

Morphology and Physicochemical Performance of Water-soluble Carboxymethyl Chitosan/Polyurethane Blend Film

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Summary: A series of water-soluble carboxymethyl chitosan (CMCS)/polyurethane (PU) blend films with various CMCS/PU mole ratios were prepared by casting the polymer blend solution in the mixed solvents of dimethyl sulfoxide (DMSO) and water. Surface morphologies of CMCS/PU blend films were studied by scanning electron microscopy (SEM). Thermal, mechanical, and chemical properties of CMCS/PU blend films were investigated by thermogravimetric analysis (TGA), tensile tests, and contact angle tests. It was revealed that the introduction of PU could greatly affect the surface morphology and the performance of CMCS film.

Key words: Morphology; Performance; CMCS/PU blend; Film.

Introduction

Polymer blending has been an attractive alternative for producing new polymeric materials with tailored performance without having to synthesize completely new materials [1]. Other advantages for polymer blending are versatility, simplicity, and inexpensiveness [1].

Owing to the outstanding 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 applications [2-14]. Due to the unique structures and properties, chitosan has been widely studied in the fields of drug delivery system [15, 16], analgesia [17], wound dressing (i.e., artificial skin) [18], bone tissue engineering [19], vascular surgery [2], cosmetics and hair care [20], etc.

Solubility is a crucial characteristic for chitosan, improving the solubility of chitosan could facilitate the application of chitosan in medicine and food [3]. Therefore, it is still interesting to promote the solubility of chitosan. 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 chitosan [21]. Water-soluble carboxymethyl chitosan can be produced by either chemical or enzymatic hydrolysis, the chemical approach has some defects, including harsh hydrolytic conditions, low yields, and chemical modifications of the glucose rings [2, 22]. On the other hand, enzymatic methods offer advantages such as mild reaction conditions, high specificity, no glucose ring modifications [22]. Water-soluble carboxymethyl chitosan films are usually used as wound dressing (i.e., artificial skin) [18].

As known, CMCS holds brittle and hydrophilic properties, and these properties could also limit its application. The polyurethane (PU) synthesized in the work presents weak hydrophilicity and good flexibility [23-30], it is expected that the introduction of PU into CMCS film could improve the performance of CMCS film. The formation of hydrogen bonds between CMCS segments and PU chains could promote the miscibility of CMCS and PU.

However, to the best of our knowledge, no experimental work has so far been reported on the studies of the modification of water-soluble carboxymethyl chitosan film via blending with PU. In the present work, a series of CMCS/PU blend films with different CMCS/PU mole ratios were prepared by casting the polymer blend solution in the mixed solvents of DMSO and water. Morphologies of CMCS/PU blend films were investigated by SEM technique. Thermal, mechanical, and chemical properties of CMCS/PU blend films were researched by TGA, tensile tests, and contact angle tests. It was found that the introduction of PU could exert marked effects on the properties of CMCS films.

Results and Discussion

SEM Tests

The morphologies of CMCS/PU blend film surface were studied by SEM technique. Fig. 1 presents the surface photographs of CMCS/PU blend films with various PU contents (mol %): (a) 0, (b) 6, and (c) 12. As seen from Fig. 1, the introduction of PU obviously changed the surface morphologies of the polymer blend films. The surface morphologies of CMCS films changed from relatively slippy to coarser and the surface density increased with the

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increase of the PU content. As CMCS chains and soft PU segments could exert interaction by entanglement, and the introduction of the PU segments accordingly changed the surface morphologies of CMCS films. With the increase of the PU content, the surface density of the CMCS film could also relatively increased. This phenomenon indicated that the change of the surface morphologies of the polymer blend films could be attributed to the introduction of PU chains.

