

Nacre-inspired Polyglutamic Acid/Layered Double Hydroxide Bionanocomposite Film with High Mechanical, Translucence and UV-blocking Properties*

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Abstract Due to the various needs in the current applications, multifunctional composite materials with high strength and high toughness were highly desired now. Many scholars dedicated their time to find a simple, green and fast method for the preparation of multi-functional materials. In this study, inspired by the hierarchical “brick-and-mortar” structure and excellent mechanical performance of nacre, a fast green vacuum-filtration method was used to fabricate strong and multifunctional polyglutamic acid/layered double hydroxide (PGA/LDH) films mimicking nacre. The experimental results confirm that the artificial nacre has hierarchical “brick-and-mortar” structure. It exhibits excellent strength (93.5 MPa) and flexibility (easily bendable fold), combining with outstanding properties of UV-blocking and translucence properties. This work provides a way of fabricating multifunctional organic-inorganic hybrid films, which has potential applications in the areas of optical, transportation and construction fields.

Keywords Nacre-inspired; Multifunctional; Mechanical properties; UV-blocking; Hierarchical structure

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INTRODUCTION

With the development of nanomaterials preparation technology, multifunctional composite materials draw more and more attention due to the limitation of the specifically conventional functional materials research^[1]. The combination of two or more seemingly distinct properties into a unique composite is an exciting direction for the fabrication of novel multifunctional materials. Learning from nature will give us important inspiration to develop new methods and approaches to develop artificial advanced materials^[2–4].

Undergoing evolution for millions of years, many biological tissues and materials have realized perfect inner relationship between their structure and mechanical properties. These biomaterials exhibit exceptionally high tensile strength, hardness, and toughness characteristics^[5]. One of the most outstanding examples is nacre^[6], consisting of 95 vol% brittle aragonitic CaCO₃ (brick) and 5 vol% organic matrix (mortar) with layer arrangements. It is clear now that hierarchical organization and a precisely designed organic-inorganic interface play an important role in the amazing mechanical properties of this natural nanocomposite^[7–10]. Hence, a lot of bio-inspired materials have been successfully fabricated by mimicking the ordered hierarchical structure to achieve combination of stiffness, strength and toughness^[11–25]. In previous reports, natural clay mineral platelets such as montmorillonite and graphene oxide (GO) were often used to fabricate biologically inspired composites

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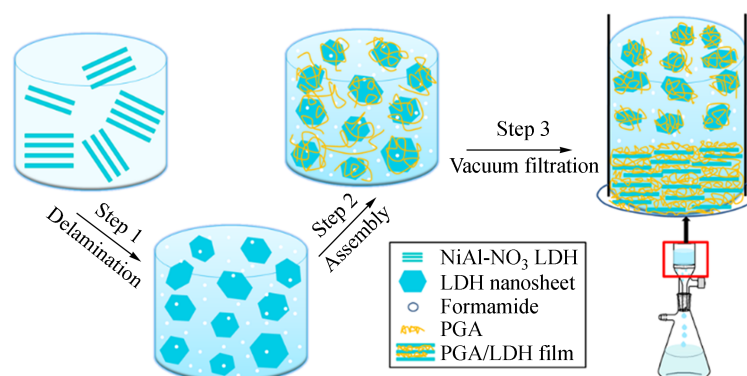
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with polymer by assembly techniques, showing fire retardant^[11, 12, 26, 27], and gas barrier properties^[21, 28–30], and high electrical conductivity^[1, 31–34]. Among these numerous platelet-like inorganic materials, layered double hydroxides (LDHs) are receiving increasing attention in the field of organic-inorganic artificial composites because they have their own unique advantages such as: (i) LDHs exhibit swelling behavior and the interlayer spacing can be adjusted based on the size, shape, and the number of the guest anions; (ii) The layer charge density and elemental composition of LDHs can be tuned during the synthetic process, which facilitates fine control over the properties of the host layer; (iii) Different synthetic methods can prepare various functional LDHs. On the other hand, LDHs are among the most studied advanced functional materials and have been widely applied in the field of catalysts and catalyst support^[35–37], anion exchangers, molecular containers^[38–40] and electrical and optical functional materials^[41–43].

