Polymer 91 (2016) 187–193

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Enhancement of fracture toughness in organic/inorganic hybrid nanolaminates with ultrathin adhesive layers

Bongjun Yeom [a, *], Ahreum Jeong [a], Jubong Lee [b], Kookheon Char [b, **]

[a] Department of Chemical Engineering, Myongji University, Yongin 17058, South Korea
[b] The National Creative Research Initiative Center for Intelligent Hybrids, The WCU Program of Chemical Convergence for Energy & Environment, School of Chemical & Biological Engineering, Seoul National University, Seoul 08826, South Korea

ARTICLE INFO

Article history:
Received 12 January 2016
Received in revised form
21 March 2016
Accepted 24 March 2016
Available online 26 March 2016

Keywords:
Nacre
Organic/inorganic hybrid nanolaminates
Layer-by-layer assembly
Fracture toughness
Interfacial adhesion

ABSTRACT

Nacre is composed of highly ordered organic/inorganic hybrid nanolaminated structures showing exceptional toughness. However, artificial fabrication of such nanoscale layered structures still remains a challenge in the area of nanocomposite films. In this study, we fabricated organic/inorganic hybrid nanolaminated films by using the layer-by-layer (LbL) deposition method, and obtained high fracture toughness by adjusting the interfacial interactions. Artificial composites with an inorganic content of 89.2 vol%–99.1 vol%, comparable to that of nacre, were fabricated via a bottom-up process with assist of the LbL method. In addition, the interfaces between organic/inorganic layers were discretely defined with the interfacial roughness of only 1.9 ± 1.2 nm, as determined by high-resolution X-ray reflectivity (HR-XRR). More importantly, the insertion of adhesive layers that were only 8 Å-thick resulted in a significant increase (291-fold) in the fracture toughness at organic contents of 8–10 vol%. Therefore, tuning of the interfacial interaction has a significant effect on the release of fracture energy in hybrid laminated films.

1. Introduction

Nacre, the mother of pearl, has attracted significant attention owing to its unique optical properties and excellent mechanical properties. These arise from its highly ordered layered structures that are composed of 300–900 nm thick calcium carbonate platelets alternatively stacked with 10–40-nm thick organic layers [1,2]. The fracture toughness of nacre is 3000 times higher than that of calcium carbonate ($CaCO_3$), which is composed of 90–95 vol% of nacre, and is hence of particular interest to materials scientists. Therefore, many studies have focused on elucidating the mechanism that governs fracture toughening, and attempts have been made to design artificial nanocomposites based on this principle [3–5]. Previous studies have identified two major toughening mechanisms, which are described as follows: (1) Highly-ordered sandwiched structures can efficiently dissipate fracture energy by forming a zigzag-shaped fracture path through organic layers laid between inorganic platelets. (2) The strong interfacial adhesion between organic/inorganic layers plays a significant role in transferring the fracture stress. Adhesive molecules located in the organic layer presented saw-tooth patterns in stress–strain curves during force–extension tests, as examined by using an atomic force microscope (AFM) [6]. This strong adhesion results from the combination of various inter/intra molecular interactions such as electrostatic interactions, hydrogen bonding, van der Waals interactions, and covalent bonding.

The layer-by-layer (LbL) assembly method has been widely used to prepare functional thin films, and various types of polyelectrolytes and nanomaterials have been used as components [7–9]. Various molecular interactions, such as electrostatic interactions, hydrogen bonding, and other chemical/physical interactions, provided the adsorption driving forces that resulted in film assembly. Therefore, LbL assembly methods have been used as a facile route to render surfaces and interfaces with the desired functionality. In fact, LbL methods have been used to fabricate artificial organic/inorganic hybrid laminated structures in order to mimic structure of nacre. Tang et al. fabricated montmorillonite clay platelet/polyelectrolyte hybrid films, and determined mechanical properties such as the tensile strength and modulus [10]. Moreover, aluminum oxide platelets/chitosan hybrid films were

