When the crack propagates towards a free surface, the stress intensity factor is magnified. A magnification factor\textsuperscript{222,226} is used to modify the semi-infinite stress intensity factor:

$$K_I = \frac{\alpha}{1-c/R} \sqrt{\frac{E}{H}} \frac{P}{c^{3/2}}$$ \hspace{1cm} [3]

Thus, the critical length of crack for unstable crack growth is determined by

$$\frac{dK_I}{dc} = 0 \text{ at } c = 0.6R$$ \hspace{1cm} [4]

And therefore, by incorporating $c = 0.6R$ back to Eq. [3], the fracture toughness is

$$K_{IC} = \frac{\alpha}{0.1859} \sqrt{\frac{E}{HR^{3/2}}}$$ \hspace{1cm} [5]

By equating equations. [1] and [5], we obtain:

$$\gamma = \frac{\alpha}{0.1859} \sqrt{\frac{E}{H}}$$ \hspace{1cm} [6]
where $E$ and $H$ are measured from independent nanoindentation tests. The details for $E$ and $H$ measurements of the UCaRI are reported elsewhere.\textsuperscript{52}

5.2.4 Fabrication of micropillars

The micropillars are fabricated using a FEI Strata\textsuperscript{®} DB235 FIB. The micropillars are fabricated by FIB milling with a 30 kV gallium ion beam. All samples are first machined using a 5 nA beam current for rough milling, followed by finer milling steps at lower currents (500 pA -1 nA). For each sample, at least five micropillars are milled at randomly selected locations. SEM images are taken after the FIB milling to measure the radii of the micropillars.

5.2.5 Nanoindentation and post-indentation imaging

The nanoindentation tests are performed using a diamond Berkovich indenter in Hysitron TI-950\textsuperscript{®} nanoindenter. The nanoindenter has an optical microscope with magnification of 20 - 200×. To ensure the precision of the indenter with the user-identified target, a tip-to-optic calibration is performed before every pillar splitting indentation test. During the tip-to-optic calibration, a permanent indent on a pristine sample surface (away from micropillars) is made by indenting the Berkovich indenter under 3 - 5 mN. The optic location is then aligned to the indent position, thus the offset between microscope and indenter is calibrated.

Force-controlled nanoindentation tests are performed at a constant loading rate of 200 $\mu$N/s. The force-displacement data is collected at 200 Hz. The critical load, $P_c$, for each force-displacement curve is determined as the maximum force before the point where a jump in displacement is observed in the test.
After nanoindentation, SEM images of the pillars are acquired using a JEOL 7500F HRSEM to confirm that the indentation is performed at or near the center of the pillars. If the indented location is not aligned near the center of the pillar, or if the nanocomposites delaminated from Si wafer underneath, the data of this pillar is excluded. For each PINF, typically 4 - 5 pillars are tested. Across samples, the indented locations differed from the pillar center by a distance of $0.36 \pm 0.19 \mu m$, as measured from post-indentation SEM images.

5.2.6 Finite element analysis for residual stress

FEA is performed using Abaqus® v6.9. An axisymmetric model is established where a nanocomposite micropillar with radius = 2.5 μm and height = 3 μm on a 1 μm thick silicon substrate. In total, there are 13000 CAX8RT elements in the model. The interface is tied in all degrees of freedom. The bottom surface of silicon is a fixed boundary and the left vertical boundary (dashed line in Figure 5.1A) is an axisymmetric boundary. The material properties – Young’s modulus (E), Poisson’s ratio (ν), and thermal expansion coefficient (α) values are assigned to the nanocomposite and silicon substrate based on realistic estimates: $E_{\text{PINF}} = 30 \text{ GPa}$, $\nu_{\text{PINF}} = 0.25$, $\alpha_{\text{PINF}} = 70 \times 10^{-6} \text{ K}^{-1}$ for the nanocomposite, and $E_{\text{Si}} = 130 \text{ GPa}$, $\nu_{\text{Si}} = 0.3$, $\alpha_{\text{Si}} = 2.8 \times 10^{-6} \text{ K}^{-1}$ for the silicon substrate. In first step, the temperature is reduced from 150 °C to 25 °C (See Figure 5.1A and Figure 5.1B) with the right vertical boundary fixed in radial direction to simulate the cooling process after annealing and before FIB milling. The right vertical boundary is then released as free boundary in second step. Then, the residual stress is calculated.
FEA results indicate a uniform residual stress distribution of 350 MPa in the PINF after annealing and cooling (Figure 5.1B). After FIB milling, large free surfaces are created, which reduces the residual stress significantly across the micropillar (Figure 5.1C and Figure 5.1D). The maximum radial stress and hoop stress are both located at the interface of PINFs and silicon wafer, and that there is only minimal stress (less than 30 MPa) near the top surface of the micropillar, where the indentation is performed to propagate a crack.

