

Structure and Properties of Carboxymethyl Chitosan Film Modified by Poly(L-lactic Acid)

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A series of water-soluble carboxymethyl chitosan/poly(L-lactic acid) (CMCS/PLLA) blend films with various poly(L-lactic acid) mole contents were prepared by the solution casting method. Surface morphologies of CMCS/PLLA blend films were investigated by scanning electron microscopy. Thermal, mechanical and chemical properties of the polymer blend films were studied by differential scanning calorimetry, thermogravimetric analysis, tensile tests and surface contact angle tests. It was displayed that the introduction of poly(L-lactic acid) could modify the properties of carboxymethyl chitosan films.

Keywords: Carboxymethyl chitosan, Poly(L-lactic acid), Blend film, Morphology.

INTRODUCTION

Because of the excellent biodegradability, biocompatibility, nontoxicity, antibacterial and wound-healing activity, chitosan with a repeated structure of (1,4)-linked 2-amino-2-deoxy- β -D-glucan has attracted much attention for its potential applications¹⁻⁹. Due to the unique structures and properties, chitosan has been widely studied in the fields of drug delivery system^{10,11}, analgesia¹², wound dressing (*i.e.*, artificial skin)¹³, bone tissue engineering¹⁴, vascular surgery¹, cosmetics and hair care¹⁵, *etc.* Water-soluble carboxymethyl chitosan has lots of special biological, chemical and physical properties, such as antifungal, antibacterial and antitumor activities, which are different from ordinary chitosan¹⁶. Water-soluble carboxymethyl chitosan films are usually used as wound dressing (*i.e.*, artificial skin)¹³. Also, the better hydrophilicity of CMCS could limit its application.

As known, poly(L-lactic acid) (PLLA) with better biocompatibility, biodegradability and hydrophobicity could be used for biomaterials¹⁷⁻¹⁹. The introduction of PLLA with better hydrophobicity into carboxymethyl chitosan (CMCS) film is expected to improve the physicochemical properties of CMCS film. To the best of our knowledge, no experimental work has so far been reported on the studies of the modification of water-soluble chitosan film *via* blending with PLLA. In the present work, a series of CMCS/PLLA blend films with different PLLA mole contents were prepared by the solution casting method. Surface morphologies of CMCS/PLLA blend films were studied by SEM technique. Thermal, mechanical and chemical properties of the polymer blend films were studied by DSC,

TGA, tensile tests and surface contact angle tests. It was revealed that the introduction of PLLA chains could exert marked effects on the properties of CMCS films.

EXPERIMENTAL

The water-soluble carboxymethyl chitosan (degree of deacetylation: 99 %; degree of carboxymethylation: 65 %; $M_w = 80000$) was purchased from Aladdin Chemistry Co. Ltd. (China). The poly(L-lactic acid) (PLLA) ($M_w = 5000$) was purchased from Jinan Daigang Biomaterial Co. Ltd. (China). Dimethyl sulfoxide and other solvents are of analytical grade and used without further purification.

Preparation of CMCS/PLLA blend film: The polymer blend films were prepared by casting a 30 wt % polymer blend solution in the mixed solvents of DMSO and distilled water (volume ratio of DMSO to water: 1:1) onto clean glass plates and drying them under vacuum at 60 °C. It is also found that when PLLA mole content in polymer blend is over 14 %, the polymer blend can not form a continuous film.

Scanning electron microscopy (SEM) investigation was carried out using a scanning electron microscope (Sirin 200, FEI, Holland). Gold was sputtered on the samples in vacuum. Acceleration voltage was 10 kV and photographs of the surface of the polymer blend films were taken. DSC measurements were made on a DSC Q100 (TA, USA) differential scanning calorimeter, the temperature calibrated with indium in nitrogen atmosphere. About 8 mg sample was weighted very accurately. The temperature was controlled within the range between 0 °C and 300 °C, the heating rate was 10 °C/min. Thermogravimetric analysis (TGA) was carried out on a NETZSCH STA 4490C