Until recent years, there has been a rapid growth in publications related to the application of LDH platelets as the inorganic bricks in the fabrication of biologically inspired organic-inorganic hybrid films^[20, 21, 44–46]. For example, Yao *et al.*^[13] assembled LDH platelets on the air/water interface and developed spin-coating into the fabrication of lamellar photoluminescent LDH/chitosan hybrid films; Han *et al.*^[47] followed an alternative approach in the design of LDH platelet-poly(vinyl alcohol) matrix nacre-mimetic artificial nanocomposites; Dou *et al.*^[21] obtained (XAl-LDH/PAA)_n-CO₂ films with brick-mortar-sand structure that display ultrahigh gas barrier properties by layer-by-layer (LBL) technique and subsequent CO₂ adsorption. We have also built heparin (HEP)/LDH completely renewable ultrathin films with enhanced strength and blood compatibility by LBL technique^[48]. Despite such a recent success to mimic nacre, there exists a profound problem that needs to be overcome to realize large-scale applications: all of the previous approaches toward biomimetic layered structures are sequential, thus inherently laborious and time-consuming. Meanwhile, multifunctional biologically inspired LDH-polymer films have been rarely reported. Hence, it still remains a significant technical challenge to find a rapid, efficient, environmentally friendly method to fabricate high performance composites with high LDH loading and multifunctionalities.

In this study, polyglutamic acid (PGA), a green, biocompatible, easily obtainable and environmentally friendly glycosaminoglycan was used which has the highest negative charge density of all known biological polyanions^[49]. Generally, because Ni²⁺ and N atoms have stronger complexing ability, therefore, the NiAl-NO₃ LDH with high crystallinity could be prepared directly, which could easily be delaminated in the formamide to get positively charged unilamellar LDH nanosheets. PGA is chosen as “mortar” to interact with positive charged NiAl-NO₃ LDH nanosheets (brick) by strong electrostatic interactions. Meanwhile, a great number of hydroxyl groups on the surface of LDH nanoplatelets as well as in the PGA molecules will facilitate the formation of a hydrogen bond network at the organic-inorganic interface. Bioinspired, nacre-like PGA/LDH films in practical sizes are fabricated by the vacuum-filtration method (Scheme 1). The large size films help us to exploit more multifunctional applications when compared with our group’s previously reported ultrathin films^[48] by the LBL fabrication technique. Moreover, this meets the requirements of future construction and coating applications. The experimental results confirm that the inorganic nanosheets are aligned well with a high loading amount of LDHs, up to 41.7 wt%. In addition, in contrast to the previous report, HEP/LDH films^[50] by vacuum filtration have high strength and hardness, but very brittle. The artificial nacre PGA/LDH films exhibit excellent strength (93.5 MPa), and can be bendably folded. The hybrid films show a combination of outstanding properties of UV-blocking and translucence properties, thus indicating their potential application in special window materials protecting objects from being damaged by UV light. We hope that these advanced PGA/LDH bioinspired films could prove beneficial for transportation, construction, or protection, or as a replacement for conventional petroleum based plastics.



Scheme 1 Fabrication of the artificial nacre-like PGA/LDH film

The NiAl-NO_3 LDH powder is first delaminated by formamide solution. Then, the exfoliated LDH nanosheet and aqueous solution of PGA are stirred together to guarantee full adsorption of PGA on LDH nanosheets. Finally, the PGA/LDH hybrid building blocks are aligned into the nacre-like structured composite by self-assembly induced by vacuum filtration.

EXPERIMENTAL

Materials

Analytical grade reagents polyglutamic acid (PGA, $M_w = 1000$ kDa) was purchased from Nanjing Sai Tai Si Biological Technology Co., Ltd. and used as received. $\text{Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Al(NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and NaOH were purchased from Sinopharm Chemical Reagent Co., Ltd. and used as received. Polyamide membrane filters (220 nm pore size) were purchased from Shanghai Xinya.

