

Preparation and characteristics of chitosan-g-PDMS copolymer

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Summary

Chitosan-g-poly(dimethyl siloxane) (PDMS) copolymer was prepared by grafting PDMS prepolymer onto chitosan. PDMS prepolymer was prepared by ionic ring opening polymerization of octamethylcyclotrisiloxane (DD) using n-buthyllithium (BuLi). The tensile strength and elongation of chitosan-g-PDMS copolymer were mostly constant regardless of PDMS prepolymer grafting %. While critical surface energy of chitosan is about 32 dyne/cm, that of chitosan-g-PDMS copolymer was a little decreased to 25~29 dyne/cm by grafting PDMS onto chitosan.

Introduction

In the recent years, much attention has been focused on the utilization of natural resources in respect of environmental pollution. Among some natural resources, chitin obtained from the protective cuticle of crustacea, insects and the cell walls of some fungi and microorganisms and chitosan, derived from it by deacetylation have been attracted much attention due to its unique properties. Especially, chitosan has been used to detect trace ions and to recover the heavy metals from sea water or wastes and to be utilized coagulating waste in the food processing plants(1-4) because of its native chelating properties. And also, chitosan has been used in biomedical fields because of its favorable characteristics such as biocompatibilty and reported to be useful for pharmaceutical preparations (5, 6). But chitosan's main disadvantage for clinical application is its high critical surface energy, caused thrombogenity phenomenon when it contacts blood. In general, if surface energy of medical material are high when it is exposed to blood, thrombogenity phenomenon is occurred due to adsorption between protein or cell in blood and surface of medical material.

The other side, siloxane derivatives such as PDMS are a high performance polymer with unique physical and chemical properties such as high thermal and oxidative stability, UV resistance, low glass transition temperature, low surface energy, good electrical property, and high permeability to many gases(7,8).

Therefore, in this paper, studies were carried out to prepare chitosan-g-PDMS copolymer by introducing PDMS onto chitosan. Also, it was investigated the change of crystallinity, tensile strength, and critical

surface energy according to grafting PDMS onto chitosan.

Experimental

Materials and Reagents

Chitosan was supplied by Tokyo Kasei Co. D₄ was supplied by United Chemical Technology and then used after sublimation. n-BuLi was supplied by Aldrich Chem. Co. CH₃SO₂Cl and dimethylformamide were supplied by Junsei Chem. Co. Ltd. All other commercially available chemicals were reagent grade and used without further purification.

Preparation of Chitosan-g-PDMS Copolymer

Preparation of Chlorinated Chitosan (Chitosan-Cl)

Chitosan-Cl was prepared as follows. 0.5g of chitosan and 200mL of DMF were charged into four necked flask, equipped with a stirrer, reflux condenser, N₂ inlet and then stirred over 30min. And excess CH₃SO₂Cl as chlorinated agent was added into flask and maintained at 65°C for 24hrs. The reaction mixture was added to excess acetone in order to remove unreacted residue. And precipitated material was filtered and washed over several times with acetone. Thus, chitosan-Cl was obtained by drying in vacuum oven at 40°C for 24hrs.

Preparation of PDMS Prepolymer.

PDMS prepolymer was prepared by reference to Gordon's method(9). 0.05mol of D₄ and 40mL of tetrahydrofuran were charged into flask, and stirred over 30min. PDMS prepolymer was obtained by adding 0.025mol of n-BuLi as initiator into flask and then maintained at 0°C for 12hrs.

