Mechanical properties of graphene oxide–silk fibroin bionanofilms via nanoindentation experiments and finite element analysis

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Abstract: Understanding the mechanical properties of bionanofilms is important in terms of identifying their durability. The primary focus of this study is to examine the effect of water vapor annealed silk fibroin on the indentation modulus and hardness of graphene oxide–silk fibroin (GO–SF) bionanofilms through nanoindentation experiments and finite element analysis (FEA). The GO–SF bionanofilms were fabricated using the layer-by-layer technique. The water vapor annealing process was employed to enhance the interfacial properties between the GO and SF layers, and the mechanical properties of the GO–SF bionanofilms were found to be affected by this process. By employing water vapor annealing, the indentation modulus and hardness of the GO–SF bionanofilms can be improved. Furthermore, the FEA models of the GO–SF bionanofilms were developed to simulate the details of the mechanical behaviors of the GO–SF bionanofilms. The difference in the stress and strain distribution inside the GO–SF bionanofilms before and after annealing was analyzed. In addition, the load–displacement curves that were obtained by the developed FEA model conformed well with the results from the nanoindentation tests. In summary, this study presents the mechanism of improving the indentation modulus and hardness of the GO–SF bionanofilms through the water vapor annealing process, which is established with the FEA simulation models.

Keywords: graphene oxide; silk fibroin; layer-by-layer (LbL); nanoindentation; finite element analysis (FEA)

1 Introduction

Nanomaterial-based thin films are widely studied in several engineering fields owing to their excellent material properties and diverse potential applications [1–7]. Several fabrication methods have been used to develop such nanomaterials-based thin films, including solvent casting, painting, spray processing, printing, spin coating, the floating technique, pulsed laser deposition technique, and the layer-by-layer (LbL)

method [8–17]. Among these thin films, graphene oxide (GO)-based thin films, which are synthesized via the LbL method, are noteworthy as they can be used to fabricate multifunctional engineering products [18–21]. GO-based functional films can be used to enhance the electrical conductivity and mechanical durability for certain engineering products [22–24]. Several types of additives have been added in fabrication processes to enhance the functional properties of GO-based thin films [25, 26]. Specifically,

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bionanomaterials have been widely used to improve the engineering functionality and biocompatibility of GO-based thin films. Because biomaterials are biocompatible and biodegradable, they can replace various eco-friendly conventional engineering materials [27–29]. In addition, it is important to understand the mechanical behaviors of biomaterials that are used as vital components of durable and robust engineering applications. The key of the biomaterial-based implants is that they need to have considerable mechanical properties that allow appropriate damage tolerance [30, 31]. Moreover, the biomaterials-based microcapsule that is impregnated with a drug component should possess a favorable hardness to enter the cell membrane. In addition, it should internalize the drug component into the target cells to create a durable drug delivery system [32, 33].

Various functional materials can be employed to build hierarchical layered thin film structures [34–38]. Among these materials, silk fibroin (SF), which is a natural polymer derived from silk cocoons, has received substantial research interest owing to its outstanding strength, favorable amphiphilic properties, and biocompatibility [39–41]. Recently, SF was combined with GO to develop functional bionanofilms that have a strong interfacial strength between the SF and GO layers [42–44]. Moreover, the water vapor annealing process was employed to improve the mechanical durability of the GO–SF bionanofilms [45]. The indentation modulus and hardness are critical factors for the protective coating films and functional carrying structures [46, 47]. Nacre-mimetic GO–SF bionanofilms can be suitable materials in their applications owing to their tailorable mechanical properties via thermal treatment and in applying several weight percentage combinations between the GO and SF [48]. Although several studies are being performed to understand the mechanical properties of the GO–SF bionanofilms, there is still a lack of fundamental knowledge about the interfacial structure of their layers that is related to their hardness and indentation modulus [49, 50].