Fabrication of Highly Oriented PGA/LDH Film

(1) The synthetic process and exfoliation of Ni-Al LDH were similar to that described in our previous work^[48]. A sample of PGA (1, 2, 3 g) was dissolved in a small amount of deionized water. Then it was diluted with formamide to an indicated anion concentration (water/formamide volume ratio of 1/3). (2) The exfoliated, positively charged LDH nanosheets were synthesized by vigorously agitating 0.1 g of Ni-Al-NO_3 LDH in 100 mL of formamide in a two-necked flask under a N_2 gas flow for 24 h. (3) To adsorb one monolayer of PGA onto the LDH platelets, the PGA dispersion was slowly added to a stirred solution of LDH. When PGA solution (1 wt%, 2 wt% or 3 wt%) was added to exfoliated LDH colloids, the solution was stirred for at least overnight to complete polymer adsorption and to obtain a fine dispersion of the stabilized LDH platelets. (4) The colloidal dispersion was vacuum filtered through polyamide membrane filter (220 nm pore size, Shanghai Xinya). In the presence of vacuum pressure, LDH nanosheets coated with PGA molecules were deposited on the membrane filter with packed interlocking structure and preferential plane orientation. (5) The membrane filter was torn off and the PGA/LDH film was dried at 90 °C in an oven. The weight fraction of platelets in the hybrid film (ω_p) was varied by controlling the concentration of PGA used in the preparation process.

UV-shielding Test

The UV-shielding performance of the PGA/LDH film was evaluated by the photo catalytic degradation of Rhodamine B aqueous solution in the presence of TiO_2 nanoparticles using a 400 W high-pressure mercury lamp as the source of irradiation^[50]. The experiments were conducted as follows: a suspension consisting of 30 mL of Rhodamine B aqueous solution ($0.01 \text{ g} \cdot \text{L}^{-1}$) with 20 mg of TiO_2 nanoparticles was stirred in dark for 1 h to ensure complete dispersion of TiO_2 nanoparticles and adsorption/desorption equilibrium. The suspension was then charged into a single-necked flask covered by a layer of aluminum foil to exclude light. The mouth of the flask was left open, allowing light to enter. The photocatalytic degradation of Rhodamine B was carried out under constant stirring. Then, 3 mL of the suspension was sampled every 10 min and centrifuged to remove TiO_2 nanoparticles. After that, the absorbance at 552 nm was determined. Nacre-like PGA/LDH film and weighing paper of the same thickness as the film served as controls.

Characterization

X-ray diffraction (XRD) data of PGA/LDH film were recorded by a Shimadzu XRD-6000 diffractometer under the following conditions: 40 kV, 40 mA and Cu K α radiation. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet NEXUS-470 infrared spectrophotometer using the KBr pellet technique. The UV-Vis transmittance spectra of the film were recorded in the range from 200 nm to 800 nm on a Shimadzu-3600 spectrophotometer. Scanning electron microscopy (SEM) was performed on a JEOL JSM7500FA field emission microscope, typically operated at 3.0 kV. The acceleration voltage was increased to 10 kV for energy-dispersive X-ray analysis (EDX) measurements. Loading of LDH inside the free-standing film was determined with a thermogravimetric analyzer (TGA) TA SDTQ600, at a temperature ramp-up rate of 10 K $\cdot$ min $^{-1}$ while being purged with air at a flow rate of 100 mL $\cdot$ min $^{-1}$. The mechanical properties were tested using a Shimadzu AGS-X at a loading speed of 1 mm $\cdot$ min $^{-1}$ with a gauge length of 5 mm. All the samples tested were cut into 10 mm in length and 3 mm in width.

RESULTS AND DISCUSSION

The preparation process began with a fine colloidal dispersion containing discrete LDH nanoplatelets, as proven by AFM and TEM (Fig. S1 in supporting information, SI). To avoid the agglomeration of LDH, the PGA dispersion was slowly added to a vigorous stirring solution of LDH. The PGA molecules could easily attach onto exfoliated LDH nanosheets to yield hybrid building blocks by strong electrostatic and hydrogen-bonding interactions. The aligned self-assemblies were maintained throughout the whole sample despite the rapidness of the process. The modification prevented the LDH platelets from being re-aggregated in the process of vacuum filtration. The resultant films are visually uniform, glossy and of high optical quality (translucency).

