Mechanical and chemical robustness of the aluminum oxide-infiltrated block copolymer films and the resulting aluminum oxide coatings

Jihyung Lee, Vahid Hasannaeimi, Thomas W. Scharf, Diana Berman *

Materials Science and Engineering, University of North Texas, Denton, TX 76205, United States of America

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ABSTRACT
Block copolymer (BCP) templates have been widely used for the design of functional organic-ceramic composites and ceramic structures. In this study, we explore the mechanical characteristics of such structures designed using sequential infiltration synthesis (SIS). We demonstrate that SIS significantly reinforces the BCP template and decreases their sensitivity to temperature and chemical environment. We also probe tribological characteristics of nanoporous alumina films obtained from the organic-ceramic composites after the BCP template removal. We determined with atomic force microscopy (AFM) that the lateral forces between the tip and the substrate are highly affected by the surface reactivity, surface structure, area of contact, environment, and porosity accessibility and interconnectivity. As confirmed by the quartz crystal microbalance (QCM) analysis, the high accessibility of the pores in the alumina film to the water penetration leads to a decrease in the friction for the ~4 μm in size colloidal tip sliding against the nanoporous alumina in contrast to the bulk alumina. The effect diminishes once the size of the AFM probe becomes comparable to the size of the pores, which is attributed to the limited water flow under the tip to support the applied during sliding stresses. Understanding the surface structure and its effect on the mechanical and frictional characteristics of materials is important for the predictive design of coatings that can sustain thermomechanical stresses and can be used to enhance the lubrication of fluids in various mechanical systems.

1. Introduction
Polymer-ceramic and all-ceramic nanostructured materials exhibit a wide spectrum of useful and sometimes unique mechanical, electrical, magnetic, thermal, and optical properties [1–4]. Discovery of the sequential infiltration synthesis approach (SIS) [5,6] allowed designing nanostructured materials with precise control over porosity, composition, and thickness characteristics. Composite organic/inorganic three-dimensional periodic and random structures that are synthesized using the SIS [7] are converted into nanoporous ceramics by thermally or etching resistance of lithography masks used for patterning nanosized features [17,18], owing to ceramic clusters inside the composites their favorable properties.
Mechanical and tribological characteristics of bulk ceramic films and bulk structures, in particular aluminum oxide, were previously studied across different environments and sliding conditions [19]. Alumina has been widely used as one of the standard materials for ball bearings. An alumina coating improved the wear resistance of a steel substrate [20] and a counterpart steel surface [21] when exposed to sliding in a dry environment. Upon immersion in the water environment, the friction and wear resistance of alumina films further decreased, though corrosion of steel counterparts significantly affected the overall wear observations [21]. In addition to this, prolonged sliding of alumina in the water environment increased the wear of alumina which is attributed to the high load and speed-induced water attack on alumina leading to the formation of aluminum hydroxide [22]. The use of alumina surfaces under mild sliding conditions allowed to improve the tribological properties of moving components, such as artificial hip joints [23]. Alumina-on-alumina bearings were used for total hip arthroplasty to minimize the wear of materials and prevent
osteoletic reaction [24]. Alumina was also considered as a component of metal-ceramic matrices and composite coatings which allowed to improve wear resistance of copper-alumina [25] or aluminum-alumina-graphite composites [26].

In the case of the porous alumina, the majority of the existing studies focused on understanding the mechanical properties of materials produced via anodizing of originally polished samples [27–29]. It was shown that anodizing could used to lower the friction between the alumina surfaces and a corundum ball by reducing the contact area of the sliding interfaces, though the further increase in the porosity of the films could lead to high brittleness of the samples and accelerate formation of abrasive wear debris [30]. Additionally, anodized alumina was used as a substrate for various films, such as amorphous carbon nanorods, which allowed to improve their adhesion and wear resistance [31,32], or as a reservoir for lubricants released during sliding [33,34]. Even though multiple efforts are dedicated to understanding the

![Fig. 1.](image1.png)  
Fig. 1. (a) Schematic of the swelling and infiltration of the non-swollen BCP and the swollen in ethanol BCP. (b) Mass gains measured using the QCM for the P4VP, PS, non-swollen BCP, and swollen BCP after 5 SIS cycles. (c) FTIR spectrum of P4VP, PS, and BCP polymers. (d) FTIR spectrum for swollen BCP, non-swollen +5SIS, and swollen +5SIS BCP measured as related to the initial non-swollen BCP.