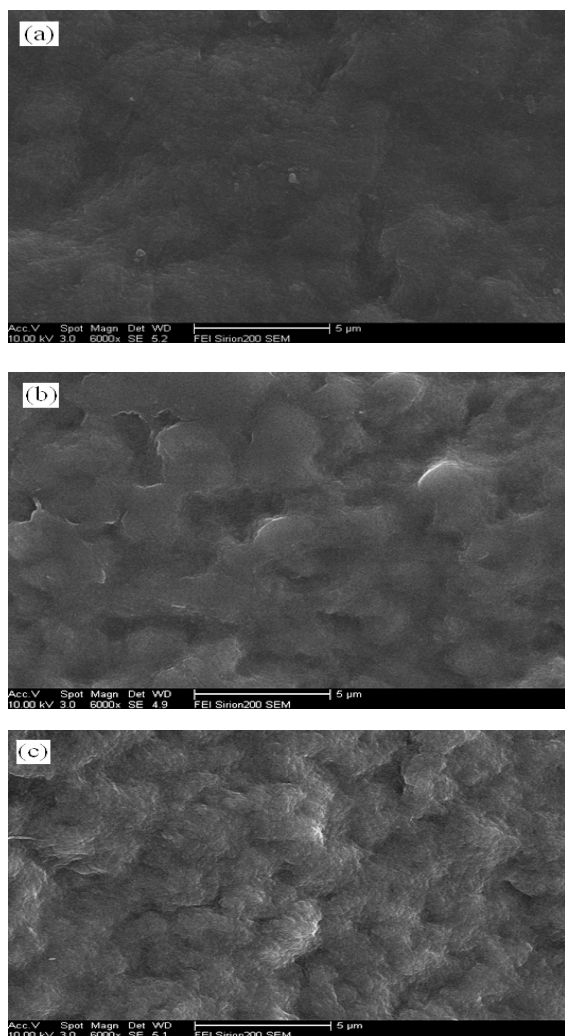


Fig. 1: SEM photographs of CMCS/PU blend film surface with different PU contents (mol %): (a) 0, (b) 6, and (c) 12 (magnification 6000 ×).

TGA Analysis

Fig. 2 indicates the DTG curves of CMCS/PU blend films with various PU contents (mol %): (a) 0, (b) 6, and (c) 12, the corresponding data

are listed in Table-1. As shown in Fig. 2 and Table-1, the maximum decomposition temperature of the CMCS segments in polymer blend films decreased with the increase of PU content in polymer blend. As known, the formation of the hydrogen bonds between the flexible PU chains and the CMCS segments could partially destroy the intermolecular or intramolecular hydrogen bonds of the CMCS segments. This situation demonstrated that the decrease of the maximum decomposition temperature of CMCS segments in polymer blend film could also be attributed to the introduction of the flexible PU chains.

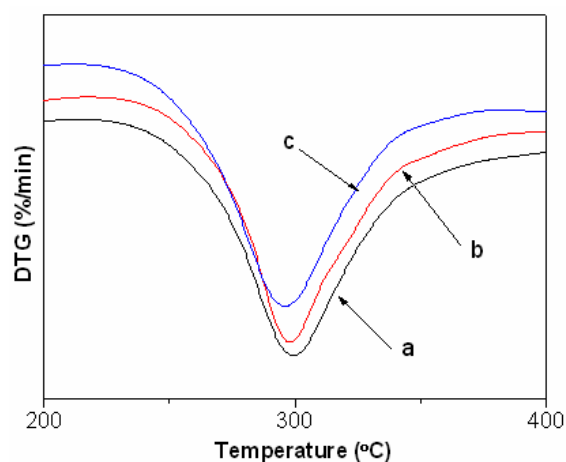


Fig. 2: DTG curves of CMCS/PU blend films with various PU contents (mol %): (a) 0, (b) 6, and (c) 12.

Table-1: The maximum decomposition temperature of CMCS/PU blend film with various PU mole contents

PU content (mol %)	Maximum decomposition temperature (°C)
0	299.7
6	298.0
12	296.1

Tensile Tests

Fig. 3 shows the relationship between the tensile strength of CMCS/PU blend film and the PU mole content. As is shown in Fig. 3, the tensile strength of the CMCS/PU blend film decreased with the increase of PU content. As discussed above, the synthetic PU chains are flexible, and the PU chains could interact with CMCS segments by entanglement or forming intermolecular hydrogen bonds. This phenomenon proved that the decrease of the tensile strength of the polymer blend film was concerned with the introduction of the flexible PU chains.

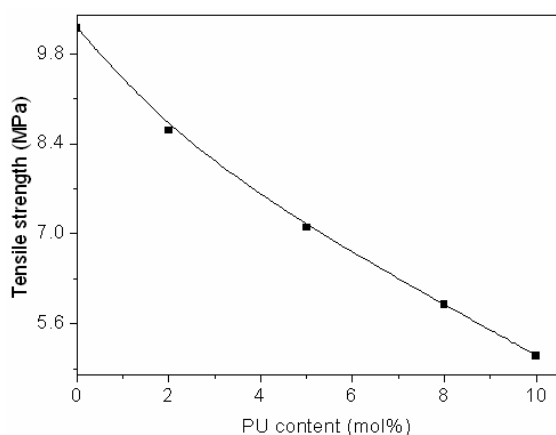


Fig. 3: Relationship between the tensile strength of CMCS/PU blend film and PU mole content in polymer blend.