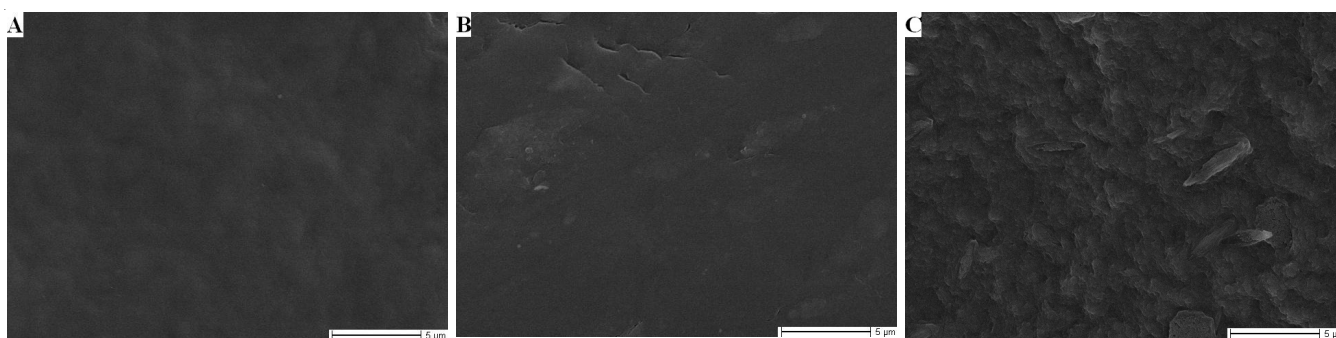


Fig. 1. SEM photographs of CMCS/PLLA blend film surface with various PLLA mole contents: (a) 0, (b) 7 and (c) 14 %

TG-DTA analyzer (Germany) at a heating rate of 10 °C/min under nitrogen atmosphere over the temperature range of 30-500 °C. Samples of approximately 13 mg were used for the measurements. Tensile tests were carried out with an Instron 4468 machine (Digital Instruments Inc., USA). The crosshead speed was set to 100 mm/min. For each data point, five samples were tested and the average value was taken. A 5 μ L drop of pure distilled water was placed on the polymer blend film surface using a syringe with a 22-gauge needle. The static contact angle was measured with an optical contact angle meter CAM 200 (KSV Instrument Ltd., Finland). The measurements of each contact angle were performed within 10 s after each drop to ensure that the droplet did not soak into the compact. The surface contact angles were the mean of five determinations²⁰.

RESULTS AND DISCUSSION

The morphologies of CMCS/PLLA blend film surface were studied by SEM technique. Fig. 1 presents the surface morphologies of CMCS/PLLA blend films with various PLLA mole contents: (a) 0, (b) 7 % and (c) 14 %. As it can be seen from Fig. 1, the introduction of PLLA changed the surface morphologies of the polymer blend films. The surface morphologies of the polymer blend films became more coarse with the increase of PLLA mole contents in the polymer blend. As CMCS chains and the PLLA segments could exert interaction by entanglement, suggesting the change of the surface morphologies of the polymer blend films could be attributed to the introduction of the PLLA chains.

DSC analysis: Table-1 shows the glass transition temperature of CMCS segments in polymer blend with various PLLA mole contents. As is shown in Table-1, the glass transition temperature of CMCS segments in the polymer blend decreased with the increase of PLLA contents. As mentioned above, CMCS segments and PLLA chains could exert interaction through entanglement and the interaction could partially destroy the intermolecular or intramolecular hydrogen bonds of CMCS segments, indicating that the decrease of the glass transition temperature of CMCS segments in the polymer blend could also be attributed to the introduction of the PLLA chains.

TG analysis: Fig. 2 indicates the TG curves of CMCS/PLLA blends with various PLLA mole contents: (a) 0, (b) 7 and (c) 14 %, the corresponding data are listed in Table-2. As seen from Fig. 2 and Table-2, the initial decomposition temperature

PLLA mole content (%)	Glass transition temperature (°C)
0	106.2
7	99.1
14	95.9

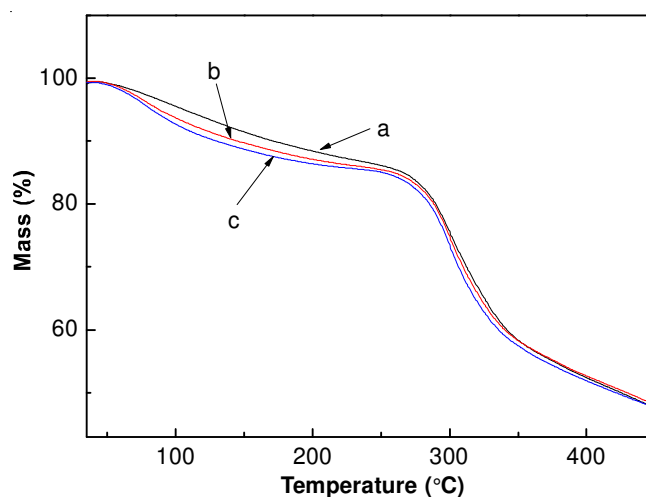


Fig. 2. TG curves of CMCS/PLLA blends with various PLLA mole contents: (a) 0, (b) 7 and (c) 14 %

PLLA mole content (%)	Initial decomposition temperature (°C)
0	260.2
7	259.1
14	257.9

of the CMCS segments in the polymer blend slightly decreased with the increase of PLLA mole contents. As noted, the interaction between CMCS chains and PLLA segments could partially destroy the intermolecular or intramolecular hydrogen bonds of CMCS segments, indicating that the decreased decrease of the initial decomposition temperature of the CMCS segments in the polymer blend was related with the introduction of the PLLA chains.