![Fig. 2.](image2.png)  
Fig. 2. (a) Nanoindentation results for PS and P4VP before and after 5 SIS infiltration cycles. (b) Nanoindentation results for non-swollen and swollen BCP before and after 5 SIS infiltration cycles.
mechanical and tribological properties of the anodized materials [35,36], mechanical characterization of nanoporous alumina designed by SIS remains a relatively unexplored area.

In this study, we explore mechanical and tribological characteristics of the composite polymer-alumina and single-component nanoporous alumina films designed by the SIS. The nanoindentation studies indicate improvement in the mechanical properties of the composite structures. Using atomic force microscopy (AFM), we compare lateral forces resisting sliding of sharp and colloidal tip over the nanoporous alumina in ambient air, or under immersion in the liquid environment. Quartz crystal microbalance (QCM) analysis confirms the accessibility of the pores for water penetration. We demonstrate that the access of the porosity to the liquids leads to a decrease in the friction of colloidal tip sliding against the nanoporous alumina in contrast to the bulk alumina. Our results create a new understanding of the tribological performance of materials and propose a new approach for controllable testing of the lubrication efficiency.

2. Experimental procedure

2.1. Sample preparation

Two types of samples were considered in the current study, bulk aluminum oxide films and nanoporous aluminum oxide films. Bulk alumina films of ~50 nm thickness confirmed by stylus profilometry were grown on a silicon substrate using the Cambridge Nanotech Savannah 100 atomic layer deposition (ALD) system [37]. Nanoporous alumina films were grown using the previously described sequential infiltration synthesis (SIS) method which involves diffusion-controlled penetration and subsequent chemisorption of inorganic precursor molecules inside a polymer template [38-40]. The polymer template was prepared by spin-coating a 3% polystyrene-block-polyvinyl pyridine (PS-b-P4VP, 75 k-b-25 k) in the toluene solution on the bulk alumina resulting in ~100 nm thick BCP film. After swelling in ethanol at 75 °C for 1 h which, as previously reported [40], results in random
orientation of the P4VP domains in the film, the templates were exposed to 5 SIS cycles. To remove any residual ethanol, the samples were dried in the nitrogen flow overnight before the SIS process. It should be noted that the SIS process is performed at 90 °C which ensures further evaporation of residual ethanol from the swollen films thus creating the additional porosity in the polymer template. One cycle of SIS was performed at 90 °C as follows: 10 mTorr of the trimethylaluminum (TMA) precursor was admitted with 20 sccm nitrogen flow into the reactor for 400 s to infiltrate the BCP template; after the excess reactant was evacuated, 10 mTorr of water vapor with 20 sccm of nitrogen was admitted for 120 s; the chamber was then purged with 100 sccm of nitrogen to remove non-infiltrated byproducts. After the SIS, the polymer template was removed by the ultraviolet ozone cleaning for 20 h. This procedure was previously reported to effectively remove the polymer template while being compatible with the QCM system and preventing the heat-induced defects in the material. The thickness of the resulting nanoporous alumina film was confirmed from the ellipsometry data (M-2000 V ellipsometer) to be ~200 nm.

2.2. QCM measurements

QCM measurements were performed to analyze the infiltration effectiveness of the BCP and confirm the accessibility of the pores of the resulting after the polymer removal alumina oxide to water penetration. The samples of bulk alumina and nanoporous alumina films were prepared using the procedures mentioned above by growing thin films on the top surfaces of the AT-cut 1 in. diameter titanium-coated QCMs with 5 MHz base resonant frequency (Filtech).