Surface Contact Angle Tests

Fig. 4 presents the relationship between the surface contact angle of CMCS/PU blend film and PU mole content. As it can be seen from Fig. 4, the surface contact angle of the polymer blend film increased with the increase of PU mole content in the polymer blend, indicating that the hydrophilicity of the polymer blend film decreased. As mentioned above, the synthetic PU chains hold weak hydrophilicity, suggesting that the increase of the surface contact angle of the polymer blend film was related to the introduction of PU chains with weak hydrophilicity.

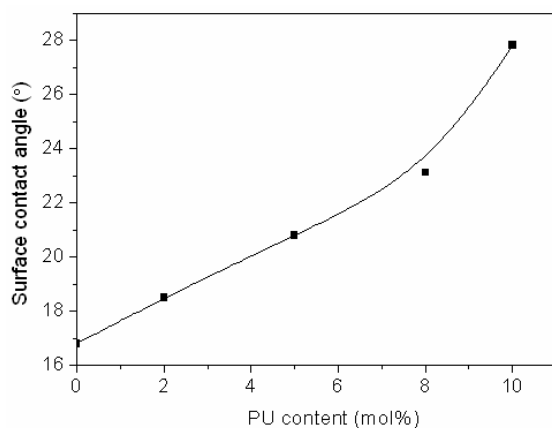


Fig. 4: Relationship between the surface contact angle of CMCS/PU blend film and PU mole content in polymer blend.

Water-Resistant Pressure Measurements

Fig. 5 indicates the relationship between the water-resistant pressure of CMCS/PU blend film and PU mole content. As seen from Fig. 5, the water-resistance pressure of the polymer blend film increased with increasing the PU mole content in the polymer blend, suggesting that the hydrophobicity of the polymer blend film increased. As discussed above, the synthetic PU segments possess weak hydrophilicity, indicating that the increase of the water-resistant pressure of the polymer blend film was connected with the introduction of PU segments with weak hydrophilicity.

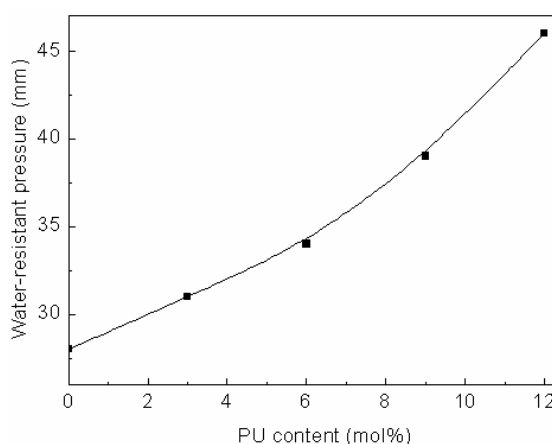


Fig. 5: Relationship between the water-resistant pressure of CMCS/PU blend film and PU mole content in polymer blend.

Experimental

Materials

The water-soluble carboxymethyl chitosan (degree of deacetylation: 99%; degree of carboxymethylation: 55%; $M_w = 90000$) was purchased from Aladdin Chemistry Co. Ltd. (China). Poly(propylene glycol) (PPG) ($M_w = 2000$) was purchased from Zibo Dongda Chemical Industrial Co. Ltd. (China), and dried under vacuum to remove water before use. Butanediol (BDO), 2,4-toluene diisocyanate (TDI), dibutyltin dilaurate (DBTL), and dimethylformamide (DMF) are of analytical grade and used without purification. Dimethyl sulfoxide (DMSO) and other solvents are of analytical grade and used without further purification.

Synthesis of PU Polymer

Polyurethane polymer based on 2,4-toluene

diisocyanate (TDI), poly(propylene glycol) (PPG), and butanediol (BD) were prepared with butanediol as chain extender, dimethylformamide (DMF) as solvent, and dibutyltin dilaurate (DBTL) as initiator [31, 32]. Briefly, a 500 ml round-bottomed, four-necked flask was fitted with a mechanical stirrer, thermometer, condenser, and a dropping funnel. TDI and PPG as a solution in DMF were put into the reactor with dibutyltin dilaurate as initiator. Reaction was carried out at 60 °C in a water bath under a nitrogen atmosphere. After 1 h of polymerization at 60 °C, BD was added into the reaction vessel. After another 20 min, anhydrous ethanol was added to stop the polymerization. The molecular weight of PU polymer was about 15000. Fig. 6 presents the scheme of PU polymer synthesis.