The TGA curves of pure LDH, PGA, and PGA/LDH films with various LDH loadings are illustrated in Fig. 1. All PGA/LDH films showed higher residues than pure PGA. The residues were 42.4%, 37.3% and 33.6% for the 1 wt%, 2 wt% and 3 wt% PGA/LDH films, respectively. From these data, the inorganic LDH loadings (ω_p) of the 1 wt%, 2 wt% and 3 wt% PGA/LDH films could be calculated as 41.7 wt%, 30.0 wt%, and 16.2 wt%, respectively. The residual contents of PGA and LDH at 800 $^{\circ}$ C in air were 28.0 wt% and 62.5 wt%, respectively. The weight fraction of LDH in PGA/LDH multiplied by 62.5% plus the weight fraction of PGA in PGA/LDH multiplied by 28% equals the residual contents of PGA/LDH. Therefore, the weight fraction of LDH was calculated to be about 41.7 wt% (1 wt% PGA/LDH), 30.0 wt% (2 wt% PGA/LDH), 16.2 wt% (3 wt% PGA/LDH).

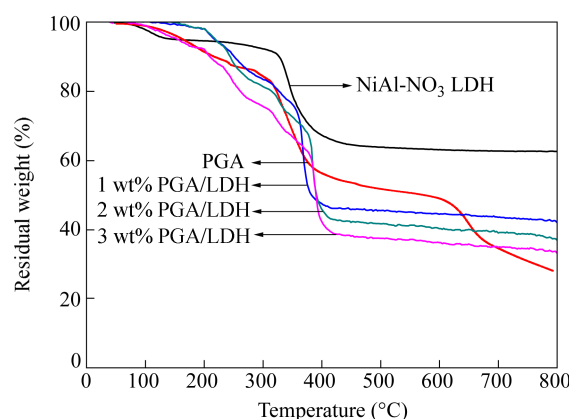


Fig. 1 TGA results for LDH powder, PGA polymer and various PGA/LDH film

Structure and Morphology of Hybrid PGA/LDH Films

The effect of the LDH content on the microstructures of composites was examined by SEM as shown in Fig. 2. For pure PGA film, the cross-section of sample was flat and smooth (Fig. 2a). In contrast, an ordered layered

structure like that of nacre appeared when hybrid film was formed (Figs. 2b–2d). For 1 wt% and 2 wt% PGA/LDH films (the LDH concentrations of which are 41.7% and 30%, respectively), the sheet-like layers are parallel to the film surface and interpenetrated into adjacent layers. This phenomenon also appeared in biomimetic (clay^[11, 26, 51], GO^[8, 32, 52], Al₂O₃^[53, 54], LDH^[13, 21, 55])-polymer composite films. As shown in previous reports^[16], an intercalated layered structure was formed when the montmorillonite (MMT) concentration was between 30 wt% and 70 wt%. This law also applies to the process of the preparation of PGA/LDH films. However, for low LDH concentrations (Fig. 2d), although the layered structure is not obvious, the LDH platelets could still be oriented orderly by vacuum filtration.

