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Self-bonding sandwiched membranes from PDMS and cellulose nanocrystals by engineering strategy of layer-by-layer curing

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ABSTRACT

Multilayer materials attracted intense scientific interests in view of their special interlayer structure and potential application in diverse fields. Different from the conventional approach of layer-by-layer assembly, in this study we proposed an engineering approach of layer-by-layer curing from polydimethylsiloxane (PDMS) elastomer and rigid cellulose nanocrystals (CNC). The covalent-bonding from the crosslinking curing reaction as the driving force ensured the strong interlayers adhesion, and meanwhile the nanoreinforcing effect from silylated CNC in the composite layers provided the tailor-made physicochemical properties for the fabricated multilayer membranes. The multilayer structures indicating the good interlayers' adhesion and structural integrity of the di- and tri-layer membranes were observed from the microscopy characterization. In comparison with the monolayer PDMS membrane, the developed CPC trilayer membrane (possessing the sandwiched structure of two composite layers and one neat layer) exhibited the advancement on the storage modulus, special optical scattering and hazing, dielectric permittivity and barrier performance, derived from the nanoscaled reinforcing and obstruction effects of rod-like natural nanoparticles (Si—CNC).

1. Introduction

The multilayer materials from the technology-driven layer-by-layer (LbL) assembly attracted considerable interest during the last two decades, allowing for the functional applications in the catalysis, optics, energy, biomedicine with the design of diverse compositions and structures [1]. In the development of multilayer materials, the preservation of structural integrity from the strong interlayer adhesion (commonly called as the driving force) is essential to prevent the defects of the multilayers construction and ensure the resultant performances. Typically, the driving forces to dominate the conventional LbL assembly procedure on the basis of molecular interactions include the electrostatic, hydrogen-bonding, charge-transfer, host-guest and covalent-bonding interactions [2]. The idea of electrostatic adsorption from the oppositely charged building blocks is regarded as the most popular approach to achieve the multilayer architecture [3]. However, the practical application of this approach to prepare the multilayer materials is restricted by the limitations involving the confined selection of specific charged molecules (or requirement of chemical treatments), tedious processing durations (repeated immersion/adsorption/rinsing treatments), low mechanical stability and weak robustness [4]. As an alternative interaction to assemble multilayers, the covalent bonding can serve as the strong driving force to strengthen the structural stability of multilayer materials with the chemical reaction and integration of various enhancing components [5–7]. Taken the covalent bonding as the driving force to develop the strong interlayer adhesion, this approach has been considered as the promising strategy to produce highly stable and robust multilayer materials. Nevertheless, several limitations on the covalent-bonding LbL strategy still restricted its development in the construction of multilayer materials, particularly involving the low applicability, possible side product and complex chemical methodology and processing.

With the purpose of regulating structure and property of each layer, diverse nano-objects were reported to be introduced into the multilayer materials with the nano-reinforcing effect. The main challenge for the nanoparticle enhancement to the multilayer materials is to preserve the original interlayer adhesion to avoid the layers' separation and to maintain the integrity of the multilayer system, in the presence of rigid nanoreinforcing phase. Cellulose nanocrystal (CNC) is a rod-like and highly-crystalline nanoparticle isolated from natural cellulose resources, which has been proved to be the potential replacement to the inorganic nanofillers in diverse composites with its numerous advantages, including the nontoxicity, renewability, rigidity, large aspect ratio, superior specific modulus, good biocompatibility and

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biodegradability etc [8,9]. It has been reported that the longitudinal moduli (E_L) of individual CNC is as high as the steel with the value of 206 GPa [10], but possesses only 18% density of the steel (1.46 *vs.* 7.90 g/cm^3). Regarding the studies of CNC in the development of multilayer materials, the typical strategy is the LbL assembly with the simple combination of negative CNC (generally H_2SO_4-hydrolyzed CNC with the surface negative charges) and polyelectrolytes from electrostatic interactions via the spin-coating process [11–14]. However, the multilayer materials obtained from this strategy have the structure of distinct layers separation with the CNC layers and polyelectrolyte layers. Therefore, the nano-reinforcing effect only comes into the polymeric region surrounding the CNC layer, but exhibits weak effectiveness to the neat polymer far away from the CNC layer. Furthermore, the low structural stability and interlayer adhesion still restrict the practical application of this approach to construct the engineering multilayer materials.

Different from the conventional approach of layer-by-layer assembly, in this study an engineering strategy covering the layer-by-layer curing was proposed from the covalent-bonding interaction as the driving force to construct the trilayer membranes with the components of PDMS and tunicate CNC. The objective of this study is the realization of both engineered processing (LbL curing) and covalent-bonding interaction (curing crosslinking) as the driving force to construct the multilayer materials, which may solve the limitations of traditional LbL assembly technique on the tedious processing durations and weak interlayers' interactions. Taking the chemical curing reaction to strongly adhere the interlayers can ensure the integrity and reliability of the multilayer system, which can be regarded as an engineering strategy with the “green”, highly-efficiency and simple-operation processing. The rigid and highly-crystalline CNC was incorporated into the composite layer but not served as the separated enhancing layer, which improved the mechanical and optical properties of multilayer membranes. Moreover, the presence of low loading levels of tunicate CNC in the composite layers remarkably affected the dielectric and barrier properties together with surface scratch behaviors of multilayer membranes, which may extend the functional application of these structural nanomaterials in diverse high value-added fields.