The complex stress and strain fields on the materials that are generated during mechanical tests can be examined through finite element analysis (FEA) [51–53]. Several researchers have investigated the overall indentation behavior using FEA [54–60]. Tadayon et al.

studied the hierarchical fiber architecture of spider fangs and tarsal claws to understand the mechanical properties that are adapted to their specific functional necessities [61]. A local hardness and reduced modulus of architecture was calculated by the nanoindentation technique, and FEA-predicted stress distribution was mapped to understand the hierarchical fiber architecture. Salinas et al. investigated a crossed lamellar microstructure of the *Strombus gigas* shell [62]. By using the nanoindentation technique and performing an FEA simulation, a significant correlation of the mechanical properties was observed between the orientation of the crossed lamellar micro-structure and the indenter geometry. Bhattacharya et al. compared the load–depth response of the indentation test on three specimen materials through FEA and experiments. The FEA results were observed to be reliable when compared to the experimental results. The differences between the FEA and experimental results arose from the differences in the yield stress, work hardening rate, and tip geometry [57]. In addition, Zhang et al. investigated the mechanical properties, namely the Young's modulus and hardness, of bone through indentation tests and FEA. The viscoelastic/plastic constitutive model was used in the FEA. Several testing parameters such as the maximum load, load/unload rate, and holding time were then considered [58].

In this study, the mechanical properties of the GO–SF bionanofilms, which were fabricated via the LbL technique, were investigated to understand the durability of these films in terms of the indentation modulus and hardness via nanoindentation experiments and FEA simulations (Scheme 1). To verify the effect of water vapor annealed SF on the indentation modulus and hardness of the LbL fabricated bionanofilms, nanoindentation experiments were conducted with two types of GO–SF bionanofilms, namely before and after water vapor annealing GO–SF bionanofilms. The indentation modulus and hardness of the GO–SF bionanofilms were considered in defining the tip area function between the surface of the indenter tip and that of the target sample [63]. The indentation modulus and hardness behaved differently for each of the GO–SF bionanofilms. The results indicate that densely packed hierarchical structures were formed between the GO and SF layers through water vapor

Scheme 1 Overall research outline: bionanofilm fabrication process using LbL assembly technique with graphene oxide (GO) and silk fibroin (SF), GO-SF bionanofilms before and after annealing, and nanoindentation test and FEA.

annealing, thereby enhancing the indentation properties owing to strong interfacial strength between the layers. FEA models of the LbL laminated bionanofilms have been established to simulate the mechanical behaviors of the GO-SF bionanofilms, which includes details of the stress and strain distribution under the indentation loading condition. To exemplify the effect of water vapor annealing on the FEA modeled GO-SF bionanofilms, a Prony series expansion was utilized. In addition, we demonstrated that the load-displacement curves of the GO-SF bionanofilms comply with the experimental data and the FEA simulation results.

2 Material and methods

2.1 Materials

2.1.1 Preparation of graphene oxide (GO)

Graphene oxide (GO) was prepared by Hummer's method [64]. In short, graphite powder (0.8 g) was exfoliated via sulfuric acid (18.5 mL, 95%), sodium nitrate (0.4 g), and potassium permanganate (2.4 g) in an ice-bath, and then in a water-bath. After the exfoliated process, DI-water (37.5 mL) was poured into the exfoliated graphite solution dropwise, and the solution was double boiled into a heated water-bath (approximately 95 °C) for 2 h. Afterwards, DI-water (112.5 mL) and hydrogen peroxide (30%, 12.5 mL) were added into the solution and stirred for 1 h, respectively. The solution was sediment down, and the supernatant of the solution was changed with DI-water by repeating the process three times. To obtain the

graphene oxide, the refined solution was filtrated using a vacuum pump and filtration paper (particle retention: 1 µm) and was dried in a 60 °C chamber.