* Corresponding author.
** Corresponding author.
E-mail addresses: byeom@mju.ac.kr (B. Yeom), khchar@plaza.snu.ac.kr (K. Char).

http://dx.doi.org/10.1016/j.polymer.2016.03.078
0032-3861/

prepared via alternating deposition by using dip and spin coating [11]. The fracture toughness of hybrid films has, however, rarely been evaluated, except in the case of Al_2O_3/PMMA (polymethyl methacrylate) composites prepared via the freeze casting method [12]. These alumina composites have a layered structure which ranges from tens to hundreds of microns in size, and is therefore significantly larger than the nano-scale layered structure of nacre. In previous work, we investigated on the fracture toughness of hybrid nanolaminated films; determining the effect of interfacial adhesion only was, however, difficult [13].

As such, in the current study, we prepared highly ordered organic/inorganic hybrid nanolaminates by using the LbL method as an artificial model of nacre. We determined the effect of interfacial adhesion on the fracture toughness of the composite films. Organic/inorganic hybrid nanolaminates were prepared by alternating deposition of silicate layers and polyelectrolytes multilayers, using hard inorganic platelets and soft organic layers, respectively. The ~200-nm-thick inorganic silicate layers and 1–20-nm-thick polymeric layers were prepared via dip coating and a spin-assisted LbL method, respectively [8]. In addition, the interfacial interactions were finely adjusted by use of an adhesion promoter that exhibited bi-functionalities consist of Si–OH groups and amine groups. Two series of samples were synthesized with and without adhesion-promoting layers. In addition, high-resolution X-ray reflectivity (HR-XRR) and cross-sectional field emission scanning electron microscopy (FE-SEM) were used to examine the internal structures of these samples; these examinations revealed the constituent, well-organized stacks of organic/inorganic layers separated by discrete interfaces. The inorganic materials constituted 89.2 vol%–99.1 vol% of the structure, similar to the case of nacre, whereas conventional artificial nanocomposites have an inorganic content of <10 vol% [11,12,14]. Nanoindentation results showed that the fracture toughness of the film with organic content of 10.8 vol%, in case of the adhesion-promoted series, could be significantly increased by two orders of magnitude comparing to the film with organic content of 1.9 vol%. However, the fracture toughness of films synthesized without the adhesion-promoting layers, decreased with increasing organic content. Fibril-like “nanoligaments” were formed after indentations under large loads; these ligaments have the same morphologies as those formed during fracture testing of natural nacre [2,6].

2. Experimental

2.1. Materials

Tetraethoxysilane (TEOS), 3-aminopropyltriethoxysilane (3-APTES), poly(diallyldimethylammonium chloride) (PDAC) (Mw = 200 000–350 000) and poly(sodium 4-styrenesulfonate) (PSS) (Mw = 70 000) were used as received from Aldrich.

2.2. Preparation of inorganic precursor and adhesion promoter

Silica sol used as an inorganic layer was synthesized by hydrolytic condensation of TEOS via sol–gel reaction. 5.14 g of H_2O and 0.075 g of HCl (35 wt %) were added to 15 g of TEOS during vigorously stirring. After stirring overnight at room temperature, 30 g of ethanol was added to silica sol and filtered with 0.2 μm filter before coating. Polymerized 3-APTES (p-ATS) was used as adhesion promoter carrying amine moiety and silanol groups. p-ATS was synthesized by adding 5 wt % of 3-APTES to H_2O, then stirred overnight. Transparent solution of p-ATS was filtered with 0.2 μm PTFE filter before use.