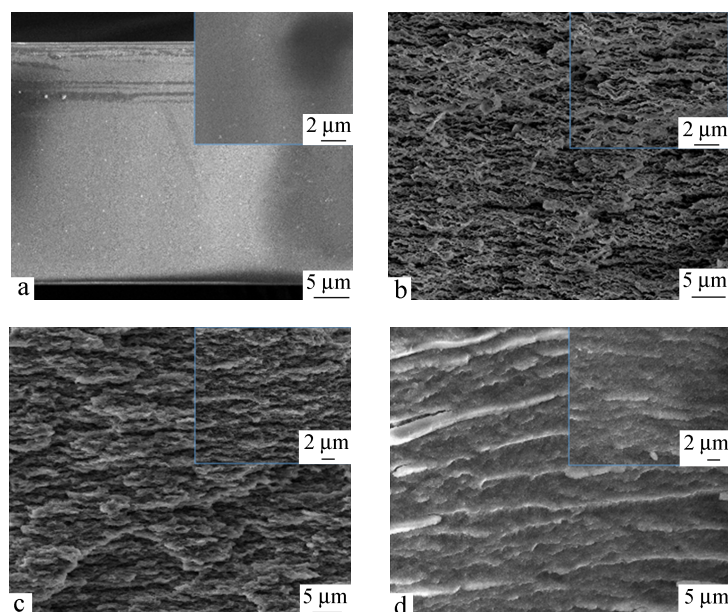


Fig. 2 SEM images of the cross-section: (a) pure PGA film; (b) 1 wt%, (c) 2 wt% and (d) 3 wt% PGA/LDH films after mechanical testing and film failure

SEM images of the nacre-like hybrid film clearly reveal the strong orientation of the LDH nanoplatelets paralleled.

The ordered stacking of PGA/LDH thin film was confirmed by XRD measurement (Fig. 3a) from which a so-called superlattice reflection of the inorganic-organic repeating nanostructure was observed. There were two peaks at *ca.* 6° and 7.85° appearing in all PGA/LDH thin film. They corresponded to the $d_{003} = 1.38$ nm and $d_{003} = 1.06$ nm of the hybrid films, demonstrating that the film had two long-range stacking orders due to two model structures in the composite materials (Fig. 3b). A model is the intercalation PGA/LDH structure, allowing for a thickness of about 0.48 nm for the LDH nanosheets^[48]; the layer height of PGA in the A model was estimated to be about 0.6 nm. B model is the adsorption PGA/LDH structure; the layer height of PGA was estimated to be about 0.9 nm. Meanwhile, the intensity of peak at 6° increased with increasing LDH loading, indicating a long-range, ordered periodic structure along the normal direction of the layer plane. The tendency was confirmed by SEM images of the cross-section that layered structure got more regular as the LDH loading increased. On the contrary, the intensity of the peak at 7.85° became weaker with increasing LDH loading, indicating that when 3 wt% PGA solution was added to exfoliated LDH colloids, LDH nanosheets were not fully dispersible in high concentration PGA solution and aggregation of some LDH nanoplates was resulted; then with the vigorous stirring, the PGA and LDH easily formed intercalation PGA/LDH structure.

In the FTIR spectra of the pristine PGA film and the pristine NiAl-NO₃ LDH powder (Fig. 3c), the band between 3500 and 3200 cm⁻¹ can clearly be ascribed to the O–H stretching vibration of free hydroxyl groups. A great number of hydroxyl groups on the surface of LDH nanoplatelets as well as in the PGA molecules would

facilitate the formation of a hydrogen bond network at the organic-inorganic interface^[56], which suppressed the O—H stretching vibration and made O—H bands of the film narrower than PGA^[51]. In the FTIR spectra of the PGA/LDH composite material, the absorption around 1630 cm^{-1} was associated with the stretching vibration and bending vibration of water molecules^[56], demonstrating the presence of water molecules in the hybrid PGA/LDH film due to PGA's hydrophilicity. And this is the reason why the PGA/LDH film is more flexible than HEP/LDH film^[50]. In the FTIR spectra of NiAl-NO₃ LDH, since the NiAl-NO₃ LDH powder is first delaminated by formamide solution, the LDH N—O stretching vibration peak^[48, 57] at 1384 cm^{-1} red shifted to 1350 cm^{-1} under the effect of polar solvent formamide. For PGA/LDH composite material, due to the electrostatic and hydrogen bonding interactions between PGA and LDH, N—O stretching vibration peak at 1384 cm^{-1} blue shifted to 1390 cm^{-1} .

