Synthesis of PVA-graft-Chito-oligosaccharide

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INTRODUCTION

Poly(vinyl alcohol) (PVA) is generally prepared by the saponification of poly(vinyl ester)s, such as poly(vinyl acetate) (PVAc). Fibers and films of PVA are known to possess high tensile and impact strength, high tensile modulus, and excellent alkali, oil and solvent resistance[1]. Also, PVA has gained increasing attention in a variety of biomedical fields due to its bioinertness[2]. PVA hydrogels resemble organic tissues and have a high elastic modulus even though their water content is very high.

Chitosan is a β-(1-4)-2-amino-2-deoxy-D-glucose and manufactured by N-deacetylation of chitin. Since chitosan has a cationic nature due to amino groups, chitosan shows good antimicrobial activity[3] and is attracted to most tissues, including skin and bone. Chitosan has been shown useful in such biomedical applications as drug carrying, immobilization of biological molecules, membranes and wound-healing because of its excellent biocompatibilty[4]. However, the range of applications of chitosan fibers and films is limited by its poor mechanical properties (e.g brittleness and rigidity). Therefore, practically, it is interesting to prepare biomaterials having good biocompatibility and mechanical properties.

In this study, we synthesized a new biopolymer combining the various functions of chitosan as biopolymer and the good mechanical properties of PVA by grafting chito-oligosaccharide onto PVA. The graft polymer (PVA-graft-chito-oligosaccharide) (PGC) was characterized by ^{1}H-NMR, DSC, X-ray diffractometer and its mechanical properties and antimicrobial activity were investigated.

EXPERIMENTAL

Solution polymerization of vinyl acetate(VAc)

VAc was solution-polymerized at 40 ℃ using 2,2'-azobis(2,4-dimethylvaleronitrile) (ADMVN) as an initiator in tertiary butyl alcohol (TBA) as a solvent.

Saponification of PVAc

Determination of molecular weight and degree of saponification(DS) of PVA

Deacetylation of chitosan

Depolymerization of chitosan[5]

2 g of chitosan was dissolved in 100 ml of a 2% acetic acid aqueous solution and 0.125 (mol/mol of chitosan) of $NaNO_2$ was slowly added to the chitosan solution with stirring and the mixture was stirred at 25 ℃, for 3 hours.

Reaction of chito-oligosaccharide with NMA

1 g of depolymerized chitosan (chito-oligosaccharide, DP_n = 9) was dissolved in 10 ml of a 2% acetic acid aqueous solution and 0.5 (mol/mol of chitosan) NMA and a small amount of the polymerization-inhibitor (2,6-di-tert-butyl-4-methyl-phenol) were added to the chitosan solution.

Grafting of chito-oligosaccharide-NMA (CO-NMA) on PVA

PVA was dissolved in water at 95 ℃ for 6 hours and the PVA aqueous solution was slowly cooled down to room temperature. CO-NMA was dissolved in water at 20 ℃ for 1 hour. The CO-NMA aqueous solution and a NaOH aqueous solution were added to the PVA aqueous solution. The reaction mixture was stirred for different times and at different temperatures.

Preparation of PVA and PGC film

Measurements

^{1}H-NMR, X-ray diffractometer, differential scanning calorimeter, tensile tests, and antimicrobial activity.

RESULTS AND DISSCUSSION

PVA was prepared by the saponification of PVAc. DP_n and DS of the PVA were 3,300 and over 99%, respectively. The chitosan of which degree of deacetylation of 94.5% was produced by alkali treatment. In depolymerizing chitosan, sodium nitrite, which is able to perform depolymerization reaction on mild conditions, was used. DP_n of the depolymerized chitosan (chito-oligosaccharide) was about 9.

Chito-oligosaccharide was grafted onto PVA through introduction of the bifuctional compounds, NMA. The grafting reaction, as shown in Fig. 1, was achieved through two separate steps. The first one is the reaction of chito-oligosaccharide with NMA in acid medium. The NMA content bonded to chito-oligosaccharide (DP_n = 9) was about 1 per 6 glucose units. The second one is the reaction of CO-NMA with PVA in alkaline medium. PVA undergoes a Michael addition reaction with compounds containing activated double bonds in alkaline medium. A double bond in conjugation with a carbonyl group is susceptible to nucleophilic attack.

Thermal properties of the PGC were examined by DSC. Fig. 2 shows the DSC curves of PVA and PGCs. The melting endotherm of PVA is large and sharp in comparison with that of PGC. With the increase in chitosan content of PGC, the endothermic peak of PGC tends to broaden and shift to lower temperature, and the intensity of the peak is reduced. This result indicates that the crystallinity of PGC was lowered and the regularity of the crystalline region was destroyed due to the chito-oligosaccharide grafted on PVA. It was reported that the T_m of PVA was depressed and the crystallinity of PVA was diminished by blending of chitosan[6]. In comparison with PVA/chitosan blend, the depression of T_m and reduction of crystallinity of PGC are more remarkable even though chitosan content is much lower.

PVA is a flexible chain crystalline polymer. The flexible PVA backbone is favorable for close molecular packing and crystallization, but the bulky and rigid backbone of the chitosan is unfavorable for crystallization. The decrease of crystallinity of PGC is due to the stiff molecular chain of chito-oligosaccharide grafted on PVA, which has a significant effect on the overall mobility in PGC and retards the rate of crystal growth. That is, crystallization of PGC is hindered by the bulky and rigid backbone of chito-oligosaccharide grafted on PVA. Thus, the crystallinity and the regularity of crystalline region of PGC decreased with an increase of chitosan content.

