

Rapid Communication

Nacre-inspired Green Artificial Bionanocomposite Films from the Layer-by-Layer Assembly of Montmorillonite and Chitosan*

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Abstract The simple LBL technique was introduced to fabricate green nacre-like chitosan/montmorillonite (CHI/MMT) films. The results of SEM and XRD analysis demonstrate that the produced CHI/MMT composite films stacked densely together to bring out well-defined nacre-like brick-mortar structure. The nanoindentation technique is used to characterize the mechanical properties of the layered nanocomposite films, which show enhanced mechanical modulus (up to ~6.64 GPa) compared with the pure chitosan.

Keywords: Nacre-inspired; Layer-by-layer films; Chitosan; Montmorillonite; Nanoindentation.

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INTRODUCTION

The material of seashell nacre is well known for excellent properties and functionalities. Their distinctive mechanical qualities are attributed to a highly regular brick-mortar arrangement of organic and inorganic elements, which combines the strong elasticity of protein layers and the rigid strength of aragonite tablets. By mimicking the layered microstructure and function of nacre, a series of nacre-like artificial materials^[1–6] have been produced by the assembly of various artificial inorganic building blocks with polymers. For example, Podsiadlo and colleagues^[7] have taken an alternative approach in the design of a montmorillonite clay platelet-poly(vinyl alcohol) matrix nacre-mimetic artificial nanocomposite; ice-crystal templates of the microscopic layers were designed to form a brick-mortar microstructured Al₂O₃/poly(methyl methacrylate) composite by Deville^[8]; Bonderer^[9] assembled Al₂O₃ platelets on the air/water interface and developed spin-coating into the fabrication of lamellar Al₂O₃/chitosan hybrid films.

Among numerous platelet-like inorganic materials, montmorillonite (MMT) sheets have been extensively investigated as reinforcing platelets for the fabrication of biologically inspired organic-inorganic hybrid films. The importance of utilization of clays as the inorganic bricks is threefold: (1) the natural abundance of this

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nanomaterial imparts low cost to its application; (2) the anisotropic, sheet-like structure is of great importance for control of transport properties through the films; and (3) like many other nanomaterials having single-crystalline, defect-free structure, the individual nanosheet possesses exceptional mechanical properties, with in-plane modulus of elasticity (E) calculated on the order of ~ 270 GPa^[10]. In the last decade, more and more attention has been paid to the replacement of conventional petroleum-based plastics by materials based on assembling layered clays and biopolymers. There has been a trend in chemistry to reduce the human impact on the environment. The increasing importance of materials from renewable sources has put chitosan (CHI) in the spotlight, especially due to its good biocompatibility, biodegradability, low toxicity and low cost, and it has been exploited in many applications^[11–13]. Also important is that chitosan is the only positively charged, naturally occurring polysaccharide, for chitosan may then interact strongly with negatively charged entities. So the chitosan molecules are very easily coated onto exfoliated MMT nanosheets to yield the hybrid building blocks by strong electrostatic and hydrogen-bonding interactions^[14].

Among the different approaches being currently explored to fabricate artificial nacre-like films^[15–18], such as freezing casting, electrophoretic deposition, paper-making method and vacuum filtration^[19], the layer-by-layer (LBL) assembly technique stands out as one of the simplest and most versatile method for fabricating structured and functional thin films^[20,21]. Comparing with other methods, this technique allows the production of complex multilayer structures with an accurate control of the composition and thickness, in addition, it can be applied to different substrates with different sizes and it is versatile and applicable to a wide range of materials, *e.g.* biomolecules, especially since it is performed under mild conditions. LBL can interact and assemble accumulatively upon varying the driving force, which mainly includes electrostatic interaction, hydrogen bonding, charge transfer, covalent bonding and hydrophobic interaction. Hence, the layered structure of nacre is easily copied by LBL technique.

Herein, in this paper we introduce the LBL technique to fabricate green nacre-like CHI/MMT films, which have shown enhancement of the mechanical properties (up to ~ 6.64 GPa) compared with the pure chitosan. Importantly, the CHI/MMT film is beneficial on environment due to its biodegradability, so the film can be used as the replacement of conventional petroleum-based plastics.