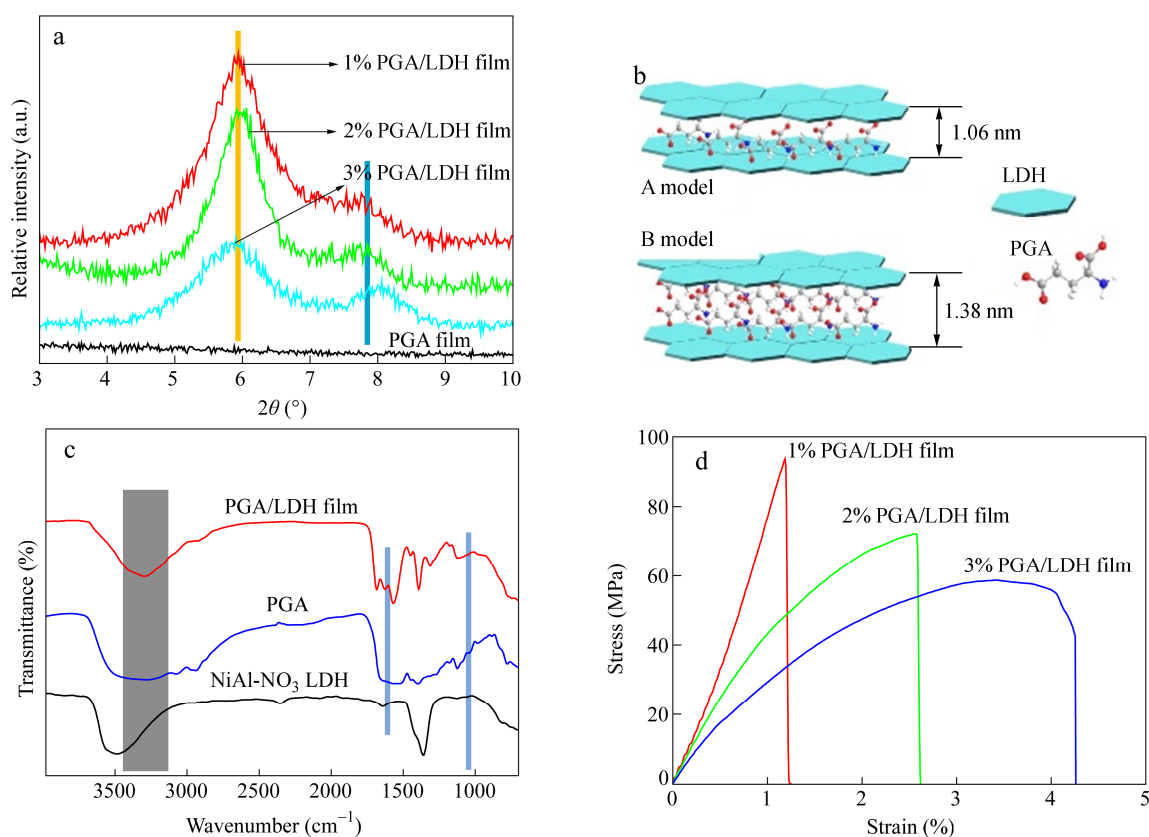


Fig. 3 (a) XRD patterns of the PGA and (1 wt%, 2 wt% and 3 wt%) PGA/LDH film; (b) Structure models of the PGA/Ni-Al LDH system; (c) FTIR spectra of NiAl-NO₃ LDH, PGA, and PGA/LDH film, respectively; (d) Tensile stress-strain curves of the (1 wt%, 2 wt% and 3 wt%) PGA/LDH film

Multifunctionalities of Hybrid PGA/LDH Films

Mechanical properties

Illustration in the Fig. 4(a) testifies that the sample can be folded without the risk of fracture, indicating its flexibility ensured by the hydrophilic polymer PGA with the presence of water for hydration in the hybrid PGA/LDH film as verified by FTIR spectra. Besides the arrangement of LDH and crystallinity of the PGA matrix, LDH content has a great effect on the mechanical performance of composites. Typical stress-strain curves of composites are presented in Fig. 3(d). Upon the mixing of inorganic LDH platelets in the PGA matrix, the tensile strengths of the resulting PGA/LDH hybrid films were markedly enhanced with increasing LDH content. It could be perceived that 3 wt% PGA/LDH films showed well defined yield points and plastic