![Diagram](image-url)

Figure 5.1 (A) An axisymmetric finite element analysis model and the boundary conditions, (B) the hoop stress after annealing and cooling and before FIB milling, and the residual stress in (C) radial and (D) hoop direction in FIB milled micropillar.
5.2.7 Estimating interfacial area between nanoparticles with infiltrated polymer

We consider a simplified case where two contacting TiO$_2$ NPs with particle radius $r_0 = 15$ nm, elastic modulus $E = 200$ GPa, and work of adhesion $141$ mJ/m$^2$,$^{32}$ interacting via weak van der Waals forces. The interfacial area between the TiO$_2$ NPs calculated using Derjaguin-Muller-Toporov (DMT) contact model$^{227}$ is $2.6$ nm$^2$ (contact radius $a_0 = 0.9$ nm).

As illustrated in Figure 5.2A, after the polymer infiltration process, a thin layer of polymer coats the NPs, resulting in an increased interfacial radius, $a_1$. At $\phi_{PS} = 0.03$, with only $0.3$ nm of polymer coating ($r_1 = 15.3$ nm), the interfacial contact radius increases dramatically from $a_0 = 0.9$ nm to $a_1 = 3$ nm, correspondingly the interfacial contact area also increases from $2.6$ nm$^2$ to $28.1$ nm$^2$. At the interface, the area of PS is approximately $9.8$ times as large as the TiO$_2$ NP interfacial area.

Another estimation is calculated using a 3D model in the Surface Evolver v2.70. TiO$_2$ NPs in contact are modeled using 2 semi-spheres with radius $15$ nm. The amount of infiltrated PS is set to $\phi_{PS} = 0.03$, and the contact angle between the TiO$_2$ NP and PS is set to $10^\circ$. Surface Evolver solves for the equilibrium distribution of the polymers by minimizing the total surface energy of the whole system. As seen in Figure 5.2B, the polymer, shown in gray, coats the NPs, outlined by the blue dashed line, and forms meniscus. The interface area increases by $146$ times with infiltrated polymer, relative to that of the bare contacting TiO$_2$ NPs.
5.3 Results and Discussion

Nanoporous PINFs composed of TiO₂ nanoparticles and PS are fabricated via UCaRI. Specifically, a bilayer structure consisting of a disordered packing of TiO₂ NPs on top of a PS layer is generated via sequential spin coating, and then the bilayer is thermally annealed to form a PINF. The volume fraction of PS is determined by the initial ratio of the polymer to NP layer thickness, i.e. \( \phi_{PS} = \frac{h_{PS}}{h_{NP}} \), where \( h_{PS} \) and \( h_{NP} \) are the thicknesses of the PS and TiO₂ NP layer before annealing. After PINF formation via UCaRI, the uniform distribution of polymer in PINFs has been confirmed using scanning electron microscopy (SEM). Nanoporous PINFs with a high volume fraction of nanoparticles (\( \phi_{NP} \sim 0.55 \)) and varying polymer volume fraction (0.01 \( \leq \phi_{PS} \leq 0.32 \)) with corresponding porosity (\( p = 1 - \phi_{NP} - \phi_{PS} \)) of 0.45 to 0.13. Neat PS and neat NP films are also fabricated. The film thicknesses are in the range of 2 μm – 5 μm.

It is nontrivial to measure fracture toughness in small volume samples, such as thin PINFs. Conventional fracture toughness measurement techniques for bulk specimens are not applicable to thin films due to geometry constraint of the specimen, which renders the
sample preparation, crack initiation, and application of load challenging. Alternatively, nanoindentation-based techniques have been investigated.\textsuperscript{222-224,229,230} One such technique that has been recently developed is the pillar splitting method.\textsuperscript{222} In this method, the film is first milled into a micropillar geometry using focused ion beam (FIB), then the pillar is loaded in force-controlled nanoindentation using a sharp indenter tip that causes the pillar to split. A jump in tip displacement in the nanoindentation data signifies the crack propagation or the pillar splitting process and allows the critical load at which the fracture occurs to be readily identified from the force-displacement curve. This technique is appropriate for micro-scale fracture toughness characterization of PINFs and has been validated on other materials in previous reports.\textsuperscript{222}