Preparation of Chitosan-g-PDMS Copolymer Membrane

0.5g of chitosan-Cl and 7.5g of PDMS prepolymer were charged into identical synthesis apparatus for chitosan-Cl, and then maintained at 40°C for 24hrs. After reaction mixture was dissolved with acetic acid, unreacted chitosan-Cl with solid state was filtered out. And then, it was added to excess ethylacetate in order to remove unreacted PDMS prepolymer. And precipitated materials were filtered and washed over several times with acetone. Finally, chitosan-g-PDMS copolymer was obtained by drying in vacuum oven at 40°C for 24hrs. And chitosan-g-PDMS copolymer membrane was prepared by solvent casting technique using 10% acetic acid solution. The chemical structure of chitosan-g-PDMS copolymer was confirmed by measuring the FT-IR and ¹³C NMR spectrum. PDMS grafting % of chitosan-g-PDMS copolymer was obtained as,

$$\text{Grafting \%} = \frac{\text{Weight of chitosan-g-PDMS copolymer} - \text{Weight of chitosan}}{\text{Weight of chitosan}} \times 100$$

Characterization and Analysis

FT-IR spectra were obtained from KBr pellets of chitosan and chitosan-g-PDMS copolymer with FT-IR spectrometer(Shimadzu DR-8011).

¹³C NMR spectra were obtained from chitosan and chitosan-g-PDMS copolymer with solid state CP/MAS ¹³C NMR spectrometer(Bruker ARX-300).

X-ray diffraction patterns were obtained from chitosan and chitosan-g-PDMS copolymer with X-ray diffractometer(Rigaku Denki Model RAD-C) The X-ray source was CuK_α radiation with 40kV, 30mA, 1 °/min.

Tensile strength and elongation were obtained from chitosan and chitosan-g-PDMS copolymer with Instron Universal Machine(Model 1000).

Contact angles were obtained from chitosan and chitosan-g-PDMS copolymer with Contact Angle Meter(KRÜSS G-10). Contact angles of chitosan and chitosan-g-PDMS copolymer membrane to various solvents, shown in Table 1 were measured at 37°C using the sessile drop technique(10). The values were obtained average at least three different drops.

Table 1. Critical surface tension of various solvents at 37°C

Solvent	Surface Tension(dyne/cm)
<i>m</i> -Cresol	34.50
Ethylene glycol	46.92
Nitroaniline	57.00
Water	72.50

Results and Discussion

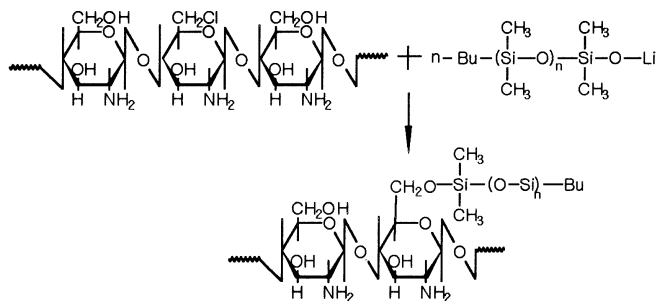
Characterization of Chitosan-g-PDMS Copolymer

Chitosan-g-PDMS copolymer was prepared by the reaction of chitosan-Cl and PDMS prepolymer at 0°C for 24hrs. The reaction mechanism of chitosan-g-PDMS copolymer was briefly shown in scheme 1. The FT-IR and ¹³C NMR spectra of chitosan-g-PDMS copolymer were shown in Fig. 1 and 2, respectively. The FT-IR spectrum[Fig. 1(B)] showed a new peak around 1020~1100cm⁻¹ due to Si-O-Si absorption peak and 1275cm⁻¹ due to Si-CH₃, as indicated grafting PDMS onto chitosan. And also, ¹³C NMR spectrum[Fig. 2(B)] showed a new weak peak around -4.5ppm due to Si-CH₃. From these results, it is confirmed that chitosan-g-PDMS copolymer has a structure, shown in scheme 1.

X-ray Diffraction of Chitosan-g-PDMS Copolymer

X-ray diffraction curves of chitosan and chitosan-g-PDMS copolymer under various conditions were shown in Fig. 3 and 4. As shown in Fig. 3, the characteristic peak of chitosan[Fig. 3(A)] showed strong, but that of chitosan-g-PDMS copolymer showed weakly around $2\theta = 9.8^\circ$ and 21° , respectively. That is to say, by introducing PDMS onto chitosan, crystalline region in copolymer was decreased. And also, as shown in Fig. 4, the characteristic peak of chitosan-g-PDMS copolymer around $2\theta = 9.8^\circ$ and 21° gradually decreased with increasing of PDMS grafting %. From these results,

it is found that the crystalline region of chitosan was gradually decreased by grafting amorphous PDMS onto chitosan.