2.1.2 Preparation of silk fibroin (SF)

Silk fibroin aqueous solution was prepared from *bombyx mori* cocoons [65]. Briefly, silk cocoons were cleaved, degummed, and dissolved with sodium sulfate solution (0.02 M) and lithium bromide solution (9.3 M). Thereafter, the dissolved silk solution was repeatedly subjected to dialysis by applying a dialysis cassette (3,500 MW cutoff) with DI-water replacements. To purify the silk solution, centrifugation (9,000 rpm, 10 min) was performed twice while collecting supernatant after completing a process. The SF solutions were stored inside a refrigerator (4 °C) for a month and a half.

2.2 Method

2.2.1 Fabrication of bionanofilms

GO-SF bionanofilms were prepared with a spin-assisted layer-by-layer (SA-LbL) method to assemble graphene oxide and silk fibroin stacking alternately one layer by one layer until desirable bilayers were stacked [66, 67]. Initially, an Si wafer (20 mm × 20 mm) was cleaned using DI-water and sonification (15 min). Subsequently, graphene oxide (0.3 wt%) and silk fibroin (0.1 wt%) aqueous suspension were spun layer by layer on the cleaned Si wafer. During the SA-LbL, the bionanofilms were rinsed with DI-water to eliminate the excessively stacked material. By using the fabricated GO/SF bionanofilms, water vapor

annealing post-treatment was conducted through a well-established procedure [41]. The bionanofilms were placed on a beaker that was filled with water in half, followed by covering the entrance of the beaker with a plastic wrap. The beaker embracing bionanofilms was in an 80 °C chamber for 1 h.

2.2.2 AFM imaging for bionanofilms

The surface characteristics of the prepared bionanofilms were studied using an atomic force microscope (AFM; NX-10, Parksystems). The morphology of the bionanofilms was observed using the contact mode with a MikroMasch cantilever conical tip (HQ:XSC11/Al BS), which has a force constant and tip radius of 0.2 N/m and 8 nm, respectively. The soft tapping mode was employed to scan the topographical AFM images of the bionanofilms. The scanning rate was selected as 0.5 Hz for all the scanned images. The topographical AFM images of the bionanofilms were scanned with 40 μm × 40 μm selected surface areas.

2.2.3 Nanoindentation test

To study the mechanical properties of the GO-SF bionanofilms, the nanoindentation experiment was performed using a nanoindentation device (Nano Indenter XP, MTS Inc.). Accordingly, a diamond Berkovich tip was used. The indentation moduli and hardness of the GO-SF bionanofilms were measured using the load–displacement curve measurement function of the nanoindentation system. The indentation modulus and hardness of the GO-SF bionanofilms can be identified by applying Eqs. (1) and (2).

$$\frac{dP}{dh} = \frac{2}{\sqrt{\pi}} M \sqrt{A} \quad (1)$$

$$H = \frac{P_{\max}}{A} \quad (2)$$

where P is the load, h is the indentation depth, M is the indentation modulus, H is the hardness, $P_{\max}$ is the maximum load, and A is the contact area [68]. The contact area can be defined using an area function that can be obtained by the Fused–Quartz substrate. The area function of the Berkovich tip can be expressed as

$$\text{Area function } (A_i) = \sum_{i=0}^5 C_i h_c^{1/2^i} \quad (3)$$

where C_i is the coefficient that is defined by the indentation experiment on the Fused–Quartz substrate, and h_c is the indentation depth that is obtained by the indentation measurements on the Fused–Quartz substrate. To define the most accurate area function, the indentation depth range on the Fused–Quartz substrate corresponds to 20% of the total thickness of the target samples (GO-SF bionanofilms). The coefficient C_i can be determined by conducting the indentation experiment at a variable penetration position.