QCM allows for non-disruptive highly sensitive in-situ analysis of the modifications of the material [41–44]. For the measurements, the QCM with a coating on the top electrode was fixed in a PTFE holder and the changes in the resonant frequency and the mechanical resistance of the QCM oscillations in air and after immersing in water were monitored using the SRS QCM 200 system. The change in the frequency of the QCM oscillations was attributed to the coupled effect of a viscous medium and the mass gain due to alumina infiltration or water penetration inside the pores [15,45]:

$$\Delta f = \frac{-2f_0^2}{A \sqrt{\rho_q \mu_q}} \Delta m - f_0^{3/2} \frac{\rho_o \eta_o}{\eta_L \rho_L}$$

where $f_0$ is the fundamental frequency of the QCM, $\rho_o = 2.648 \text{ g/cm}^3$ is the density of quartz, $\mu_o = 2.947 \times 10^{11} \text{ g cm}^{-1} \text{s}^{-2}$ is the shear modulus of quartz, $\rho_L = 0.9982 \text{ g/cm}^3$ and $\eta_L = 0.01 \text{ g/(cm s)}$ are the density and viscosity of water, respectively. In the case of the bulk alumina films, the expected frequency change upon immersing in water is 715 Hz.

In addition to the frequency shift, immersion of the QCM in liquids results in changes in the mechanical resistance of the QCM oscillations, measured in Ohms. This resistance is quantitatively added to the oscillator circuit to sustain stable QCM oscillations in a viscous environment [46]. For the bulk alumina-coated QCM with a smooth surface immersed in liquid, the mechanical resistance can be calculated as [47]:

$$\Delta R = (2L_u) \left[ \frac{4\pi \rho_q \eta_q}{\rho_o \eta_o} \right]$$

where $L_u$ is inductance for the dry resonator. In the case of the water environment, the expected mechanical resistance value is 320 Ohms.

Fig. 4. Analysis of the mechanical properties and water access characteristics of the nanoporous alumina in comparison to bulk alumina films. (a) Schematic of the swollen BCP and swollen BCP + 5SIS samples. (b) Nanoindentation results indicate a decrease in the mechanical strength of the coating as expected from the introduction of the porosity in the film. Results of the QCM analysis used to characterize the water penetration inside the porosity of the nanoporous alumina film by monitoring changes in the (c) resonant frequency and (d) mechanical resistance of the QCM oscillations.
2.3. AFM surface analysis

AFM analysis was performed using the Bruker Multimode 8 AFM in tapping mode for evaluation of surface morphology of the films and in contact mode for analysis of lateral forces between the AFM tip and the alumina samples. Tapping mode measurements for the in-situ analysis of structural changes and the chemically-induced modifications were performed in an ambient air environment and in ethanol using the silicon tip (Bruker) with a scanning speed of 0.5 Hz. For the chemical robustness experiments, the temperature variations were applied using the heating stage attachment to the AFM allowing to control the temperature of the measurements from room temperature to 75 °C. The measurements at elevated temperatures were performed after 15 min of the temperature equilibration.

2.4. AFM tribology analysis

Lateral force measurements were done in ambient air and deionized water (DI) environment using a regular silicon nitride tip (Bruker AFM) and a colloidal gold-coated tip (NanoAndMore USA Corp.) at 90-degree
scanning angle direction over a 5 μm × 5 μm scanning area. For the experiments performed in the DI water environment, the samples and the tips were enclosed in a liquid cell filled with water and completely covering the tip and the sample to prevent the impact from capillary forces. The applied normal load during the tests was fixed to 30 nN.

