

# Preparation and characterization of biodegradable poly(L-lactide)/chitosan blends

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## Abstract

In order to improve the properties of chitosan and obtain new fully biodegradable materials, blends of poly(L-lactide) (PLLA) and chitosan with different compositions were prepared by precipitating out PLLA/chitosan from acetic acid–DMSO mixtures with acetone. The blends were characterized by Fourier transform infrared analysis (FTIR), X-ray photoelectron spectroscopy (XPS), differential scanning calorimetry (DSC), <sup>13</sup>C solid-state NMR and Wide-angle X-ray diffraction (WAXD). FTIR and XPS results showed that intermolecular hydrogen bonds existed between two components in the blends, and the hydrogen bonds were mainly between carbonyls of PLLA and amino groups of chitosan. The melting temperatures, cold crystallization temperatures and crystallinity of the PLLA component decreased with the increase in chitosan content. Blending chitosan with PLLA suppressed the crystallization of the PLLA component. Although the crystal structure of PLLA component was not changed, the crystallization of the blends was affected because of the existence of hydrogen bonds between two components, which was proved by WAXD results.

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## 1. Introduction

Chitosan (CS), a biodegradable, biocompatible and relatively inexpensive natural polymer, is produced from deacetylation of chitin with a degree of deacetylation over 75%. In recent decades, CS has become a major

component used in vascular surgery, tissue culture, and tissue regeneration as a hemostatic agent [1]. Among some interesting applications, CS scaffolds have also been investigated for use in tissue engineering. However, CS has a high modulus of elasticity, owing to the higher glass transition temperature and crystallinity [2]. The film brittleness and membrane permeability of CS limit its broader application as a biomaterial.

In order to overcome its shortcomings, two methods are applied to improve its morphology and ductility. One is to chemically synthesize CS copolymers. Since the molecular chains of CS hold functional groups, many novel polysaccharide derivatives containing

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poly(ethylene glycol) (PEG) [3], poly(vinyl alcohol) (PVA) [4] and poly(methyl methacrylate) (PMMA) [5] were synthesized by copolymerization. Depending on chemical structure and composition, the properties of these copolymers vary widely. When CS is grafted with PEG, the modulus of elasticity and the elongation at break are improved by the suppression of crystallinity of each component [3]. Moreover, the drug release behavior of copolymers based on CS can be adjusted by changing the kinds of grafted polymers and their graft degree [6]. The other method is to prepare blends consisting of CS and other polymers, for example cellulose [7], PVA [8] and poly(ethylene oxide) (PEO) [9,10]. Taking advantage of amino and hydroxyl groups on the molecular chains, CS is very useful in the development of composite materials such as blends or alloys with other materials. The blends of CS and PEO were found to be slightly incompatible, but it did not lead to phase separation. The best mechanical properties were obtained with the composition of CS/PEO = 30/70, which was a stoichiometric composition between PEO and CS monomer units. The blending of CS with other polymers not only changes its morphology but also improves its toughness. Compared with chemical copolymerization, blending is still a relatively simple, cost effective, and convenient way to improve the properties of CS.

Currently, there is considerable interest in the blending of CS with biodegradable polyesters because it is an effective approach to reduce environmental pollution from plastic wastes. Inoue's group [11–14] reported blending films of poly(3-hydroxybutyrate) (PHB)/chitin, PHB/CS, poly( $\epsilon$ -caprolactone) (PCL)/chitin and PCL/CS by solution-casting technique using 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) as common solvent, and then investigated their thermal properties and crystallization behavior. The results showed that chitin and CS components suppressed the crystallization of PHB and PCL components, resulting in decreasing crystallinity of PHB and PCL components. The biodegradability of chitin and CS components was improved by blending with PHB, especially for CS components. Cheung et al. studied the blends of PHB/CS and P(HB-co-HV)/CS by solid-state NMR, and found that CS was miscible with both PHB and P(HB-co-HV) at all compositions [15]. Recently, Suyatma investigated mechanical and barrier properties of biodegradable films made from CS and poly(lactic acid) (PLA) blends [16]. They prepared the blends by solution mixing and film casting using 1% acetic acid and chloroform as solvent, and found that the mechanical properties of the films decreased because there was no specific interaction and no compatibility between two components. In all cases, it can be found that the choice of common solvents is close related with morphology properties of the blends. In fact, there are few common solvents for CS and aliphatic polyesters,

except HFIP. So far there have been few studies on blending CS and polyesters because HFIP is very expensive and difficult to dry.

Among many biodegradable polyesters, poly(L-lactide) (PLLA) has attracted the most attention because it is not only highly biodegradable, but can also be derived from renewable natural resources such as corn starch [17]. PLLA is also superior to other aliphatic polyesters in terms of thermal, mechanical properties and transparency of the processed materials [18]. PLLA does not have any active functional groups on the backbone, besides the hydroxyl and carboxylic groups at the chain ends; therefore, it is difficult to be modified chemically. Hence, blending is preferable for modifying the properties of PLLA and CS. With improved toughness, controlled biodegradability, and chemical functionalities, such blends can be good candidates for new biomaterials. Compared with blends utilizing other biodegradable polyesters, for example PHB, blends based on CS and PLLA are likely to have more widespread application as biomedical materials because PLLA is cheaper and is easier to produce directly by chemical polymerization. As one of our series of studies into the blends of biodegradable polyesters and CS, this article examines PLLA/CS blends prepared by precipitation with FTIR, XPS, DSC,  $^{13}\text{C}$  solid-state NMR and WAXD. The effect of intermolecular interaction between two components on crystallization is also addressed.

## 2. Experimental

### 2.1. Materials

PLLA was synthesized by ring-opening polymerization of L-lactide monomer in the presence of stannous octanoate as catalyst, which was used after purification by precipitation in methanol from chloroform solution. Its average molecular weight and polydispersity were determined by GPC as  $3.74 \times 10^4$  and 2.83, respectively. CS, kindly supplied by Xiamen University, was used without further purification. The degree of deacetylation of CS determined by colloidal titration was 89%. Stannous octanoate was purchased from the Aldrich Chemical Co. The other reagents were used as received.

### 2.2. Preparation of samples

PLLA was dissolved in DMSO [concentration, 2% (w/v)], and then CS was also dissolved in acetic acid–DMSO (1:100, v/v) to obtain 1% (w/v) solution. After both solutions were well homogenized, the CS in acetic acid–DMSO was mixed with PLLA in DMSO. The mixtures were precipitated in acetone after being stirred for 6 h at ambient temperature, and then filtered to obtain the blends with appropriate weight ratios in the

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