PINF micropillar fracture specimens are fabricated by FIB milling. Figure 5.3A and Figure 5.3B show the cross-section of a PINF ($\phi_{8k_{PS}} = 0.32$) and a micropillar milled from the PINF, respectively. Pillars with varying radii ($R = 1.9 - 3.6 \mu$m) are fabricated to test the sensitivity the pillar splitting method to radius while satisfying the geometric constraint such that the pillar aspect ratio $2R/h > 1$,\textsuperscript{222} where $h$ is the film thickness. A large shallow circle (Figure 5.3B) is milled around the pillar to facilitate alignment of the indenter to the center of pillars during testing.

The pillars are tested in force-controlled nanoindentation experiments in which a diamond Berkovich indenter is used. SEM image of a fractured pillar is shown in Figure 5.3C. The PINF micropillar is split into three roughly equal parts, consistent with the geometry of Berkovich indenter and prior reports.\textsuperscript{222,223,231}
Figure 5.3 (A) Cross-sectional SEM image of UCaRI PINF composed of 8k PS and TiO$_2$ nanoparticles ($\phi_{8k\text{PS}} = 0.32$), (B-C) a FIB-milled PINF micropillar on the same PINF (B) before and (C) after the nanoindentation-based pillar-splitting fracture test.

The force-displacement (FD) curves for several PINFs with different volume fractions of 8k PS and different molecular weights of PS at $\phi_{PS} = 0.01$ are shown in Figure 5.4. Jumps in displacement in the FD curves are clearly seen; these jumps correspond to unstable crack propagation in the pillar and are used to identify the critical load, $P_c$, at which fracture occurs. For a given molecular weight (8k PS) shown in Figure 5.4(A) as the volume fraction of polymer increases, the peak force required to split the pillar increases; whereas at a fixed $\phi_{PS} = 0.01$, we also see increasing peak force for increasing polymer molecular weight, as shown in Figure 5.4(B).
Figure 5.4. Force displacement curves of PINFs with (A) different volume fractions of 8k PS and (B) different molecular weights of polymer at $\phi_{PS} = 0.01$. The displacement is normalized by the maximum displacement, $d_{max}$, of each indentation test. The critical fracture load, $P_c$, is determined as the maximum load prior to the jump in displacement, indicating pillar fracture.

Figure 5.5. SEM images of the fractured micropillars and the schematics of their crack type for (a) neat nanoparticle film with $\phi_{PS} = 0$ and (b) a PINF with $\phi_{8k} PS = 0.27$. The cracks and plastic zones are represented by grey and blue, respectively.
SEM images of the specimens after testing show that the crack type varies between neat NP films and PINFs. For example, fractured micropillars of neat NP films (Figure 5.5A) showed minimal plastic deformed material under the indenter and large through thickness cracks, similar to radial/median cracks.\textsuperscript{232} For the TiO\textsubscript{2} NP/8k PS PINFs (Figure 5.5B), a relatively large plastic deformed area and Palmqvist-like cracks is observed. The crack type is related to the elasticity and plasticity\textsuperscript{222,233} and fracture toughness\textsuperscript{232} of the material. Moreover, we observe complete breakage of the pure NP pillar (Figure 5.5A), clearly indicative of a catastrophic, brittle fracture. Whereas in the case of the PINF pillar (Figure 5.5B), the indenter pillar conformed to the indenter tip geometry and appears to undergo a more homogeneous deformation, a signature of plasticity in the PINF structure.\textsuperscript{213,234} Furthermore, we note from the force-displacement curve in Figure 5.4A that the PINFs with more infiltrated polymer experience lower load drops, consistent to the crack morphology of PINFs displaying increased plasticity.
Combining peak force data from the force-displacement curves, pillar radii measurement, elastic modulus, and hardness measurements, we calculate the fracture toughness, $K_{IC}$, of the PINFs using Eq. [1]. Figure 5.6 shows the fracture toughness of the nanoporous TiO$_2$ NP/8k PS and TiO$_2$ NP/173k PS PINFs as a function of $\phi_{PS}$. By tuning $\phi_{PS}$, the PINF fracture toughness can be tuned from $0.071 - 0.65$ MPa·m$^{1/2}$. The fracture toughness of PINFs with $\phi_{173kPS} > 0.10$ and $\phi_{8kPS} > 0.24$ exceed even that of neat PS films ($K_{IC} \approx 0.34$ MPa·m$^{1/2}$), as shown in Figure 5.7. With increasing $\phi_{PS}$ the hardness and modulus of the PINFs also increase. 52 Thus, by infiltrating NP packings with polymer, we see simultaneous hardening, stiffening, and toughening effects. This observation agrees with prior reports of enhanced stiffness and toughness in nanoconfined polymers. 8,218 Polymer chains confined