EXPERIMENTAL

Materials

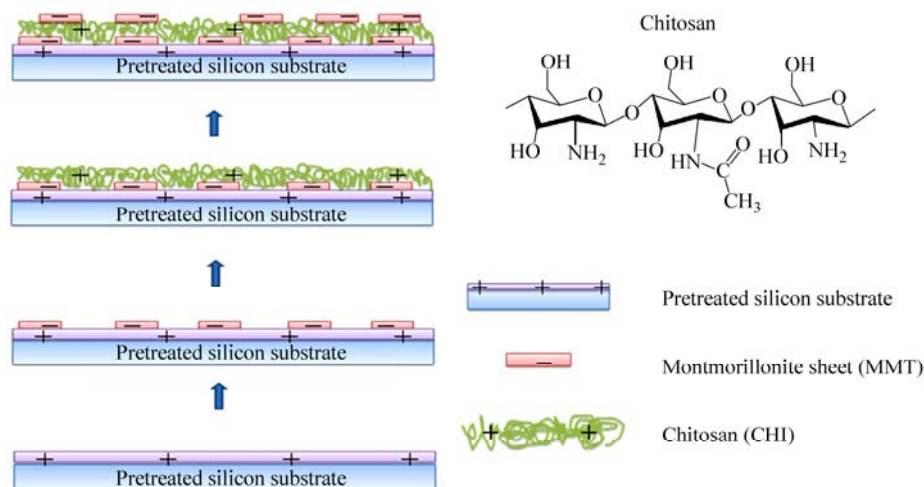
Chitosan ($M_w \sim 10$ kD) and glacial acetic acid were purchased from Sinopharm Chemical Reagent Co. Ltd. Sodium montmorillonite (Na-MMT) clays were purchased from Zhejiang Fenghong Clay Co. Ltd. All chemicals were of analytical grade and used as received without further purification.

Preparation of Nacre-like CHI/MMT Films

In a typical procedure, a mixture of Na-MMT in the deionized water (0.5 wt%) was stirred thoroughly for one week and then centrifuged at 10000 r/min for 20 min to remove unexfoliated Na-MMT. Chitosan (2 wt%) was dissolved in an aqueous solution containing 2 wt% glacial acetic acid and was stirred 24 h before use.

Substrates, such as a silicon wafer, was cleaned by immersion into hot ‘piranha’ solution (1:3 $H_2O_2:H_2SO_4$) for 30 min, followed by thoroughly rinsing with deionized water and anhydrous ethanol several times, and dried under a flow of nitrogen. The substrates were then modified with 3-aminopropyltriethoxysilane (ATES) by heating to reflux in toluene with 5 wt% ATES for at least 6 h to obtain chemically bonded $-NH_2$ groups on the surface. The surface was rinsed with toluene and dichloromethane to remove any remaining ATMS, dried under a flow of nitrogen gas, and immersed in dry dichloromethane containing pyridine (2% *V/V*). A positive surface charge was induced by dipping the substrate in HCl ($pH \approx 1 \sim 2$) before starting the deposition.

First, the pretreated substrate was dipped into the colloidal MMT suspension containing MMT nanosheets for 10 min, followed by rinsing with copious amounts of deionized water. The substrate treated with negatively charged MMT nanosheets was then immersed into the CHI aqueous solution for 10 min and washed with water afterwards. Subsequently, a series of alternative deposition operations for MMT nanoplatelets and CHI was repeated n times to produce multilayer films of (CHI/MMT) $_n$ (Scheme 1). The final films were dried with a nitrogen gas flow.



Scheme 1 Fabrication of the artificial nacre-like CHI/MMT films

Characterization of Nacre-like CHI/MMT Films

X-Ray diffraction (XRD) data of (CHI/MMT)_n films were recorded by a Shimadzu XRD-6000 diffractometer under the following conditions: 40 kV, 40 mA, Cu K α radiation. Fourier transform infrared (FTIR) spectra were measured on a Nicolet iN10MX infrared spectrophotometer. The morphology and dimension of the samples were examined with a HITACHI S4800 scanning electron microscope (SEM), operating at an accelerating voltage of 10 kV. Transmission electron microscopy (TEM) was performed using a JEOL JEM-2100F transmission electron microscope at an acceleration voltage of 200 kV. The mechanical properties of the LBL films were tested using the HYSITRON TI-950 TriboIndenter, where a Berkovich shape indenter was used. The hardness and Young's modulus were calculated and recorded.