Scheme 1. Preparation of chitosan-g-PDMS copolymer.

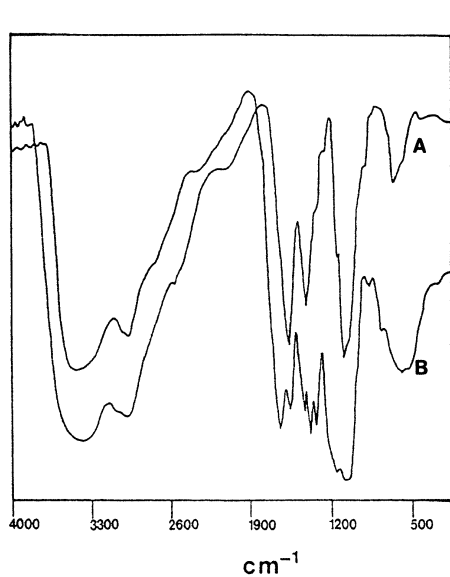


Fig. 1. FT-IR spectra of chitosan(A) and chitosan-g-PDMS copolymer(B).

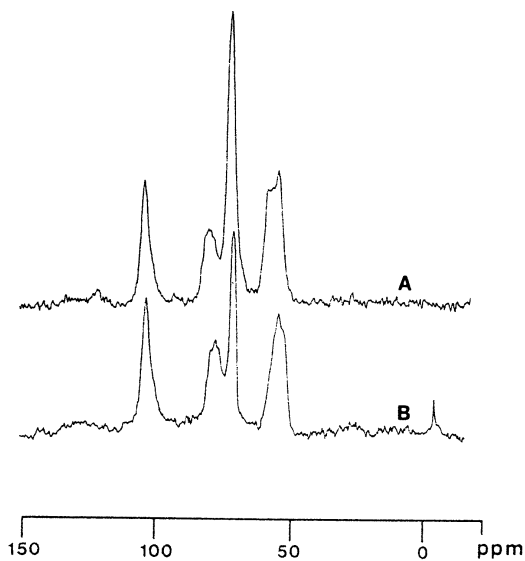


Fig. 2. ^{13}C NMR spectra of chitosan(A) and chitosan-g-PDMS copolymer(B).

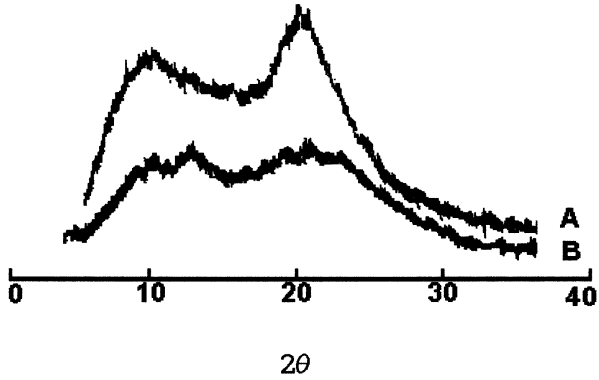


Fig. 3. X-ray diffraction patterns of chitosan(A) and chitosan-g-PDMS copolymer(Grafting % : 35)(B).