2.2.4 Finite element analysis

To validate the results of the nanoindentation experiment, FEA was conducted with ABAQUS, which is a widely used CAE software. The FEA model was designed on a nanoscale. A Berkovich tip is defined as a three-sided pyramid shape with a height of 0.6 μm and a centerline to face angle of 65.3°. In this work, the blunt tip was defined with a radius of 15 nm, and the indenter was then meshed with 3-D discrete rigid elements by assuming no deformation on the tip. The substrate that consists of GO and SF has a brick shape with a thickness of 500 nm. It was modeled with a composite LbL laminate with the viscoelastic property. A Prony series expansion was considered to describe the viscoelastic behavior. The relaxation modulus $E(t)$ is defined as

$$E(t) = E_{\infty} + \sum_{i=1}^n E_i e^{-\frac{t}{\tau_i}} \quad (4)$$

where E_{∞} is the equilibrium modulus, E_i is the elastic modulus, and τ_i is the relaxation time. A pair of E_i and τ_i is determined by the Prony series. Here, instantaneous modulus E_0 can be represented as

$$E_0 = E_{\infty} + \sum_{i=1}^n E_i \quad (5)$$

Therefore, the relaxation modulus $E(t)$ can be represented as

$$E(t) = E_0 - \sum_{i=1}^n E_i \left(1 - e^{-\frac{t}{\tau_i}} \right) \quad (6)$$

To simulate the indentation experiment, the contact between the tip and substrate should be considered.

In this study, a frictionless condition was assumed for simplifying the tangential behavior. A symmetric model was used for the simulation to reduce the computational time.

3 Results and discussion

3.1 Morphology of the GO–SF bionanofilms

The surface morphology of the GO–SF bionanofilms before and after annealing and the thickness of the bionanofilm was examined using AFM (Fig. 1). The surface roughness of the GO–SF bionanofilm before and after annealing are 16.1 ± 4.1 nm and 10.4 ± 2.1 nm, respectively. The values of the surface roughness indicate that the GO–SF bionanofilms that were fabricated by the SA-LbL techniques possess a smooth surface as reported in the Refs. [42, 45]. Moreover, the structural shape of the surface morphology between the two different GO–SF bionanofilms varied. Specifically, a globular type structural shape was observed through the GO–SF bionanofilm before annealing (Fig. 1(a)). Meanwhile, a more fibrillar type structural shape was discovered in the GO–SF

bionanofilm after annealing (Fig. 1(b)). Notably, SF molecular structures can be formed in the nanofibrillar structural type from the globular cluster-like structures after water vapor annealing [45]. The change in the structural type surface morphology of the GO–SF bionanofilms can affect the interfacial strength between the layers of the GO–SF bionanofilms, which implies that the overall indentation modulus and hardness of the GO–SF bionanofilms can be significantly changed through water vapor annealing. This will be discussed with the indentation test results in Section 3.3. The edge region of the GO–SF bionanofilms on Si substrate was scanned by performing AFM to measure the average thickness of GO–SF bionanofilms, which was approximately 519 nm (Figs. 1(c) and 1(d)).

3.2 Calibration of the indentation tests

By performing multiple indentation experiments on the Fused-Quartz substrate (indentation modulus: 69.5 GPa), the area function of the Berkovich tip was determined with various coefficients at each indenting depth. Multiple loads were applied to measure the mechanical properties of the Si substrate within a target indentation depth range of 5–50 nm. By using the

Fig. 1 Representative AFM topography images (z -scale: 150 nm) of the GO–SF bionanofilms: (a) before annealing and (b) after annealing. (c) 3D topography image of the GO–SF bionanofilm on a Si substrate, and (d) the surface profile data of the GO–SF on the Si substrate to determine the thickness of the bionanofilm.

determined area function, the indentation modulus and hardness of the Si substrates were measured through the indentation experiment. The statistical results of the modulus and hardness are shown in Fig. S1 in the Electronic Supplementary Material (ESM). The modulus and hardness of the Si substrate are approximately 168.9 GPa and 12.1 GPa, respectively (Figs. S1(a) and S1(b) in the ESM). These values for the indentation modulus and hardness of both Si substrates correspond to the existing studies [69, 70]. According to the indentation results of the Si substrates, it can be determined that this indentation system has been calibrated.