Before the measurements, the lateral forces were calibrated using the wedge calibration method [48].
2.5. Characterization

Modifications of the polymers during swelling and after 5 SIS cycles were characterized using a Nicolet 6700 Fourier Transformation Infrared spectrometer (FTIR) with a 1000–4000 cm⁻¹ spectral range. The surface imaging of the samples before the measurements was performed using the FEI Nova scanning electron microscope (SEM). The elemental composition of the deposited films was confirmed using the X-ray photoemission spectroscopy (XPS) analysis performed with a PHI 5000 Versaprobe Scanning X-ray Spectrometer. Nanoindentation was conducted using a Bruker (TI-Premier) nano-indenter with a diamond Berkovich tip at a load of 1000 μN. At least five indents were made on each specimen to determine the statistical variation, with 100-μm spacing between two indents to avoid any potential overlap of the plastic zones.

3. Results and discussion

3.1. Mechanical properties and chemical robustness of BCP + alumina composites

Swelling and infiltration-induced modifications in the BCP, as well as P4VP and PS, films are summarized in Fig. 1. As previously reported [40], the BCP film expands from ~100 nm to ~200 nm upon swelling in ethanol (Fig. 1a). Mass gain measurements acquired using the QCM indicate the largest degree of the alumina infiltration in the swollen BCP (Fig. 1b), equal to ~36 μg per ~63 μg of the BCP (where ~16 μg belongs to the P4VP component). Similar results were observed in our previous study focusing on the evolution of the BCP during swelling and infiltration [40]. In contrast, for the non-swollen BCP, the mass gain is equal to ~14 μg, indicating that only ~40 nm of the polymer top layer is infiltrated with the alumina [40]. In the case of the P4VP and PS the added by SIS mass gains are ~24 μg and ~3.7 μg respectively, with observed mass gain for PS being attributed to the growth of the alumina coating on the PS film [49].

FTIR measurements (Fig. 1c and Fig. 1d) characterize the effects of the chemically-induced modifications during swelling and infiltration with 5 SIS cycles of TMA + water. As indicated in Fig. 1d, swelling of the BCP increases absorption for CH bending (CH₃ and CH₂ compounds at 1580, 1500, 1450, and 1410 cm⁻¹) [50], becoming the infiltration sites during the SIS process. CH₃ compounds were previously reported as alumina infiltration sites of the P4VP polymer [38]. Therefore, the infiltration of the reactive CH₃ sites before the swelling is expected to suppress the polymer swelling process.

Mechanical properties of the BCP samples before and after the infiltration are characterized using the nanoindentation technique [51] (Fig. 2). The indentation tests were performed to limit the indentation depth to the thickness of the films. PS shows a very negligible change in the mechanical properties (Fig. 2a), which further indicates that PS is not sensitive to the SIS process. Meanwhile, the results indicate higher indentation resistance for the P4VP film than for the PS film which is in agreement with the previously reported observations [52]. The indentation resistance of the P4VP is further increased with the alumina infiltration (Fig. 2a). A similar trend is observed for the non-swollen and swollen BCP films after the SIS infiltration (Fig. 2b), though their indentation resistances are defined by the combination of the infiltrated polar and non-infiltrated non-polar domains. It should be noted that swelling of the BCP significantly reduces the indentation resistance of the films as a result of the incorporation of the void spaces. After the SIS, the observed improvement in the indentation resistance is more dramatic for the swollen BCP than for the non-swollen BCP or PS and P4VP alone (Fig. 2b), though the resulting indentation resistance values for the swollen BCP + 5SIS samples remain lower than for the non-swollen polymers. This improvement indicates more efficient infiltration of the swollen BCP, up to the overall thickness of the film as it was observed in earlier studies [38]. Meanwhile, the infiltration of the non-swollen BCP that is highly driven by the diffusion-based infiltration of the TMA vapors is limited only to the top (~40 nm) layer of the polymer. The observed indentation load-displacement curves, therefore, suggest the composite response of the materials to the mechanical stresses defined by individual properties of the polymer film, swollen or non-swollen, as well as by the infiltrated alumina.