deformations. In contrast, as the LDH content continued to increase upon decreasing the PGA concentration to 2 wt% PGA/LDH films had improved strengths, and the plastic deformations became inconspicuous. When the LDH content surpassed 41.7 wt%, decreasing the PGA concentration to 1 wt%, the composites failed at obviously lower strains. The strength was further improved, and no yield and plastic deformation were observed. Nevertheless, these PGA/LDH hybrid films became brittle, owing to the fact that the elongation at break gradually decreased with the augmentation of the LDH content in the films. The structures of the LDH platelets resembled those of nanoclay. As shown in previous reports^[14, 16], clay-polymer composites were much more fragile than the corresponding pure polymer matrices. Thus, it stands to reason that the hybrid films became brittle upon incorporating LDH into the PGA matrix. From all of the analysis of data above, it can be concluded that the LDH content plays an important role in the mechanical performance of PGA/LDH films. It can be seen that the tensile stress and tensile modulus of these films increased with the increase of LDH loading, and it is noteworthy that the tensile strength and the strain of the 1 wt% PGA/LDH films reached up to 93.5 MPa and 1.25%, respectively. The tensile fractured morphologies were observed by SEM to further investigate the mechanical properties of these PGA/LDH films (Fig. 2).

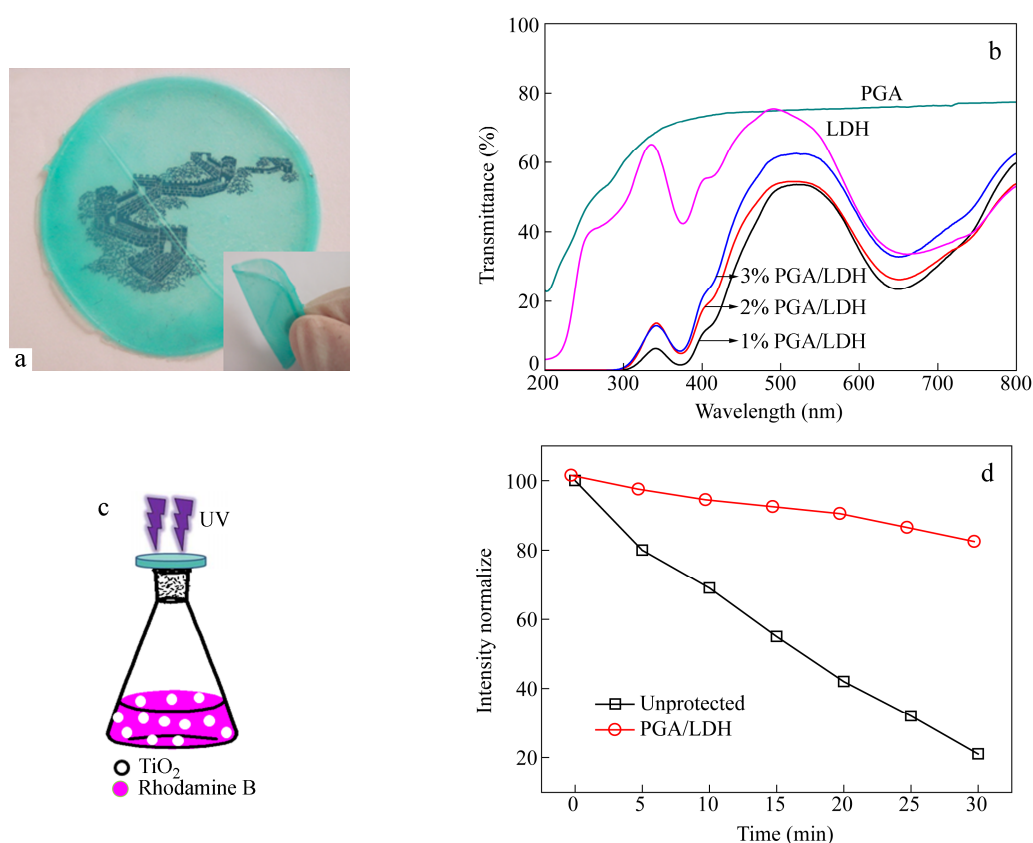


Fig. 4 (a) Hybrid PGA/LDH film placed on the paper with the printed “Great Wall” logo, inset: photograph of folded sample; (b) UV-Vis spectra (transmittance) of PGA, LDH and PGA/LDH films; (c) Schematic illustration of UV shielding performance testing of the PGA/LDH film; (d) Photocatalytic degradation profile of Rhodamine B unprotected and protected by PGA/LDH film