3.3 Nanoindentation tests of the GO/SF films

The nanoindentation tests were performed with different types of GO–SF bionanofilms. The first group is the GO–SF bionanofilm before water vapor annealing, and the second group is the GO–SF bionanofilm after water vapor annealing. These two types of films are coated on the top surface of both Si substrates. The indentation experiments were conducted to obtain the mechanical properties, such as the indentation modulus and hardness, of those films using the load–displacement curves. The loading force condition was on the top surface of each bionanofilm during the nanoindentation experiments. Figure 2 presents the representative load–displacement curves before and after annealing the GO–SF bionanofilms. In both curves, no plastic deformation was observed during the nanoindentation tests. There are no substrate-effects on these results because of the small indentation depth: less than 20% of the total thickness of the bionanofilms in all cases of the indentation experiment is up to 0.75 mN indentation for the loading condition. The viscoelastic properties of GO–SF bionanofilms can be thoroughly considered with the application of a constant loading rate region at the maximum load and at the specified unloading segment [71, 72]. Thus, two platform regions were observed throughout the load–displacement curves at the maximum loading segment and the end of the unloading segment (Fig. 2).

Figure 3 presents the results of the indentation modulus and hardness of the GO–SF bionanofilms on the Si substrates. The indentation modulus and

Fig. 2 Representative load–displacement curves of the GO–SF bionanofilms before and after annealing.

hardness of each sample were measured using the determined area function of the Berkovich tip. In each case, there were no considerable deviations on the indentation modulus and hardness of the bionanofilms. The GO–SF bionanofilms that were fabricated before and after annealing possessed an indentation modulus of 22.1 ± 7.1 GPa and 45.5 ± 4.8 GPa, respectively. Moreover, the hardness of the GO–SF bionanofilms before and after annealing were measured to be 0.8 ± 0.2 GPa and 2.3 ± 0.6 GPa, respectively. In addition, the average indentation modulus of the GO–SF bionanofilms after annealing was 106% higher than that before annealing, and the hardness of the GO–SF after annealing increased with an increase of 200% than that before annealing. Therefore, the GO–SF bionanofilms before annealing have lower values for the indentation modulus and hardness rather than the GO–SF bionanofilms after annealing. The mechanical properties of the bionanofilms can be increased by conducting water vapor annealing because of the enhancement of the packing density and a more aligned domain of the silk fibroin [45]. These results indicate that water vapor annealing affects the mechanical properties of the GO–SF bionanofilms according to the observed indentation modulus and the hardness behavior. Accordingly, water vapor annealing can enhance the mechanical properties of the final GO–SF bionanofilms in terms of durability.

Higher surface area densities of SF molecular structures can be realized on GO layers, demonstrating a favorable interfacial interaction at the interface via

Fig. 3 Results of the indentation modulus and the hardness of the GO-SF bionanofilms before and after annealing: (a) indentation modulus and (b) hardness. Each bar is represented as the mean $\pm$ STD.

rapid solvent evaporation after the SA-LbL process [39]. Substantial interfacial interactions can be facilitated by maximizing hydrophobic interactions, hydrogen bonding interactions, and polar-polar interactions between GO and SF owing to the densely formed SF molecules on the GO layer [39, 45]. Thus, more densely and finely formed networks of interactions between GO and SF can be developed after the water vapor annealing process (Fig. 4(a)) [39, 45]. Furthermore, the Raman spectra of the GO-SF bionanofilms indicated that peak intensity ratios of D-band (I_D) to G-band (I_G) were calculated to be 0.996 and 0.997 for the GO-SF bionanofilms before and after annealing, respectively (Fig. S2(a) in the ESM). The results demonstrated that there are similar GO-based layered structures between the GO-SF bionanofilms before and after annealing [73]. Figure S2(a) in the ESM shows that the GO-SF bionanofilms after annealing have a lower intensity at 2D than the intensity of these bionanofilms before annealing. One possible explanation for the decreased 2D band is that through water vapor annealing post-treatment, an increased content of β -sheets in SF was reconstructed, and densely packed interfacial structures were formed in the GO-SF bionanofilms [41, 45]. The thickness of the GO-SF bionanofilms before and after annealing was measured using AFM (Fig. S2(b) in the ESM), with the results yielding values of 519 nm and 489 nm, respectively, which indicated that the bionanofilms were densely packed via the water vapor annealing post-treatment. As demonstrated, water vapor annealing influenced the interfacial interaction between the GO and SF layers by manipulating the structural ordering of the GO-SF bionanofilms and