To further test the reinforcement of the composite structure induced by the alumina infiltration, we analyzed the stability of the non-swollen BCP after the immersion in the swelling environment. Fig. 3 summarizes the results observed for the swelling of the non-swollen BCP and non-swollen BCP after 5 SIS cycles when the samples are exposed to ethanol at different temperatures and imaged using the liquid-cell AFM. Upon heating in ethanol, non-swollen BCP (without alumina infiltration) shows porosity (dark spots) opening starting from 55 °C and further increasing at higher temperatures (Fig. 3a–e) thus providing the visual evidence for the temperature effect on the swelling process. Previous studies support this observation that higher temperature results in larger micelle opening effect [40]. The polar domains in which the porosity originates during the ethanol-induced swelling, at the same time act as infiltration sites for the alumina infiltration (white spots). This is supported by the observation that the non-swollen BCP after 5 SIS (with the top 40 nm of the BCP being infiltrated by alumina) shows no changes when exposed to ethanol at elevated temperature (Fig. 3f–j). These results suggest that polymer infiltration of even top 40 nm film results in complete encapsulation of the reactive domains and suppresses swelling-induced modifications in the BCP.
3.2. Mechanical properties of SIS-synthesized alumina films

In addition to the observed improvement in the mechanical characteristics of the BCP + alumina composites, the properties of the nanoporous alumina films were probed after the BCP template removal using the UV ozone cleaning. As reported previously, removal of the polymer template after the SIS procedure results in the formation of nanoporous aluminum oxide films replicating the initial structure of the polar domains in the BCP [18].

The mechanical stability under applied stresses and the water-absorbing characteristics of the porosity were further tested using the nanoindentation and QCM analyses (Fig. 4). For this, nanoporous alumina films synthesized via SIS followed by the polymer template removal (Fig. 4a) were compared to the bulk alumina films deposited by the ALD process. The mechanical strength of the materials was lowered as expected upon 70% porosity introduction (Fig. 4b). We further analyzed the access of the water to the available porosity. The change in the resonant frequency of the QCM oscillations indicates ~780 Hz frequency change being attributed to the porosity filling with water (Fig. 4c). Considering ~200 nm thickness of the nanoporous alumina films with 70% porosity, these results suggest that ~98% of the available porosity is filled with water. Such a high water penetration efficiency is supported by the hydrophilic nature of the nanoporous alumina films [15].

The larger change in the mechanical resistance of the oscillations (Fig. 4d) suggests that the water penetrating inside the porosity still experiences some degree of the decoupling from the oscillating QCM coated with nanoporous alumina film, thus allowing the flow of the liquid through the connected pores.

Fig. 5 summarizes the characterization of bulk and porous alumina films grown on the silicon substrate. While the bulk alumina films have a very smooth surface (Fig. 5a and b), nanoporous alumina films have uniformly-distributed porosity over the surface of the samples (Fig. 5f and g). Notably, the XPS analysis of both samples indicates a higher oxygen concentration for the SIS-grown porous films in comparison to bulk films (Fig. 5c and h, correspondingly), which is attributed to amorphous nature of alumina grown by SIS [53] resulting in the higher presence of oxygen groups in the defects. Also, variations in the Al:O relative concentration can be attributed to the oxygen-rich polymer removal process. Interestingly, in the case of the porous alumina (Fig. 5j), the position of the Al2p peak is shifted to the higher binding energy values than for the bulk alumina (Fig. 5e) which further emphasizes a higher number of the OH groups. This increase in the oxygen groups is expected to result in higher surface energy and better wetting characteristics of the films [54].

In addition to the nanoindentation tests, the resulting structures were further tested for their tribological characteristics using the AFM analysis. In the tests, we used two types of tips, the sharp regular tip with the tip radius of ~20 nm being comparable to the size of the pores and the colloidal tip with the tip radius of ~4 μm being significantly larger than the size of the porosity. The lateral force measurements were performed in ambient air and upon immersing in a water environment to assess the water penetration-caused changes in the tribological response of the films.