Figure 5.6. The fracture toughness for PINFs filled with 8k PS and 173k PS as a function of polymer saturation level, $\phi_{PS}$. The dotted line indicates the fracture toughness value of the pure 8k and 173k PS films, respectively. The error bars represent the standard deviation of uncertainty propagation from experimental measurements of critical loads, pillar radius, film thickness, modulus, and hardness. The dashed line indicates the fracture toughness of neat TiO$_2$ NP film.
in the NP packings can mechanically reinforce the PINFs through several proposed mechanisms. Nanoconfinement of polymer near hard NP surfaces have been reported to show higher effective viscosity as well as glass transition temperature, which suggests the suppression of polymer chain and segmental motion,\textsuperscript{55,121} which may correlate with the mechanical stability of the PINFs. Toughening of the PINFs may also stem from the biomimetic architecture and high volume fraction of the NPs. In PINFs composed of hard NPs and soft polymer, crack preferentially propagates through the soft polymer phase, which fill the void space in the disordered NP packing.\textsuperscript{47,56} The NPs deflect the advancing crack along a narrow, tortuous path, which may blunt growing cracks and dissipate additional energy.\textsuperscript{22,144,215,221} Furthermore, during a fracture event, the advancing crack intercepts the soft polymer phase, where confined chains pull out and stretch, dissipating energy, which further toughens the PINF.\textsuperscript{57}

![Figure 5.7. The fracture toughness of neat 8k PS, 173k PS, 500k PS, and TiO\textsubscript{2} NP films. All films are at least 1.5μm thick. The fracture toughness value is determined using the nanoindentation based pillar-splitting method outlined in the Methods section.\textsuperscript{222} Each data point is obtained from the at least 2 pillar samples, and the error bar represents the standard deviation of uncertainty propagation from experimental measurement of critical loads, pillar radius, modulus, and hardness.](image-url)
Interestingly, we note a significant increase in the PINF fracture toughness at very low $\phi_{PS}$, when compared to that of the pure NP film. For instance, at $\phi_{8k \text{ PS}} = 0.03$, $K_{IC} = 0.25 \text{ MPa}\cdot\text{m}^{1/2}$, which is approximately 3.5 times that of the neat NP film ($i.e. \phi_{PS} = 0$). This is likely due to formation of polymer capillary bridges at low $\phi_{PS}$, whereby polymer accumulates preferentially at contact points between NPs, which in turns increases interparticle bonding. The propensity for the capillary bridge formation increases with stronger physical nanoconfinement, which leads to higher curvature in the NP contacts. At low volume fractions of polymer, the polymer in the PINF is analogous to water in wet granular material, whereby the capillary condensation of water leads to mechanical reinforcement of particle packings. Using analytical model and Surface Evolver calculations, we estimate and show that the interfacial area between NPs can be increased substantially by very low amount of polymer added, thus mechanically reinforcing the NP packing, as shown in Figure 5.2. Moreover, the Surface Evolver calculation also shows the formation of a capillary bridge between NP contacts, leading to $\sim 145$ fold increase of the NP-polymer interfacial contact area in the PINF relative to the NP contacts in neat film. Previous molecular dynamic simulations on UCaRI PINFs also show increased probability of polymer chains in contact with two NPs with decreasing $\phi_{PS}$. Furthermore, previous reports of a model cohesive granular material shows that fracture energy scales with the cross-sectional area of the polymer bridges, which agrees with our observation and calculations.

From Figure 5.6, in the range of $\phi_{8k \text{ PS}} = 0.03 - 0.32$, we observe the fracture toughness of PINFs increases superlinearly with $\phi_{PS}$. This is consistent with previous studies on the
fracture behavior of porous materials.\textsuperscript{240} This may be due to a shift in the dominant toughening mechanism. In particular, the nanoparticles may facilitate crack pinning and deflection\textsuperscript{241} leading to an increase in fracture toughness. This effect has also been observed in polymer/nanoparticle nanocomposite systems with < 20 vol\% NP loading\textsuperscript{232,242,243}.