Translucency and UV-blocking properties

Multifunctional composite materials get more and more attention of people, because conventional specific functional materials research is unable to meet the needs of human beings. UV light blocking is one of the properties in great demand in multifunctional materials as ultraviolet radiation causes chemical reactions,

weathering of polymers, fading of certain coloring, and even eye and skin damage.

In Fig. 4(a), the PGA/LDH film is self-supporting, visually uniform, glossy and translucent, which had a blue-green hue due to the color of the Ni-Al LDH. The extraordinary visible-light transparency of hybrid films was attributed to the flat and uniform orientation of the LDH platelets in the hybrid films. The structure with a strikingly strong alignment of the LDH platelets can be verified by SEM as shown in Fig. 2 and a homogeneous component distribution was concluded from the energy-dispersive X-ray analysis (EDX) element maps (Fig. S2 in SI). The optical properties of the PGA/LDH hybrid films were revealed by UV-Vis transmittance spectra. In Fig. 4(b), PGA exhibited a high transmittance in the UV and visible regions. LDH nanosheets showed partial blocking in the UV region because nanoscaled laminates of LDH sheets (60–70 nm) reflected and scattered UV radiation. This phenomenon could be ascribed to two possible aspects. On one hand, the HEP/LDH film exhibited a complete blocking to the passage of UVC (200–280 nm) radiation. Relevant regions for protection are the UVB (280–315 nm) and UVA (315–400 nm) regions, where the maximum transmittance value of the film is just 15%, yielding a very efficient blocking effect. The scattering of the laminates of LDH nanosheets and the layered interfaces between the PGA and LDH contributed to the good UV shielding properties of the PGA/LDH film. On the other hand, the strong electrostatic interaction and hydrogen bond network at the organic-inorganic interface between the LDH nanosheets and PGA molecules played an important role in the shielding of UV irradiation. The PGA/LDH film blocked radiation partially in the UVA region and totally in the UVB and UVC regions, indicating its potential application in special window materials protecting objects from being damaged by UV light. The UV-shielding ability of the nacre-like PGA/LDH film was examined by the photocatalytic degradation of Rhodamine B aqueous solution in the presence of TiO₂ nanoparticles (Fig. 4c)^[50, 58]. For the sake of comparison, the photocatalytic degradation behavior of unprotected Rhodamine B aqueous solutions was measured under the same conditions. As shown in Fig. 4(d), after being irradiated for 30 min, the unprotected Rhodamine B showed a loss of 80%, while the Rhodamine B protected by PGA/LDH film only showed a decrease of 19%. The small amount of loss of Rhodamine B protected by PGA/LDH film suggested good UV shielding. Rhodamine B was still partially degraded when protected by the film. It was probably the result of the incomplete shielding of UV light, which occurred mainly in the range 310–360 nm. This photocatalytic degradation test of Rhodamine B also showed good UV-shielding property of the PGA/LDH. A film with such combination of transparency and UV-blocking properties might be inspiring for a broad range of fields in optical applications.

CONCLUSIONS

In summary, we demonstrated that the multifunctional layered composite materials, nacre-mimicking PGA/LDH hybrid films successfully synthesized by fast green vacuum filtration method showed a combination of outstanding properties of high mechanical performance, flexibility, translucence and UV blocking. The easy-prepared composite films are promising for applications such as photo-protective materials, ultraviolet-proof umbrella and windows of buildings. The exploration properties and applications based on these functional assemblies are expected to promote great development in multifunctional material design and fabricating, as well as exciting improvement in a broad range of applications.

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