increasing the content of the β -sheet in the GO-SF bionanofilms [45]. The crystallinity of the SF can be changed by water vapor annealing, thereby forming a more ordered fibrillar type hierarchical structure in the GO-SF bionanofilm (Fig. 1(b)) [41]. Moreover, the β -sheet domains, which is related to the backbones of the compact-packed chains, can be increased by water vapor annealing in the GO-SF bionanofilms [41, 45]. Notably, this increases the β -sheet content in the GO-SF

Fig. 4 (a) Basic formation model of GO-SF bionanofilms before and after annealing. Schematics of the structural changes in the GO-SF bionanofilms before annealing: (b) GO-SF bionanofilms without application of the indentation load, (c) GO-SF bionanofilms with application of the indentation load. Illustrations of the structural changes in the GO-SF bionanofilms after annealing: (d) GO-SF bionanofilms without application of the indentation load, (e) GO-SF bionanofilms with application of the indentation load.

bionanofilms, and the highly-ordered morphological structures of the GO-SF bionanofilms can improve the mechanical performance of the GO-SF bionanofilms [45, 74, 75].

According to the practical discussed points in the previous studies and the morphological analysis of the GO-SF bionanofilms before and after annealing in Section 3.1, structural modification of the GO-SF bionanofilms can be identified under water vapor annealing, which may affect the indentation modulus and hardness of the GO-SF bionanofilms (Figs. 4(b)–4(e)). As demonstrated, the structural shape of the SF molecules, which consists of crystalline and amorphous regions, transformed from a disordered globular like nanocluster to more aligned hierarchical nanofibrils structures. In addition, the nanofibrillar-formed-SF can firmly cling to the GO layers with compact packed layers through water vapor annealing [45, 75]. Based on the strong interaction of the annealing effect between the GO and SF, the indentation behavior of the GO-SF bionanofilms before and after annealing can be determined. The densely packed, well-aligned SF nanofibrils between the GO layers can increase the mechanical strength of the GO-SF bionanofilms after annealing (Fig. 4(d)). In contrast, a globular-like nanocluster SF results in lower mechanical properties of the GO-SF bionanofilms before annealing (Fig. 4(b)). It is worth noting that the multilayered hierarchical nanofibrils SF that were obtained by water vapor annealing can result in greater mechanical properties, such as the indentation modulus and hardness, with an enhancing efficiency of the loading transfer and interfacial interactions between the GO and SF layers [39, 76].

3.4 FEA simulation of the GO/SF films

The indenter was meshed with linear triangular elements (R3D3 under ABAQUS). In this simulation, 3,831 elements were used for modeling the rigid indenter. The substrate was meshed with linear hexahedral elements (C3D8R under ABAQUS). The substrate model consisted of 14,560 elements, and the relative fine meshes were considered in the central part of the substrate to describe the contact analysis of the indenter. The substrate was designed as a solid, consisting of GO and SF layers with a thickness of

500 nm. For the computational efficiency, the x -axis cross-section of the model had a symmetrical plane. The bottom surface of the substrate was defined as the fixed boundary condition, and the concentrated force was applied to the tip of the indenter in the negative z -direction. We assumed that the motion of the indenter was on the z -axis. The specific model is demonstrated in Fig. 5.

For the FEA simulation, models were established for the GO-SF bionanofilms before and after annealing. The viscoelastic parameters of the FEA simulation were optimized to describe the experimental nanoindentation data with the substrates before and after annealing, which are listed in Table S1 in the ESM. The Prony series parameters, which are related to the damping characteristics of the viscoelasticity and time, are listed in Table S2 in the ESM.

