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Free-standing polylactic acid/chitosan/molybdenum disulfide films with controllable visible-light photodegradation

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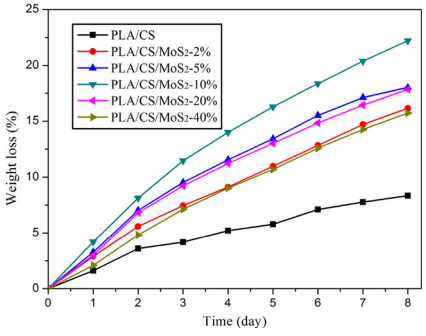
GRAPHICAL ABSTRACT



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ABSTRACT

The serious white pollution and energy crisis make it important and urgent to develop the degradable materials. The free-standing photodegradable PLA/CS/MoS_2 composite films were successfully prepared with the non-solvent induced phase separation method. The morphology, FTIR, Raman, UV–vis, fluorescence and visible light photodegradation rates of the films were investigated. The prepared PLA/CS/MoS_2 composite films could effectively absorb visible light, which were accompanied with photoluminescence. The photodegradation rates of the PLA/CS/MoS_2 films could be easily tuned by changing MoS_2 contents in a controlled way. The weight loss of the PLA/CS/MoS_2 films could reach up to ~22% after the visible light illuminating for 8 days, which were much faster than PLA/CS films. The films develop a new way to design a both photodegradable and biodegradable material, which can be used as excellent biomedical and packaging materials.

1. Introduction

The serious white pollutionand energy crisis make it important and urgent to develop degradable materials [1–3]. Polylactic acid (PLA), as a complete biodegradable material, has many advantages, such as good reproducibility, biocompatibility, biodegradability and diaphaneity [4,5]. PLA has got the approval of FDA agency and can be used potentially in many commercial and biomedical applications. Chitosan (CS), as the only cationic polymer in nature, has good hydrophilicity, biocompatibility, biodegradability and antibacterial activity [6,7]. CS is usually used as the blending modified material of PLA to solve the limitations of PLA, for example, the hydrophobicity and acid degradation products [8–10]. However, the PLA/CS blend materials are simply biodegradable materials, which are difficult to degrade in the non-

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microbial environment. Therefore, the modification of these biomaterials to degrade under light and improve the controllability of the degradation rate is a must.

The classical preparation of photodegradable plastics is divided into two basic kinds: copolymerized plastics [11,12] and additive plastics [13,14]. The copolymerized plastic can be photodegradable through introducing suitable photosensitive groups, such as carboxyl bond, carbonyl bond and double bond, into the polymer structure to change the molecular structure of polymers, so that the polymer material itself is photosensitive and thoroughly photodegradable. The additive plastic can be photodegradable through adding photosensitizer into the material to change the components of the polymer materials. The photosensitizer can absorb light to produce free radicals, transfer the energy to polymer molecules, so that the additive plastic can be photocatalytic photodegradable when exposed to light. The latter preparation method is much simpler and quicker than the former, so we chose to add the appropriate photosensitizer to PLA/CS composite films. There are many kinds of photosensitizers and photocatalysts. For example, Zhou et al. use the crystal facet-based CeO_2 homojunction and three-dimensional Bi_2MoO_6 nanostrips as photocatalysts to activate the reduction of CO_2 into methane [15,16] and 30-faceted $BiVO_4$ polyhedra microcrystals to enhance O_2 evolution from photocatalytic water splitting [17]. However, we chose molybdenum disulfide (MoS_2) as the photosensitizer to trigger for the photocatalytic photodegradation of the free-standing PLA/CS films under the visible light in this paper. Because MoS_2 has both unique properties of the transition metal sulfides materials and two-dimensional layered nanostructures, for example, good biocompatibility, mechanical properties and photoelectric properties [18–21], which can effectively absorb light.

MoS_2 includes 2H-MoS_2 and 1T-MoS_2 two phases [22]. The former is a thermodynamically-stable triangular prism phase with six sulfur atoms around each molybdenum atom, while the latter is a metastable octahedral phase. The direct band gap energy of the monolayer MoS_2 nanosheet is up to 1.8–1.9 eV and the mobility of the in-plane photogenerated carriers is as high as 200–500 $cm^2/(Vs)$ [23]. MoS_2 has been widely used in the bio-medical and photoelectric fields, for example, Huang et al. [24] modified MoS_2 nanosheets with multihydroxy hyperbranched polyglycerol (HPG) shells to improve the water dispersibility, which was used for photothermal therapy in vitro due to the excellent light-to-heat conversion capability of MoS_2; Xuan et al. [23] added MoS_2 nanosheets into the self-healing coatings to improve the antibacterial activity and detect heavy metals because of the fluorescence quenching; Wang et al. [25] synthesized MoS_2/g-C_3N_4/GO ternary composites to enhance the photocatalysiti activity for water splitting owing to the confinement effect.