2.3. Fabrication of organic–inorganic hybrid multilayer

Organic/inorganic hybrid nanolaminates were synthesized using following procedures. Si wafers were treated with piranha solutions (H_2SO_4/H_2O_2 = 7/3 (vol%)), followed by RCA treatment ($H_2O/H_2O_2/NH_4OH$ = 5/1/1 (vol%)) to render the surface negative charge. PDAC (10 mM, NaCl 0.1 M) as a cationic polyelectrolyte and PSS (10 mM, NaCl 0.1 M) as a anionic polyelectrolyte were used to prepare $(PDAC/PSS)_n$ multilayer thin film using spin-assisted layer-by-layer method. When top layer was coated with PDAC over $(PDAC/PSS)_n$, it is denoted as $(PDAC/PSS)_{n.5}$. After organic layer ($(PDAC/PSS)_{n.5}$) was coated on substrate, silica sol was dip-coated at 85 mm/min followed by heating at 150 °C for 30 min to cross-link Si–OH groups partially in TEOS film ($[(PDAC/PSS)_{n.5}]$/TEOS). Same procedures were repeated 4 times, and the film was cured at 230 °C for 1 h to increase cross-linking in TEOS layers, resulting in $\{[(PDAC/PSS)_{n.5}]/TEOS\}_4$ hybrid film denoted as T_n Series. To investigate the effect of adhesion layer at interface of organic/inorganic layers, adhesion promoter (p-ATS) was inserted between $(PSS/PDAC)_{n.5}$ organic layer and TEOS sol. These hybrid films were named as G_n Series, $\{p\text{-ATS}/[(PSS/PDAC)_{n.5}]/p\text{-ATS/TEOS}\}_4$.

2.4. Characterization of organic/inorganic hybrid multilayers

Ellipsometric thickness measurements were performed with a ellipsometer (Model L2W15S830, Gaertner Scientific Corp.) with a 632.8-nm He–Ne laser-light source. The X-ray photoelectron spectroscopy (XPS) result was obtained with AXIS (KRATOS Corp.) Contact angles of water were measured using a drop shape analysis system (Kruss, DSA 100). In XPS and contact angle measurement, all TEOS layers were preannealed at 150 °C for 30 min before use. The layered structure was characterized using field-emission scanning electron microscope (FE-SEM) and high resolution X-ray reflectivity measurement (HR-XRR). For cross-sectional measurement, film was cut after chilling in liquid N_2 for 5 min, followed by Pt sputtering, and tested by a JEOL 7401F system. XRR measurements were performed at 3C2 XRD beam line of Pohang Light Source, Pohang, South Korea. The scattering length density profile was calculated using Parrat program. The mechanical properties of hybrid film were obtained using Nanoindenter XP and G200 via depth sensing indentation in DCM and CSM mode, respectively. The crack length was examined with FE-SEM and optical microscope (Nikon OPTIPHOT2-POL) in reflection mode.

3. Results and discussion

To mimic the layered structure of nacre, organic/inorganic hybrid nanolaminates were prepared via alternating depositions of organic and inorganic layers, as shown in Fig. 1. The organic layers were obtained by depositing polyelectrolyte thin films onto the substrate via spin-assisted LbL methods, using poly(-diallydimethylammonium chloride) (PDAC) and poly(sodium 4-styrenesulfonate) (PSS) as the polycation and polyanion, respectively [8]. The thickness of the organic layer was varied to 1–20 nm by controlling the repeating number (n) of bilayers of PDAD/PSS, denoted as $(PDAC/PSS)_{n.5}$; 0.5 indicates that PDAC constitutes the outermost layer. The organic part constitutes 0.9 vol%–10.8 vol% of the structure, similar to the case of nacre. Ellipsometry measurements revealed that the $(PDAC/PSS)_n$ LbL-assembled films experienced linear growth of 6.4 nm/bilayer (See Supporting Information Fig. S1). The hard inorganic layer was obtained by depositing ~200-nm-thick silicate layer onto the organic layer with tetraethoxysilane (TEOS) sol, synthesized via the sol–gel reaction, and pre-annealing at 150 °C for 30 min. After four depositions of organic/inorganic layers, the final hybrid film was cured at 230 °C for 1 h. The