Preparation of CMCS/PU Blend Film

The CMCS was dissolved in the mixed solvents of DMSO and distilled water (vol. ratio of DMSO to water: 1:1) to obtain 30 % clear polymer solution, while PU was dissolved in the same mixed solvents to obtain 5 % clear polymer solution. According to the various mole ratios of CMCS to PU, the clear polymer blend solutions were obtained. The polymer blend films were prepared by casting the polymer blend solutions in the mixed solvents onto clean glass plates and drying them under vacuum at 60 °C. The detailed method was as follows: First, the clean glass plates were put in the oven with the temperature of 35 °C, the polymer blend solutions were put onto the clean glass plates within 5 min and keeping at 35 °C for 10 hours; Second, the temperature of the oven was adjusted to 60 °C, and the polymer blend films were dried under vacuum for 96 hours. Also, it is found that, when PU mole content in polymer blend is over 12 %, the polymer blend can not form an even and continuous film. Fig. 7 shows the proposed structure of CMCS/PU blend

showing the H-bonding interaction between CMCS and PU.

Methods

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. Thermogravimetric analysis (TGA) was carried out on a NETZSCH STA 4490C TG-DTA analyzer (Germany) at a heating rate of 10 °C/min under nitrogen atmosphere over the temperature range of 30-550 °C. Samples of approximately 14 mg were used for the TG measurements. Tensile tests were carried out with an Instron 4468 machine (Digital Instruments Inc., USA). The crosshead speed was set to 70 mm/min. For each data point, five samples were tested and the average value was taken. The static contact angle was measured with an optical contact angle meter CAM 200 (KSV Instrument Ltd., Finland). A 5 µL drop of pure distilled water was placed on the polymer blend film surface using a syringe with a 22-gauge needle. 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 determinations [33]. The water-resistant pressure (mm) measurements of CMCS/PU blend films were carried out according to a conventional method. The round sample films were used to seal the mouth of a long round tube with graduation in millimeters (tube diameter: 8 mm). Then, the tube was upset, deionized water was added into the long round tube drop by drop. As soon as the deionized water permeated the film, the height of water column was written down. For each data point, five samples were tested and the average value was taken [34].

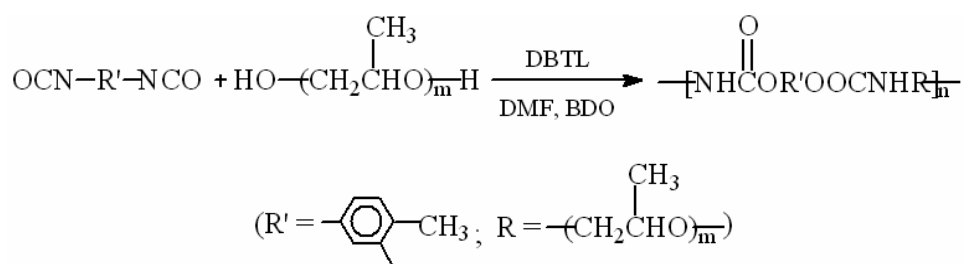


Fig. 6: Scheme of PU polymer synthesis.

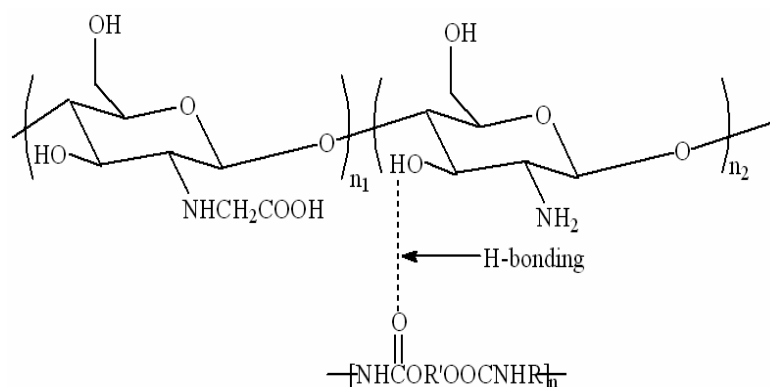


Fig. 7: Proposed structure of CMCS/PU blend showing the H-bonding interaction between CMCS and PU.

Conclusions

A series of CMCS/PU blend films with various PU contents were prepared by casting the polymer blend solution in the mixed solvents of DMSO and water. SEM photographs attested that the introduction of PU chains markedly changed the surface morphologies of the polymer blend films. TGA tests indicated that the maximum decomposition temperature of the CMCS segments in the polymer blend films decreased with the increase of PU content. Tensile tests verified that the tensile strength of the polymer blend film decreased with the increase of PU content. Surface contact angle measurements proved that the surface contact angle of the polymer blend film increased with the increase of PU content. The water-resistant pressure tests demonstrated that the water-resistant pressure of the polymer blend film increased with increasing the PU content.

Acknowledgements

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