The load–displacement curve in the nanoindentation was first investigated. The three specimens per case before and after annealing were considered in the FEA simulation. The results show that the FEA models can predict the experimental nanoindentation results for the substrates before and after annealing (Figs. 6(a) and 6(b), and Fig. S3 in the ESM). It should be noted that the substrate behavior of the viscoelastic property represented by the Prony series is significantly dependent on time [77–79]. As discussed, the experimental load–displacement curves of the nanoindentation clearly show that water vapor annealing reinforces the mechanical properties of the GO-SF bionanofilms. To describe the feature, larger parameters of the Prony

Fig. 5 FEA model of the GO-SF bionanofilm for the nano-indentation characterization.

Fig. 6 Comparison between the experiment and simulation: (a) GO-SF bionanofilm before annealing, (b) GO-SF bionanofilm after annealing. Contour plots of the FEA simulation results: (c) von-Mises stress of the GO-SF bionanofilm before annealing, (d) von-Mises stress of the GO-SF bionanofilm after annealing, (e) strain of the GO-SF bionanofilm before annealing, and (f) strain of the GO-SF bionanofilm after annealing.

series for the annealing case were used instead of the ones for the before annealing case (Table S2 in the ESM). Notably, the viscoelastic creep behavior may be more significant in the GO-SF bionanofilms before annealing with loosely packed structures in terms of smaller Prony series parameters. Meanwhile, the GO-SF bionanofilms after annealing have densely packed structures with larger values for the Prony series parameters.

The FEA simulation results of the von Mises stress and the principal strain distribution indicated that complex stress and strain fields were generated during the indentation test on the GO-SF bionanofilms (Figs. 6(c)–6(f), Figs. S4 and S5 in the ESM). The maximum stress and strain were expressed at the

point that contacts the tip of the indenter. The von Mises stress contour demonstrated that considerably higher von Mises stresses were observed in the GO-SF bionanofilms after annealing rather than in the GO-SF bionanofilms before annealing. However, the principal strain contour demonstrated that smaller principal strains were exhibited in the GO-SF bionanofilms after annealing rather than in the GO-SF bionanofilms before annealing. As suggested from the experimental indentation modulus and hardness results that were previously discussed, the results of the FEA analysis demonstrate that solid elastic mechanical behavior was dominant in the GO-SF bionanofilms after annealing, whereas viscoelastic behavior governed the GO-SF bionanofilms before annealing (refer the Supporting

Information). Thus, it is possible to highlight that the highly ordered hierarchical molecular structures formed by water vapor annealing can enhance the overall mechanical behaviors of the GO–SF owing to the presence of more elastic-solid properties.

4 Conclusions

In this study, the mechanical properties of two different GO–SF bionanofilms were examined, including before and after water vapor annealing of GO–SF bionanofilms. The indentation modulus and hardness of the bionanofilms were measured by performing nanoindentation experiments. To ensure that the system is calibrated, the mechanical properties of the bare Si substrate was measured with the area function. The application of the water vapor annealing process on the GO–SF bionanofilms improved the indentation modulus and hardness of the bionanofilms. Highly ordered hierarchical structures in the GO–SF bionanofilms that were formed by annealing enhanced the interfacial interactions between the molecules. This causes the bionanofilms to display reinforced mechanical properties. The nanoindentation FEA simulations were performed with functionally established GO–SF bionanofilm simulation models, which includes numerical factors of the viscoelastic properties. The load–displacement curves of the GO–SF bionanofilms through the FEA simulation conformed with the experimental data. Moreover, the details of the stress and strain behaviors of the GO–SF bionanofilms under the indentation loading condition have been identified, and the simulation results revealed that improved mechanical behaviors of the bionanofilms were observed in the GO–SF bionanofilms after annealing, owing to the elastic solid dominated characteristic. The findings of this study present the detailed mechanism to improve the indentation modulus and hardness of the bionanofilms. In addition, this study offers guidance in terms of building a proper FEA model to design mechanically robust bionanofilms.

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