In our present study [26,27], PLA/CS composite biodegradable films were successfully prepared with the non-solvent induced phase separation method. The prepared free-standing films have advantages of highly diaphaneity, controllable degradation rates and amazing antibacterial activity. In this paper, PLA/CS films were further modified with photosensitive MoS_2 nanosheets to improve the photoresponse of the materials. MoS_2 nanosheets could absorb visible light to produce free radicals and pass the energy on to the films to make the prepared PLA/CS/MoS_2 composite films photodegradable under visible light. Besides the morphology, FTIR, Raman, UV–vis, fluorescence and visible light potodegradation were investigated in this paper.

2. Material and methods

2.1. Materials

Polylactic acid (PLA, hydroxyl-terminated PLLA, Mw = 100,000) was purchased from Jinan Daigang Biomaterial Co., Ltd. Chitosan (CS, Mw = 100,000), chloroform, formic acid and *N*, *N*-dimethylformamide (DMF) were obtained from Sinopharm Chemical Reagent Shanghai Co. Ltd. Molybdenum disulfide (MoS_2) solution (100–400 nm, 18 mg/ml) was bought from Graphene Supermarket. Deionized water was laboratory homemade. All the materials were used without further purification.

2.2. Preparation of PLA/CS/MoS_2 films

The preparation of PLA/CS films with non-solvent induced phase separation has been reported in the previous work [27]. Then the PLA/CS film was treated by plasma for 5 min. After that the ultrasonic treated MoS_2 solution was added to the film by drop-coating method. Finally, the film was dried at 60 °C for 5 h. The obtained film was named as PLA/CS/MoS_2 film. According to the w/w ratio of MoS_2/PLA, the PLA/CS/MoS_2 composite films were further labeled as PLA/CS/MoS_2-2%, PLA/CS/MoS_2-5%, PLA/CS/MoS_2-10%, PLA/CS/MoS_2-20% and PLA/CS/MoS_2-40%, respectively. In the experiment, if there was no special description, the PLA/CS/MoS_2 film was referred to PLA/CS/MoS_2-5% by default.

2.3. Characterization of PLA/CS/MoS_2 films

Scanning electron microscope (SEM, Ultra Plus Zeiss) equipped with energy dispersive X-ray spectroscope (EDS), optical stereo-scopic microscope (OLYMPUS MVX10) and Digital camera (EOS 5D Mark II) were used to observe the morphology of the prepared films. Transmitted spectra were obtained with a fiber optic spectrometer (Ocean Optics, QE65000). The contact angle analysis was carried out using contact angle analyzer (Powereach, JC2000D1). FTIR spectra of the prepared samples were obtained with Fourier transform spectrophotometer (Nicolet 5700). Raman spectra were measured with Raman microscope (Invia microRaman) at excitation laser wavelength of 532 nm. Absorption spectra were collected with UV–vis spectrometer (a-1900 PC). Fluorescene images and spectra were obtained with fluorescent microscope (Olympus IX71).

2.4. Photodegradation of PLA/CS/MoS_2 films

The photodegradation of prepared films was investigated upon exposure to tubular xenon lamps (GXZ500, P = 500 W) and high pass filter (JB420, λ = 420 nm). The distance between samples and the light source was 10 cm. After a given time, the specimen was taken out and calculated the weight loss. The degradation activity of each sample was carried out in triplicate and the average values were reported.

The weight loss was calculated as follows:

$$Weight\ loss\,(\%) = \frac{W_0 - W_t}{W_0} * 100\% \quad (1)$$

Where W_t was the weight of film at predetermined time and W_0 was the initial weight of film.

3. Results and discussion

3.1. Morphology

The morphology of prepared PLA/CS/MoS_2 composite film was observed with optical microscope and scanning electron microscope (Fig. 1a and b). A number of MoS_2 exfoliated flakes with 100–400 nm of lateral dimensions were evenly distributed on the PLA/CS/MoS_2 composite film. The presence of MoS_2 was further proved by the EDS spectrum (Fig. 1d). The atomic percentages of the Mo and S in the film were 6% and 12%, respectively. The water contact angle (CA) of the PLA/CS/MoS_2 film (~78.7°) (Fig. 1c) was slightly larger than that of the PLA/CS film (~71.7°). The hydrophobic MoS_2 changed the interfacial tension of the material and resulted in the larger contact angle. However, the contact angle was still less than that of the pure PLA film (~79.6°). It suggested that PLA/CS/MoS_2 film could achieve the purpose of improving the hydrophilicity of PLA. The transmittance of PLA/