Tensile tests: Fig. 3 shows the relationship between the tensile strength of CMCS/PLLA blend film and the PLLA mole

contents. As is shown in Fig. 3, the tensile strength of the CMCS/PLLA blend film increased with the increase of PLLA mole contents. As reported in previous document²¹, pure PLLA film holds higher tensile strength than pure chitosan film, suggesting that the intermolecular interaction between the CMCS segments and the PLLA chains through entanglement promoted the tensile strength of the polymer blend film.

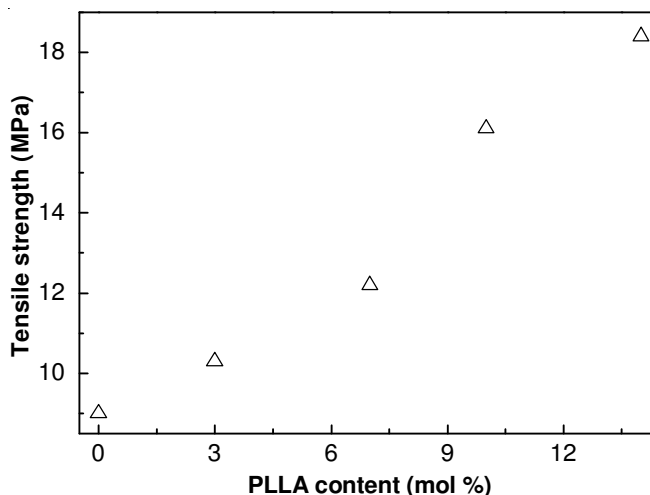


Fig. 3. Relationship between the tensile strength of CMCS/PLLA blend film and PLLA mole contents

Surface contact angle tests: Fig. 4 presents the relationship between the surface contact angle of CMCS/PLLA blend film and PLLA contents. As shown in Fig. 4, the surface contact angle of the polymer blend film increased with the increase of PLLA mole contents in the polymer blend, suggesting that the hydrophobicity of the polymer blend film increased. As noted, PLLA chains hold good hydrophobicity, indicating that the introduction of the hydrophobic PLLA chains promoted the surface contact angle of the polymer blend film. Under permitted PLLA contents, the higher the PLLA contents, the higher the surface contact angle of the polymer blend film.

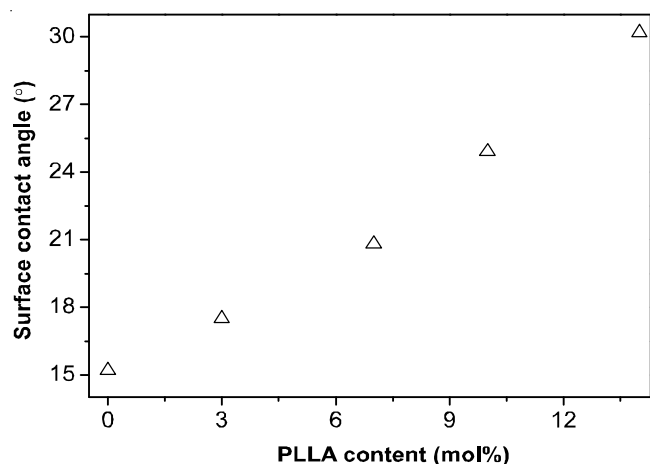


Fig. 4. Relationship between the surface contact angle of CMCS/PLLA blend film and PLLA mole contents

Conclusion

A series of CMCS/PLLA blend films with various PLLA mole contents were prepared by the solution casting method. SEM photographs showed that the introduction of PLLA chains changed the surface morphologies of the polymer blend films. DSC data indicated that the glass transition temperature of CMCS segments in the polymer blend decreased with the introduction of the PLLA chains. Thermogravimetric tests proved that the initial decomposition temperature of the CMCS segments in the polymer blend decreased with the introduction of the PLLA chains. Tensile tests verified that the tensile strength of the polymer blend film increased with the introduction of the PLLA segments. Surface contact angle measurements demonstrated that the introduction of PLLA chains increased the hydrophobicity of the polymer blend films.

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