![Graph showing fracture toughness versus polymer molecular weight for PINFs with different PS volume fractions.](image)

**Figure 5.8.** The fracture toughness for PINFs with $\phi_{PS} = 0.01$, 0.03, and 0.10, as a function of PS molecular weight. The error bars represent the standard deviation of uncertainty propagation from experimental measurements of critical loads, pillar radius, film thickness, modulus, and hardness. The dashed line indicates the fracture toughness of neat TiO$_2$ NP film.

As shown in Figure 5.6, we also observe steeper increase in the 173k PS fracture toughness at low volume fraction and higher fracture toughness at comparable polymer volume fraction relative to 8k PS. This is more clearly demonstrated in Figure 5.8, which shows the fracture toughness of PINFs as a function of infiltrated PS molecular weight, at various $\phi_{PS}$. All PINFs display enhanced fracture toughness at low $\phi_{PS}$ ($\phi_{PS} = 0.01$ and $\phi_{PS} = 0.03$).
relative to the neat NP film, which we attribute to confinement-induced polymer capillary bridge formation and increased interfacial contact area, as previously explained. Generally, this enhancement in fracture toughness increases with the infiltrated PS molecular weight, displaying up to 3.2 fold and 4.6 fold increase at $\phi_{PS} = 0.01$ and $\phi_{PS} = 0.03$, respectively, relative to the NP film. This is notwithstanding the non-sensitivity of nanoindentation-based technique to the mechanical properties of pure polymer thin films,\textsuperscript{244} as shown in Figure 5.7 and Figure 5.9. Past work has attributed the molecular weight toughening effect of nanoconfined polymer to the ability of longer chains to stretch over larger distances, hence dissipating more energy.\textsuperscript{57} Another possibility of increased fracture toughness with molecular weight may be due to long range NP bridging by elongated polymer chains under nanoconfinement.\textsuperscript{30,97} During UCaRI, the comparable pore size to the polymer equilibrium chain size necessitates the polymer chains stretch and undergo conformational changes to enter the narrow, elongated pore.\textsuperscript{55} As such, the highly stretch chains bridge multiple nanoparticles, and this NP bridging effect is increasingly pronounced with increasing polymer molecular weight, which may manifest in the mechanical reinforcement of such PINF.\textsuperscript{245}
Figure 5.9 The (a) elastic modulus and (b) hardness of neat 8k PS, 173k PS, 30k PS, 500k PS, and TiO$_2$ NP films. All films are at least 1.5μm thick. The elastic modulus and hardness are measured using nanoindentation tests. Every data point is expressed as a statistical average of nine partial loading cycle with loads 40 - 500 μN at 49 random spots on the sample, with indent depths between 100 to 200 nm. The error bars represent the standard deviation of the mean. The hardness and modulus are determined from the force displacement curves using the Oliver-Pharr method.\textsuperscript{191}

5.4 Conclusion

We generate TiO$_2$ NP/PS PINFs using UCaRI, with extremely high NP loading ($\phi_{NP} \sim 0.55$) and varying polymer volume fraction ($\phi_{PS}$) and correspondingly, varying porosity. We characterize the fracture toughness of the PINFs based on a nanoindentation-based pillar splitting method. Relative to the bare NP film, the fracture toughness of the PINFs increases with $\phi_{PS}$, even exceeding that of neat polymer films. We observe a drastic jump in PINF fracture toughness at low polymer volume fraction (\textit{i.e.} $\phi_{PS} < 0.10$), which we attribute to the formation of polymer capillary bridges in the narrow NP contact region, which significantly increases the NP-polymer interfacial area and strengthens the NP contact. By increasing the molecular weight of the polymer, we see further increase in PINF fracture toughness at low $\phi_{PS}$, which indicates the role of multiple NP bridging under nanoconfinement. Our study shows the tunability of PINF design parameter, namely polymer volume fraction and polymer molecular weight, to achieve desirable fracture
properties. With small amount of infiltrated polymer, we see great enhancement in the fracture toughness of NP packing, which shows promise to reinforce NP packings without sacrificing porosity for potential applications in lightweight composite, separation membranes, and structural coatings.
Chapter 6. Summary and Outlook

6.1 Summary

This thesis aims to further our understanding on the capillary rise infiltration (CaRI) process of polymer, which enables future scale-up processing considerations and design of nanocomposite films (NCFs) with optimal and tailored properties. The work in this thesis strives to answer several fundamental questions we pose about the CaRI process, by exploring the role of physical nanoconfinement, polymer-nanoparticle interaction, undersaturation on the polymer CaRI dynamics and partially consolidating the processing-structure-property relationship of the latter CaRI, with an emphasis on mechanical characterization.