2. Materials and methods

2.1. Materials

The raw tunicate sea pineapple (*halocynthia roretzi*) was collected from the marineland at Weihai city of China. The silicone elastomer (Sylgard 184) of polydimethylsiloxane (PDMS) and curing agent were purchased from the company of Dow Corning (USA). Methyltrimethoxysilane (MTMS) as the silylating reagent was supplied by the company of Macklin (Shanghai, China). Other chemicals were purchased from the company of Aladdin (Shanghai, China) and directly used without any treatment, including potassium hydroxide (KOH), sodium hypochlorite (NaClO), glacial acetic acid and sulfuric acid (H_2SO_4).

2.2. Extraction of cellulose nanocrystals (CNC) from the tunicate sea pineapple

The rod-like CNC preparation from the raw *halocynthia roretzi* generally included two processes, purification for the tunicate cellulose extraction and hydrolysis for the CNC isolation [15,16]. The procedure and details information on the purification and hydrolysis of tunicin for the isolation of CNC were shown in Fig. S1.

2.3. Surface silylation of CNC

The silylated modification on the surface hydroxyl groups of CNC was performed with the addition of the MTMS into the 1 wt% CNC suspension for 4 h at room temperature [17]. The modified nanocrystals (Si−CNC) were subjected to the dialysis for 3 days in water to remove the physically-adsorbed silane and unreacted polysiloxanes.

2.4. Preparation of composite monolayer PDMS/Si−CNC membrane

The Si−CNC suspension (1 wt%) and PDMS (12 g, base: curing agent = 10: 1 w/w) were homogeneously mixed for 1 h with the mechanical stirring. The mixture was carefully poured into the polytetrafluoroethylene (PTFE) mold, and then removed the bubbles in the vacuum oven at room temperature for 1 h. Finally, the composite monolayer PDMS/Si−CNC was obtained after the curing treatment at 50 °C for 24 h. As the comparison, the neat PDMS membrane was also fabricated according to the similar method without the introduction of Si−CNC.

2.5. Fabrication of multilayer PDMS/Si−CNC membranes

The di- and tri-layer PDMS/Si−CNC membranes were prepared by the layer-by-layer curing approach. The monolayer mixture was fabricated by the previous method, and then pre-cured at 50 °C for 80 min. Another monolayer mixture (PDMS or PDMS/Si−CNC) was carefully poured on the surface of the pre-cured mixture for a good adhesion to obtain the dilayer pre-curing mixture. The dilayer mixture can be treated with the post-curing at 50 °C for 24 h to produce the dilayer membrane (PC), or suffered the repeated pre-curing process for the additional layer. On the basis of the proposed layer-by-layer curing approach, the multilayer membranes were fabricated containing the PDMS and Si−CNC components at different layers with the monolayer membrane (neat PDMS), dilayer membrane (PC) and trilayer membranes (PCP and CPC). In the nomenclature, the capitals “P” and “C” represented the neat PDMS layer and PDMS/Si−CNC composite layer. The compositions and thicknesses of the PDMS and Si−CNC components in diverse multilayer membranes were summarized in Table S1.

2.6. Characterization

2.6.1. Structure and properties of silylated cellulose nanocrystals

The morphology and crystalline properties of CNC before and after surface modification were analyzed by transmission electron microscopy (TEM) and X-ray diffraction (XRD). The CNC or Si−CNC suspension was diluted as about 0.1 wt% and negatively stained with the 2 wt% uranyl acetate for the TEM observation (FEI Tecnai G2 F30, USA). The XRD analysis was performed on the freeze-dried powders with the operating condition of the 2θ ranging from 5° to 40° (D8 Advance, Bruker, Germany). The surface silylation of CNC and substitution degree of Si−CNC were confirmed by the Fourier transform infrared spectrometer (FTIR), solid-state ^{13}C CP-MAS NMR spectroscopy, X-ray photoelectron spectroscopy (XPS) and atomic absorption spectroscopy (AAS). The FTIR measurement was carried out on a FTIR iS5 spectrometer (Nicolet, Madison, USA) in the range 4000–400 cm^{-1}. The solid-state ^{13}C CP-MAS NMR spectra were performed by a Bruker Avance 400 NMR spectrometer with the 4 mm CP-MAS probe, and recorded at 100.61 KHz, 12000 Hz spinning speed, 6 s relaxation delays. The silylation degree of Si−CNC was analyzed by the XPS using a ESCALAB 250Xi equipment (Thermo Fisher Scientific, USA) and the AAS with a GBC AVANTA instrument (Australia).

2.6.2. Interlayer and microstructure observation of multilayer membranes

The interlayer structure of the trilayer membranes was observed by the transflective polarizing microscope (TPM, EX20, China) with the observation of cross-sectional membranes from the cryo-fractured treatment in liquid nitrogen. The cross-sectional microstructure of the membrane was further investigated by scanning electron microscopy (SEM, Hitachi S-4800 instrument) and atomic force microscopy (AFM, MFP-3D-SA, Asylum Research, USA). The cryo-fractured cross-section