RESULTS AND DISCUSSION

The growth of CHI/MMT multilayer films was monitored by X-ray diffraction spectra measured immediately after every twenty deposition cycle (Fig. 1a). The (001) peak for natural MMT is located at $2\theta = 7.4^\circ$, corresponding to $d_{001} = 1.2$ nm. Bragg diffraction peaks at $\sim 5.2^\circ$ appeared after 20 depositing cycles, and the peak intensity increased gradually upon increasing the bilayer number, indicating multilayer long-range ordered

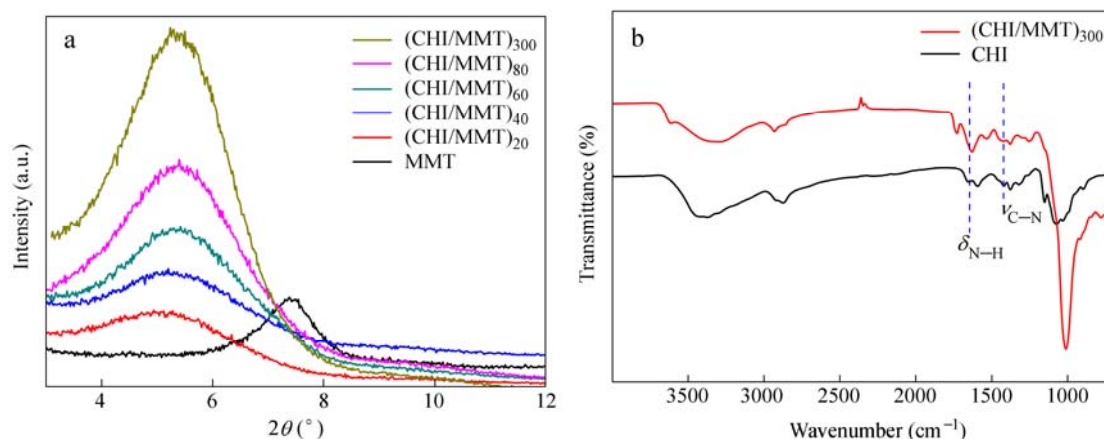


Fig. 1 (a) XRD profiles for the MMT and (CHI/MMT)_n films with 20, 40, 60, 80 and 300 bilayers, respectively; (b) FTIR spectra of the (CHI/MMT)₃₀₀ film and chitosan

superstructure was successfully constructed. The peak at $\sim 5.2^\circ$ corresponded to the 001 diffractions of the $(\text{CHI/MMT})_n$ ultra thin film, demonstrating the films with long range stacking order in the normal direction of the substrate.

Figure 2(a) shows the cross-sectional morphology of $(\text{CHI/MMT})_{300}$ multilayer film. The cross-section of $(\text{CHI/MMT})_{300}$ hybrid film was stacked densely together to form a well-defined layered structure, which was conceptually similar to the brick-mortar structure of nacre. The top-view SEM images (Fig. 2b) shows that the surfaces of the $(\text{CHI/MMT})_{300}$ film was microscopically smooth and uniform, the negatively charged MMT nanoplatelets glued together by the positive charged CHI molecules. From the FTIR spectra (Fig. 1b), peaks at 894, 1419, 1592, 2900 and 3300 cm^{-1} were related to chitosan, which were also observed after assembling of MMT nanosheets, with broader O—H bands. The absorption at 1592 cm^{-1} and 1419 cm^{-1} were assigned as $\delta_{\text{N-H}}$ and $\nu_{\text{C-N}}$ respectively, indicating the existence of the chitosan molecules on the MMT nanosheets.