Chapter 1 presents an overview on the attractiveness of polymer nanocomposite films (PNCFs) with high loadings of nanoparticles (NP) for wide-ranging potential applications and addresses the limitations of current fabrication techniques for such PNCFs. The CaRI process of polymer is presented as a straightforward technique to overcome the hurdles of conventional methods. Initial characterizations show the versatility of CaRI on various NP packings, and CaRI polymer-infiltrated nanoparticle films (PINFs) show enhanced mechanical performance. The polymer CaRI dynamics and properties may be influenced by confinement, polymer-nanoparticle interaction, and undersaturation. Thus, Chapter 1 summarizes our goals to systematically study the role of each aforementioned factor on the polymer CaRI dynamics and the corresponding CaRI PINFs’ properties.

Chapter 2 explores the effect of physical nanoconfinement on the viscosity and glass transition temperature ($T_g$) of unentangled polymer undergoing CaRI, in a weakly
interacting polymer-nanoparticle system. By tuning the confinement ratio (CR), defined as the ratio of polymer radius of gyration ($R_g$) to the average pore radius ($R_{pore}$) in the nanoparticle packing, we observe increasing viscosity and $T_g$ with increasing CR until CR $\sim 1$. This observation suggests that physical nanoconfinement slows down both segmental and chain dynamics. While it is generally accepted that weakly interacting systems tend to show enhanced polymer dynamics due to dominance of surface effects over polymer-substrate or polymer-NP interfacial effects, our observations show that in highly-loaded PINFs, physical nanoconfinement effect can dominate the overall polymer dynamics.

Chapter 3 further explores the role of polymer-NP interaction on the viscosity and $T_g$ of unentangled polymer undergoing CaRI under extreme nanoconfinement. By using polymer-NP systems with comparable CR but different interaction strengths, we observe that both systems behave similarly under extreme nanoconfinement; that is, both polymers experience similar increase in viscosity and $T_g$ at comparable CR. The correlation between the $T_g$ and viscosity increase suggest that the slowdown in chain dynamics can be attributed to the slowdown in segmental motion. Overall, we show that once again, under extreme nanoconfinement, physical confinement effects can dominate over the influence of polymer-NP interactions in determining the polymer behaviors.

Chapter 4 examines the PINF formation as a result of polymer undersaturated CaRI (UCaRI), such that there is less polymer than the void volume in the NP packing. We determine the UCaRI is a two-step process \textit{in situ} and \textit{in silico}: a rapid capillary rise process, and a gradual spreading process likely \textit{via} surface diffusion. By tuning the polymer volume fraction and annealing time, we may derive either uniform or graded nanoporous
Chapter 5 extends on the study on UCaRI PINFs, with an emphasis on their fracture behaviors. Using a pillar-splitting nanoindentation-based method, we study the fracture toughness of UCaRI PINFs as a function of polymer molecular weight and fill fraction. There is a general increasing trend of fracture toughness with polymer fill fraction, and longer chain polymer in PINFs lead to higher fracture toughness values at comparable polymer fill fraction. The role of fracture toughness enhancement of polymer in NP films is especially notable at very low polymer fill fraction, such that the structure still retains most of its original porosity but is mechanically toughened at least 2-fold relative to the bare NP film. We attribute this toughening effect to the formation of nanoconfinement-induced polymer capillary bridge, whereas increasing polymer chain length leads to increased NP bridging and subsequently increased toughening.