Fig. 6 summarizes the lateral force maps of the bulk alumina film. In the case of the sharp tip, a slight increase in the frictional force upon immersion in DI water (Fig. 6b) in comparison to ambient air (Fig. 6a) is attributed to energy losses accompanying movement of the liquid during the tip sliding. In the case of the colloidal tip sliding on the bulk alumina surface, the observed trend is the opposite. Upon transition from the air (Fig. 6c) to DI water (Fig. 6d), the friction slightly decreases. This can be caused by the lower energy of the interactions between the tip and the substrate as a result of water enclosing in the roughness of the colloidal tip.

Meanwhile, in the case of the nanoporous alumina film, the differences in the results for the lateral forces are further emphasized (Fig. 7). While in the case of the sharp tip, the immersion of the samples (Fig. 7b) leads to the friction increase as compared to dry sliding (Fig. 7a), in case of the colloidal tip the lateral force behavior reverses. Upon immersion of the colloidal tip sliding on the nanoporous alumina film surface in the DI water (Fig. 7d), the friction drops in comparison to dry sliding (Fig. 7c).

Fig. 8 presents a comparison of the changes in the frictional forces between the samples, tips, and environments. For this, the average friction values were calculated by averaging over the scanned area and then converting to nN using the wedge method calibrations performed in air and in water correspondingly. The results indicate that in the air (Fig. 8a) friction is similar for bulk and porous alumina films for the sharp tip. However, in the case of the colloidal tip, the increase in the friction for the nanoporous alumina is observed as a result of the higher surface energy of the sample as demonstrated by the XPS analysis. An increase in the friction for the colloidal tip in comparison to the regular tip is associated with the increase in the contact area for the colloidal tip in comparison to the regular tip. In DI water (Fig. 8b), friction for the bulk and porous alumina when using the regular sharp tip remains similar; however, when using the colloidal tip, a significant decrease in the friction from the bulk to the porous sample is observed. While in the case of the bulk film, most of the water is removed from the immediate tip-sample contact under applied contact pressure, water penetration inside the interconnected porosity allows using water for the load support and easier sliding of the system lubricated by the water flow. Similar systems are widely observed in nature, in case of, for example, cartilages, where the easy flow of the natural lubricants in form of synovial fluid is critically important to preventing failures of joints and associated pains [55,56].

4. Conclusions

We performed the quantitative analysis of the mechanical properties and responsiveness to exposure to different environments of SIS-synthesized BCP/alumina composites and porous alumina structures formed after the BCP removal. Our results indicate that alumina incorporation in swollen and non-swollen BCPs leads to improvements in their mechanical characteristics. In addition to the increased strength, the composite structures show high resistance to swelling in ethanol at elevated temperatures, thus suggesting that the infiltration of the polar domains encapsulates the reactive sites of the BCP.

We also measured the tribological characteristics of the nanoporous alumina film obtained after the removal of the BCP in comparison to the bulk alumina. Using the AFM lateral force measurements, we demonstrated that in air friction increases upon transition from the sharp tip to the colloidal tip which is associated with the increase in the contact area. The results obtained with the colloidal tip offer a new perspective on understanding the importance of the porosity accessibility effect on the friction. While in case of the bulk film, the transition from the dry to the water environment results in an increase of the lateral force for the colloidal tip sliding on the alumina surface, in case of the nanoporous alumina film, water penetration inside the pores as confirmed by the QCM measurements, leads to the friction reduction. Understanding the surface structure and its effect on the frictional characteristics of materials is important for the predictive design of coatings that can be used to enhance the lubrication of fluids in various mechanical systems.

CRediT authorship contribution statement

Jihyung Lee: Investigation, Data curation, Writing - original draft, Writing - review & editing. Vahid Hasannaeei: Data curation. Thomas W. Scharf: Resources, Writing - original draft, Writing - review & editing. Diana Berman: Supervision, Investigation, Conceptualization, Writing - original draft, Writing - review & editing.
Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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