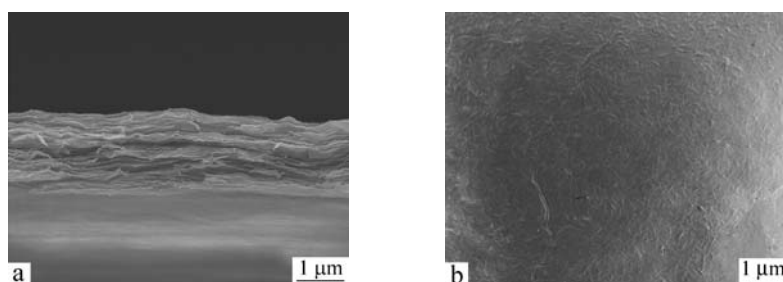
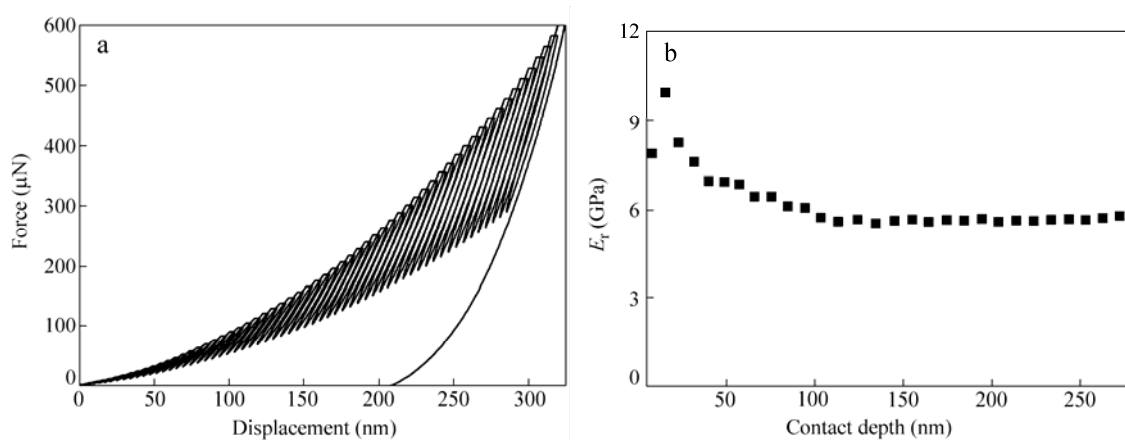


Fig. 2 (a) Cross-sectional SEM image of $(\text{CHI/MMT})_{300}$ film and (b) top view of SEM image for the $(\text{CHI/MMT})_{300}$ film

To demonstrate full nanomechanical characterization of the $(\text{CHI/MMT})_{300}$ film Hysitron's state-of-the-art TI 950 TriboIndenter, a novel partial unloading (PUL) technique, was used to obtain correct results. The PUL indents made on the sample was used to determine the hardness and elastic modulus of the film as a function of thickness, similar technique was used by a previous report^[22] of our group and Li^[23] to test mechanical characterization of shell. The data collected in the tests are displayed in Fig. 3, along with modulus (E_r) values that were calculated from the load-displacement curves using the Oliver and Pharr approach^[24]. Although the elastic modulus of the chitosan was 2 ± 0.68 GPa (Fig. S1), the modulus of the $(\text{CHI/MMT})_{300}$ film was up to 6.64 ± 0.75 GPa. This considerable increase in the mechanical properties was explained by taking into consideration the extensive plastic flow of the chitosan and the load transfer to the MMT nanoplatelets that takes place through the strong MMT-CHI interface.



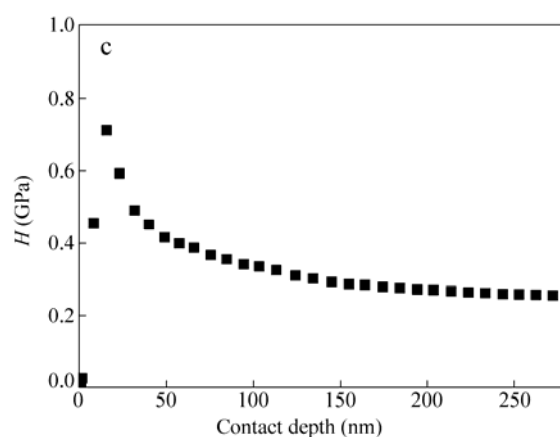


Fig. 3 The PUL test made on the (CHI/MMT)₃₀₀ film: (a) load displacement profile obtained by a PUL test, (b) the modulus values of the sample and (c) hardness of the (CHI/MMT)₃₀₀ film

CONCLUSIONS

In summary, we have developed an environmentally friendly film for mimicking nacre with regular structure by bottom-up LBL deposition of MMT nanoplatelets with natural CHI *via* strong electrostatic attraction. The obtained bionanocomposite films have an orderly brick-mortar microstructure, which leads to their good performances in mechanical properties. However, the enhancement of the mechanical property and multifunction of the CHI/MMT bionanocomposite film is still low and far from the expectations in industry. Further extension of the present strategy should allow access to a variety of regular nacre-like structure films with high mechanical properties and multifunctionality.

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