6.2 Outlook

So far, many of our works, especially those pertaining to the study of polymer CaRI dynamics, are limited to unentangled polymer. We have verified that entangled, high molecular weight polymers can infiltrate into NP packings, in spite of the extreme nanoconfinement imposed by the NPs. However, our preliminary experiments to quantify and describe the infiltration dynamics of highly entangled polymer into NP packings using \textit{in situ} spectroscopic ellipsometry with multilayer Cauchy-model data fitting show different infiltration behavior than what is observed in the unentangled polymer case. More specifically, the highly entangled polymer does not appear to invade the NP packing in a
uniform, clear front, which is characteristic to capillary rise infiltration. Instead, the polymer may be forming prewetting layer in the NP packing which spreads along the NP surface, followed by a clear front that catches up gradually. Prior studies have reported this distinctive filling processes of polymer in nanopores. The quick surface wetting is attributed to a stronger adhesive force than cohesive force, whereby the polymer favors spreading on the solid surface to reduce the interfacial energy. The cohesive force needed to sustain a continuous bulk filling is weakened by the strong physical confinement effect. Furthermore, the deviation of entangled polymer infiltration dynamics may be related to the high entropic penalty to transport through the narrow pores, as well as disentanglement effects under extreme nanoconfinement. Moreover, the front broadening of a liquid imbibition front in a nanoporous matrix may be more substantial in the case of entangled polymer undergoing CaRI.

We have performed preliminary experiments on entangled polymer systems using *in situ* spectroscopic ellipsometry and analyzed the data using the three-layer Cauchy model with a graded composite layer as described in the Method sections in Chapter 4. Figure 6.1 shows the plot of refractive index versus distance from substrate of a bilayer film composed of SiO₂ NP packing on a 173k PS film at various stages of annealing at T = 180°C. Initially, there are 2 refractive indices value, corresponding to the NP layer (n = 1.31) and the PS layer (n = 1.58), respectively. As we anneal the sample, a third refractive index value, that of the composite layer, emerges between the NP and PS layer. The refractive index, alongside the thickness of the composite layer, continuously increase throughout CaRI. This suggests the formation of prewetting polymer layer preceding the cohesive infiltration.
front. The challenge with pinpointing the exact infiltration dynamic is that the interpretation can vary depending on the model used to analyze the data. For instance, modeling the composite layer without gradient would still give reasonable fit to the data but with provides a different picture on the polymer infiltration dynamics. Furthermore, we have attempted fitting the composite with 2 distinct Cauchy layers, one describing the cohesive invading front and one describing the diffuse prewetting layer. With the additional layer however, the solution uniqueness is no longer guaranteed when there are too many variables to fit.
Refractive index as a function of distance from substrate at various annealing intervals.

The bilayer film is composed of a ~210 nm 22 nm SiO$_2$ NP layer ($n_{NP} = 1.31$) on a ~240 nm ($n_{PS} = 1.58$) and the film is annealed at 180 °C.

Because of this deviation in entangled polymer infiltration dynamics, we are unable to apply the Lucas-Washburn analysis and derive the confined entangled polymer viscosity.

In addition, it is challenging to accurately describe the nature of the infiltration front based solely on a model-dependent technique, such as in situ spectroscopic ellipsometry, whereby it is sometimes challenging to reconcile different model interpretations of the infiltration process. Thus, future studies involving complementary techniques are warranted in order
to understand the infiltration behavior of high molecular weight (entangled) polymers in nanoparticle packings. These complementary techniques may include elastic recoil detection (ERD), small angle X-ray scattering (SAXS), and small angle neutron scattering (SANS).

Another future direction involves the fabrication of biomimetic CaRI PINFs, where we use instead high aspect ratio nanoparticles to more accurately mimic the morphology of natural composites, for instance nanoplatelets in nacre. While there is abundant literature on nacre-like nanocomposites, and we believe it would be advantageous to validate CaRI as a viable process to achieve desirable optical and mechanical properties for applications in structural coatings.

![Figure 6.2](image_url)

Figure 6.2. Schematic illustration of generating nacre-inspired polymer-infiltrated nanoparticle films using CaRI. The proposed nanoparticle is gibbsite nanoplatelet, which are thin hexagonal platelets with aspect ratio $\sim 10$, and poly(methylmethacrylate) (PMMA) as the polymer.

In our preliminary work, we synthesize gibbsite nanoplatelets with average width of 300.4 $\pm$ 35.2 nm and average thickness of 28.4 $\pm$ 5.1 nm, using a hydrothermal method,$^{248}$ as shown in Figure 6.3. To deposit a gibbsite nanoplatelet layer, an aqueous suspension of the nanoplatelet is prepared, and the pH of the suspension is adjusted to $\text{pH} \sim 0 - 1$ using 1 M nitric acid to enhance the dispersion. We generate bilayer films of gibbsite nanoplatelet
packings and 8k PS using spin-coating (Figure 6.4a), and successfully demonstrated in Figure 6.4b that polymer undergoes CaRI into the gibbsite nanoplatelet layer. To more accurately mimic the morphology of nacre, we also explore other avenues of depositing the gibbsite nanoplatelets, such as flow coating or blade coating,\textsuperscript{249,250} to increase the alignment of nanoplatelets. Figure 6.5(a) shows preliminary results of films fabricated using doctor blading at various coating speed, and Figure 6.5(b) shows that this approach is promising to increase the alignment of nanoplatelets. Thus, further extensive characterizations are warranted to correlate the deposition parameters with the film morphology including alignment parameter and film thickness. Next, future work to establish the processing-structure-property relationship of the gibbsite/polymer nanocomposite films is to follow.

