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Preparation and Properties of Copolymer of Methacrylic Acid and Acrylamide onto Degraded Chitosan Initiated by HRP/H₂O₂/ACAC

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Keywords [Chitosan \(CS\)](#), [Graft Copolymerisation](#), [Horseradish Peroxidase](#), [Tanage](#)

Abstract The chitosan was degraded by hydrochloric acid and the effects of concentration of chitosan, amount of hydrochloric acid, reaction temperature and reaction time on the viscosity of chitosan were investigated. The results showed that the degraded chitosan with low viscosity could be prepared when chitosan (wt 6%) was dissolved in acetic acid solution and hydrochloric acid (wt 3%) at 90° C for 6 h to decrease the viscosity from 7.52 mPa·s to 2.48 mPa·s. Then, a graft copolymer was synthesized by copolymerization of degraded chitosan with methacrylic acid (MAA) and acrylamide (AAM) by using horseradish peroxidase (HRP)/H₂O₂/acetylacetone (ACAC) as initiator. The structures of original chitosan, degraded chitosan and the copolymer were characterized by FTIR. The copolymer was applied to the leather industry as an amphoteric retanning agent. The applied results showed that the retanned leather had the merits of good uniformity fullness softness, strong selecting filling properties, good dyeing ability and antimicrobial activity.

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First page example



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Keywords: chitosan, horseradish peroxidase, graft copolymerization, tannage

Abstract. The chitosan was degraded by hydrochloric acid and the effects of concentration of chitosan, amount of hydrochloric acid, reaction temperature and reaction time on the viscosity of chitosan were investigated. The results showed that the degraded chitosan with low viscosity could be prepared when chitosan (wt 6%) was dissolved in acetic acid solution and hydrochloric acid (wt 3%) at 90°C for 6 h to decrease the viscosity from 7.52 mPa·s to 2.48 mPa·s. Then, a graft copolymer was synthesized by copolymerization of degraded chitosan with methacrylic acid (MAA) and acrylamide (AAM) by using horseradish peroxidase (HRP)/H₂O₂/acetylacetone (ACAC) as initiator. The structures of original chitosan, degraded chitosan and the copolymer were characterized by FTIR. The copolymer was applied to the leather industry as an amphoteric retanning agent. The applied results showed that the retanned leather had the merits of good uniformity fullness softness, strong selecting filling properties, good dyeing ability and antimicrobial activity.

Introduction

Chitosan, a deacetylated product of chitin, is a high molecular weight heteropolysaccharide composed mainly of β -(1,4)-2-deoxy-2-amino-D-glucopyranose units and partially of β -(1,4)-2-deoxy-2-acetamido-D-glucopyranos. Owing to its characteristics such as antimicrobial activity, biocompatibility, non-toxicity and biodegradability, chitosan can be applied in many fields. However, chitosan can be only dissolved in a few dilute acid solutions, and this limits its applications. Therefore, many attempts have been made to degrade chitosan for the preparation of chitosan oligomers. Recently, H₂O₂ has been used in the degradation of chitosan because it is easily available and environmentally benign. However, the molecular weight of chitosan used in H₂O₂ treatment of chitosan is still high in the application of tanning agent. In contrast, hydrochloric acid could degrade chitosan and the resulting product could have low molecular weight. Therefore, the chitosan with low molecular weight has better solubility in water, which can be widely used in leather industry [1,2]. On the other hand, based on the unique molecular architectures with amino groups, sophisticated molecular designs became possible through controlled chemical modification of chitosan. Graft copolymerization, especially grafting of various vinyl monomers onto chitosan is one of the most effective and promising method, which can incorporate desirable functions, affording novel types of tailored hybrid materials composed of natural polysaccharides and synthetic polymers. The resulting graft copolymers have found new potential applications in many fields. So far, graft copolymerizations of chitosan with vinyl monomers have been explored by various methods, performed typically with AIBN, γ -ray, and traditional redox systems including Ce (IV), K₂S₂O₈, Fe²⁺-H₂O₂, etc. Among them, Ce (IV) is the most efficient initiator. However, the polymerization must be in the acid medium using ceric ion initiator and homopolymer percentage was also high, which lead to the generally low grafting efficiency. At present, some new modified methods such as enzyme catalysis polymerization are studying and using for modification in order to introduce more functional groups to chain of chitosan. Horseradish peroxidase (HRP) is a kind of enzyme and can catalyse polymerization of vinyl monomer. Compared with the above methods, graft copolymerization initiated by HRP, can take place in alkali medium. Furthermore, it has higher grafting efficiency than the other methods mentioned above [3-5].

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