PVA and PGC films were prepared in order to investigate mechanical properties. Fig. 4 shows tensile strengths and tensile moduli of the films. The tensile modulus of the PGC film was lower than that of PVA film due to low crystallinity and decrement of regularity of crystalline region. However, the tensile strength of PGC film was higher than that of PVA film and increased with an increase of chitosan content. The enhancement of tensile strength of PGC film may be due not only to intra- and inter-molecular interactions between PVA parts and chitosan parts in PGC but also to an improvement of plasticity in the films derived from lower crystallinity. The antimicrobial activity of PGC, as shown in Fig. 5, was exellent even though chitosan content is low.

CONCLUSIONS

Chito-oligosaccharide was grafted onto PVA through two separate reaction steps using NMA. The crystallinity of the graft polymer (PGC) was lowered and the regularity of the crystalline region was destroyed because the crystallization of PGC is hindered by the bulky and rigid backbone of the chito-oligosaccharide to be unfavorable for crystallization. The tensile modulus of the PGC film was lower than that of PVA film due to its low crystallinity. However, the tensile strength of the PGC film was higher than that of PVA film and increased with an increase of chitosan content. The PGC showed good antimicrobial activity.

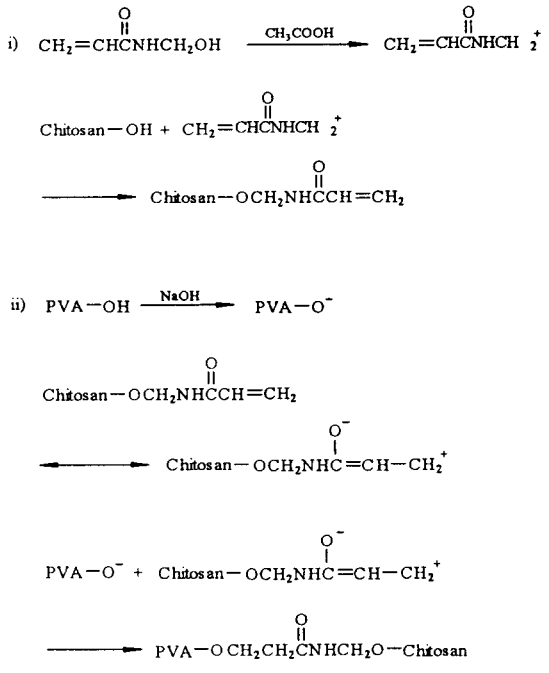

Fig. 1. Synthesis of PGC

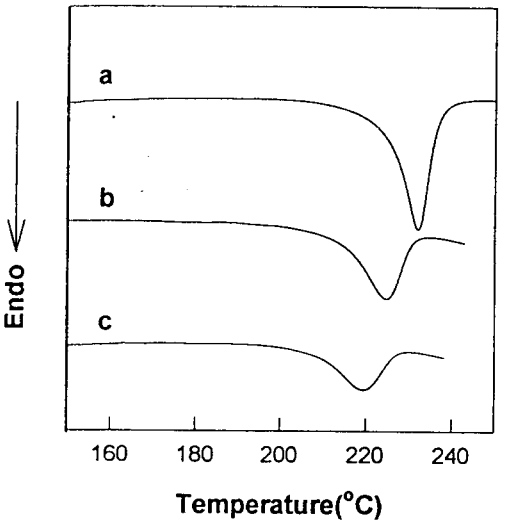

Fig. 2. DSC curves of PVA and PGCs with different chitosan contents.
a : PVA
b : chitosan content = 4.49%
c : chitosan content = 8.50%

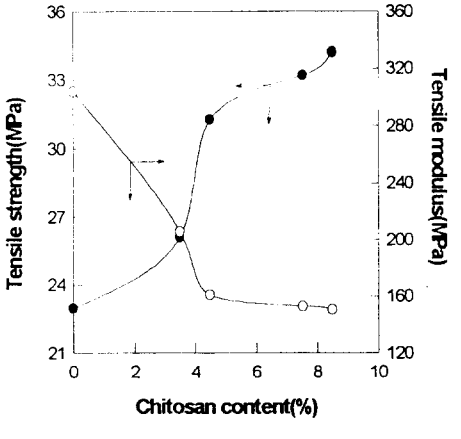

Fig. 3. Tensile strengths and moduli of PVA and PGC films with different chitosan contents.

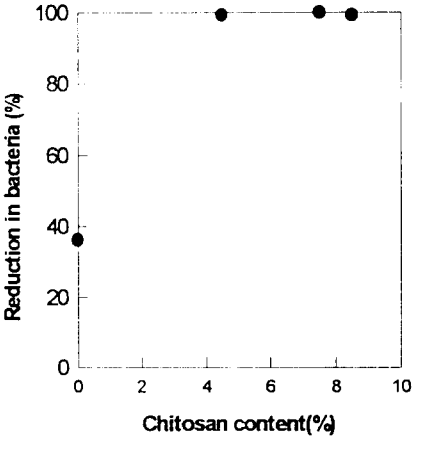

Fig. 4. Antimicrobial activity of PVA and PGCs with different chitosan contents.

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