Figure 6.3. The scanning electron microscopy (SEM) image of gibbsite nanoplatelets synthesized using a hydrothermal method. The nanoplatelets have an average width of \(300.4 \pm 35.2\) nm and average thickness of \(28.4 \pm 5.1\) nm. The scale bar is 500 nm.
Figure 6.4. The cross-sectional SEM image of the bilayer film of gibbsite nanoplatelet packing and 8k PS (a) before and (b) after CaRI. The scale bar is 500 nm.

Figure 6.5. (a) Gibbsite nanoplatelet films fabricated using doctor blading at decreasing coating speed from left to right. (b) The cross-sectional SEM image of the gibbsite nanoplatelet film deposited at low deposition speed. The scale bar is 500 nm.
APPENDIX

A1. Bulk polymer viscosity value from literature

This appendix section is meant to supplement the details pertaining to bulk polymer viscosity values in Chapter 2 and Chapter 3 for polystyrene (PS) and poly(2-vinylpyridine) (P2VP).

The bulk polystyrene (PS) viscosity value is extracted from literature\textsuperscript{133} based on Figure 6 and Figure 10. Figure 6 shows the plot of \((\log \eta_T/\eta_{217})\) versus \(1/T\), whereas Figure 10 plots Log viscosity versus \(\overline{M}_w^{1/2}\) at \(T = 217\)\(^\circ\)C. We first extract the normalized viscosity as a function of reciprocal temperature for 21k PS from curve 1 (valid for \(M_w \sim 25,5000 – 134,000\) g mol\(^{-1}\)), and 8k PS from curve 2 (\(M_w \sim 11,000 – 13,5000\) g mol\(^{-1}\)) and curve 3 (\(M_w \sim 7400\) g mol\(^{-1}\)). We then extract the viscosities of 8k and 21k PS at \(T = 217\)\(^\circ\)C are extracted using the linear interpolation of the high slope region at low \(\overline{M}_w^{1/2}\) values in Figure 10. The viscosity values as a function of temperature can then be calculated for both 8k and 21k PS. Since the normalized viscosity values extracted from step 1 is only valid at \(T > 130\)\(^\circ\)C, the viscosity values of PS at \(T < 130\)\(^\circ\)C are obtained based on Williams-Landel-Ferry model of PS\textsuperscript{73,81}:

\[
\log(a_T) = \log\left(\frac{\tau}{1000}\right) = \frac{-C_1(T - T_g)}{C_2 + T - T_g}
\]

Where \(C_1 = 13.35\); \(C_2 = 42.00\). \(a_T\) is the shift factor and \(\tau\) is the relaxation time. Viscosity and relaxation time are related through a vertical shift factor (b), that is determine by fitting the data to the data for bulk polymer in literature.
\[-\log \mu = -\log \tau - b\]

The bulk poly(2-vinyl pyridine) (P2VP) viscosity value is extracted from literature\(^{156}\) based on Figure 1 and Figure 4. Figure 1 shows the plot of \(\log a_T\) versus \(T\), whereas Figure 4 plots \(\eta\) versus \(M_W\) of bulk P2VP at \(T = 160\,^\circ C\). From Figure 1, we extract \(\log a_T\) versus \(T\) using data from VPL8 (8,400 g mol\(^{-1}\)) for 8k P2VP and from VPK7 (17,000 g mol\(^{-1}\)) for 22k P2VP. Then, we linearly interpolate the low slope region at low \(M_W\) values (\(M_W \sim 5,000 – 22,000\) g mol\(^{-1}\)) in Figure 4 to obtain the viscosity values for 8k and 22k P2VP at \(T = 160\,^\circ C\). Finally, we obtain the viscosity value as a function of temperature by solving for \(a_T = \mu/\mu_{160}\), where \(\mu_{160}\) refers to the viscosity at reference temperature \(T = 160\,^\circ C\) obtained from the previous step.
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