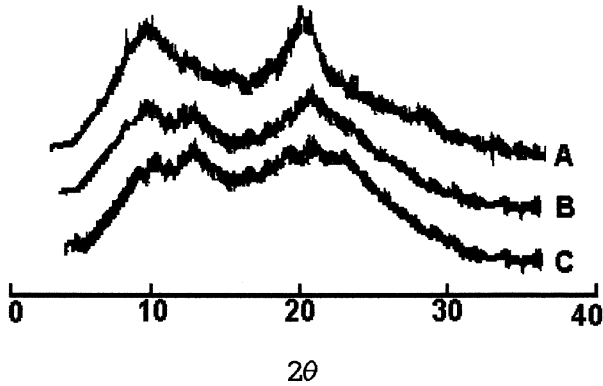


Fig. 4. X-ray diffraction patterns of chitosan-g-PDMS copolymer according to grafting %.
(A:10%, B:29%, C:35%)

Table 2. Tensile strength and elongation of chitosan and chitosan-g-PVA copolymer

	Grafting %	Tensile Strength (MPa)	Elongation(%)
Chitosan	-	14.7	15
Chitosan-g-PDMS Copolymer	10	14.8	18
	29	17.8	16
	35	16.5	14

Tensile Strength and Elongation

The tensile strength and elongation of chitosan-g-PDMS copolymer with PDMS grafting % were shown in Table 2. As shown in Table 2, while the tensile strength and elongation of chitosan were 14.7MPa and 15%, respectively, tensile strength and elongation of chitosan-g-PDMS copolymer were mostly constant about 14.8~17.8MPa and 14~18% regardless of PDMS grafting %.

Critical Surface Energy

Critical surface energy of chitosan and chitosan-g-PDMS copolymer membrane were obtained by the Zisman method(11). The summary of Zisman method is as follows. When polymer with low surface energy was wetted by liquid, the cosine of the contact angle plotted the surface tension of wetting liquid is straight line. The intercept of this line with $\cos \theta = 1$ axis is called the critical surface energy (γ_c). Typical Zisman plot of chitosan and chitosan-g-PDMS copolymer were shown in Fig. 5. Critical surface energy of chitosan and chitosan-g-PDMS copolymer membrane as determined from Fig. 5 were shown in Table 3. If critical surface energy of medical material is high, the protein or cell in blood is readily adsorbed to medical material when it is exposed to blood dose. Finally, thrombogenicity was occurred and then, it would be harmful to the human body.

In general, many theories about relation between critical surface energy and blood compatibility have been proposed so far. The optimum zone using biocompatible materials were reported by Baier, about 25~30 dyne/cm(12).

As shown in Table 3, while critical surface energy of chitosan was about 32 dyne/cm, that of chitosan-g-PDMS copolymer was decreased from 25 to 29 dyne/cm according to increasing of PDMS grafting % from 10 to 35%.

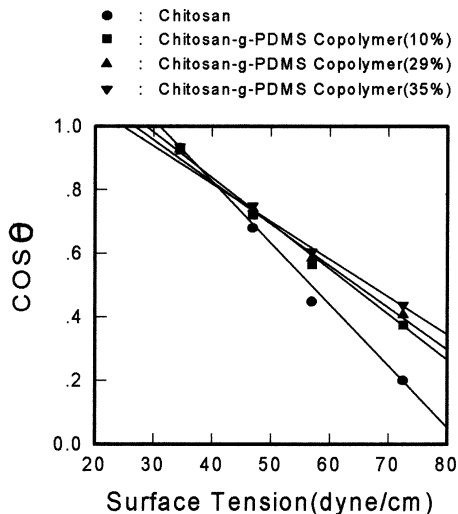


Fig. 5. Critical surface energy by Zisman plot.

Table 3. Critical surface energy of chitosan and chitosan-g-PDMS copolymer membranes

Sample	Grafting %	Critical surface energy (dyne/cm)
Chitosan	•	32
	10	29
Chitosan-g-PDMS copolymer	29	27
	35	25

Conclusion

Chitosan-g-PDMS copolymer was prepared by grafting PDMS prepolymer onto chitosan. By grafting PDMS on chitosan, the degree of crystallinity was a little decreased but tensile strength and elongation were mostly constant about 14.8-17.8MPa and 14-18%, respectively. While critical surface energy of chitosan was 32 dyne/cm, that of chitosan-g-PDMS copolymer was about 25-29 dyne/cm. From these results, chitosan-g-PDMS copolymer was supposed to be more excellent biocompatible material than chitosan.

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