Synthesis and Preliminary Studies on a β-Cyclodextrin-Coupled Chitosan as a Novel Adsorbent Matrix

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Received 1 September 1995; accepted 9 January 1997

ABSTRACT: A novel adsorbent matrix is synthesized by coupling β-cyclodextrin to chitosan using 1,6-hexamethylene diisocyanate. The matrix is found insoluble in organic as well as acidic or alkaline media. The results of our preliminary study on its interaction with cholesterol indicates that the modified chitosan could be used as a novel, reusable sorbent matrix. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 1051–1055, 1998

INTRODUCTION

Chitosan, a naturally occurring biopolymer, has been figured in several studies largely due to its extensive commercial potential.[1,2] The material has been used as a sorbent for the removal of toxic metal ions like mercury.[3] Recently, the potential of the material in medical applications, particularly in drug-delivery formulations and wound management, has been demonstrated.[4,5] β-Cyclodextrin (BCD), the oligomer of glucose, has been subjected to numerous studies, particularly in terms of its complexing ability with a variety of components.[6,7] The complexing ability of BCD has been well exploited in food and pharmaceutical industries.[8,9] The use of BCD as an adsorbent for the selective removal of components from aqueous fluids is, however, limited due to its inherent water solubility.

We presume that the product formed by anchoring BCD to chitosan would have improved its complexing ability and, additionally, the reaction converted BCD into an insoluble matrix. As far as we know, BCD-coupled chitosan and its use as sorbent has not been reported. This study reports the formation of BCD-coupled chitosan and the preliminary discussion of its usage as a reusable sorbent.

Journal of Applied Polymer Science, Vol. 69, 1051–1055 (1998)
 CCC 0021-8995/98/061051-05

EXPERIMENTAL

Chitosan (purified, viscocity grade 50) obtained from Central Institute of Fisheries and Technology, Cochin, India, was used as received. The viscosity-average molecular weight of the sample was found to be 3.05×10^5 and the extent of deactylation was 74%. β-Cyclodextrin (BCD), procured from Sigma Chemicals, U.S.A., was used after drying. 1,6-Hexamethylene diisocyanate and dibutyltin dilaurate were obtained from Fluka Chemicals AG. Cholesterol was also obtained from Sigma Chemicals, U.S.A. Other chemicals (chromatographic or analytical reagent grade) were obtained from Merck, Bombay, India.

The infrared spectra were recorded on a Perkin-Elmer Model 597 infrared spectrophotometer. A Hitachi Model S-2400 scanning electron microscope was used for obtaining the surface features of the materials. A thin layer of gold was coated prior to the observation. A Waters Associates liquid chromatographic system consisting of a Model 6000A solvent delivery pump, U6K injector, and a Model 486 tunable absorbance detector was employed for the chromatographic analysis. A μ-Bondapak C_{18} column (Waters Associates) in conjunction with methanol at a flow rate of 1 mL/min was used for the estimation of cholesterol. The column effluents were monitored at 206 nm and the chromatograms were obtained on an Omini-

scribe strip chart recorder (Texas Instruments, U.S.A.).

Synthesis of BCD-Coupled Chitosan

One gram chitosan powder was placed in 15 mL dimethyl acetamide. An excess of hexamethylene diisocyanate was added to this suspension. The mixture was stirred magnetically at a moderate temperature (60°C) after adding 0.01% dibutyltin dilaurate. The stirring was continued for about 6 h. The chitosan flakes in the suspension were recovered by filtration. The component was washed twice with dimethylacetamide. At this stage, the component was subjected to infrared spectroscopic analysis.

The chitosan reacted with 1,6-hexamethylene diisocyanate was then suspended in about 5 mL dimethylacetamide and 4 g of BCD was added. Ten milliliters dimethylacetamide was then added to this and stirred to dissolve the BCD completely. The mixture was stirred at 60°C after adding 0.01% dibutyltin dilaurate. The stirring was continued for about 2 h. Thereafter, the mixture was cooled and filtered. The modified chitosan was washed several times with dimethylacetamide and dried.

Interaction of Modified Chitosan with Cholesterol

A 5% cholesterol solution was prepared by dissolving an appropriate amount of cholesterol in methanol. About 150 mg of the modified chitosan was placed in the cholesterol solution and kept for 30 min at 37°C. The amount of cholesterol adsorbed by the modified polymer was estimated by analyzing the cholesterol solution before and after mixing with the modified chitosan. A calibration plot for cholesterol was constructed between the concentration and the height of the peak at 206 nm. This plot was used for quantification.

RESULTS AND DISCUSSION

Recently, Muzzarelli et al. showed that although chitosan is insoluble in dimethylacetamide it can be further polymerized into a poly(urea–urethane)-type polymer by reacting chitosan suspended in dimethylacetamide with 1,6-hexamethylene diisocyanate.[10] Figure 1 illustrates the infrared spectrum of chitosan reacted with 1,6-hexamethylene diisocyanate (sample A). The spectrum of chitosan is shown in Figure 2. The sharp feature of the spectrum of sample A in comparison with the spectrum of chitosan is the peak centered around 2200 cm^{-1}, characteristic of the —NCO group on the polymer backbone. The reaction of diisocyanate with chitosan is further evidenced by considering the absorption bands at 1640 cm^{-1} (—NH—CO—) as well as 2860 cm^{-1} assigned to the —CH2— stretching mode.

Figure 3 shows the infrared spectrum of sample A further reacted with BCD. The 2200 cm^{-1} band of sample A (see Fig. 1) has completely disappeared, indicating the coupling of BCD to chitosan through the —NCO group. The infrared spectrum of BCD is depicted in Figure 4. The characteristic features of BCD are a strong —OH absorption band at 3500 cm^{-1} and a strong —C—O— band around 1020 cm^{-1}. The spectrum of modified chitosan (Fig. 2) has more resemblance to the spectrum of BCD (Fig. 4). The relative intensity of the 3500 cm^{-1} band of modified chitosan (Fig. 3) is much higher than is the intensity of 3500 cm^{-1} band of sample A (Fig. 1) or chitosan (Fig. 2). The increased intensity could be attributed to the presence of more —OH groups in modified chitosan that resulted by the coupling of BCD.

It is well known that chitosan dissolves in dilute acids. The modified polymer is found insoluble in acidic pH as well as in other common solvents like chlorinated solvents, alcohols, and dimethylacetamide, indicating the reaction.

The SEM micrographs of chitosan and modified chitosan are shown in Figure 5(a,b). The modification process of coupling BCD to chitosan could alter the structural integrity of chitosan. The reaction indeed changed its native conformation, which, in fact, is reflected in the insoluble nature of the modified material in acidic medium. The morphology of modified chitosan appears to be different from that of the chitosan due to the above-mentioned aspects.

Table I summarizes the extent of cholesterol removal by the chitosan–BCD polymer from the solution. Nearly 21% of the cholesterol has been removed from the solution. We found that the cholesterol adsorbed by the polymer can be removed by rinsing the polymer with an organic solvent like chloroform, indicating the feasibility of using the modified chitosan as a reusable sorbent.

The ability of BCD to form inclusion complexes with varied components including organics has

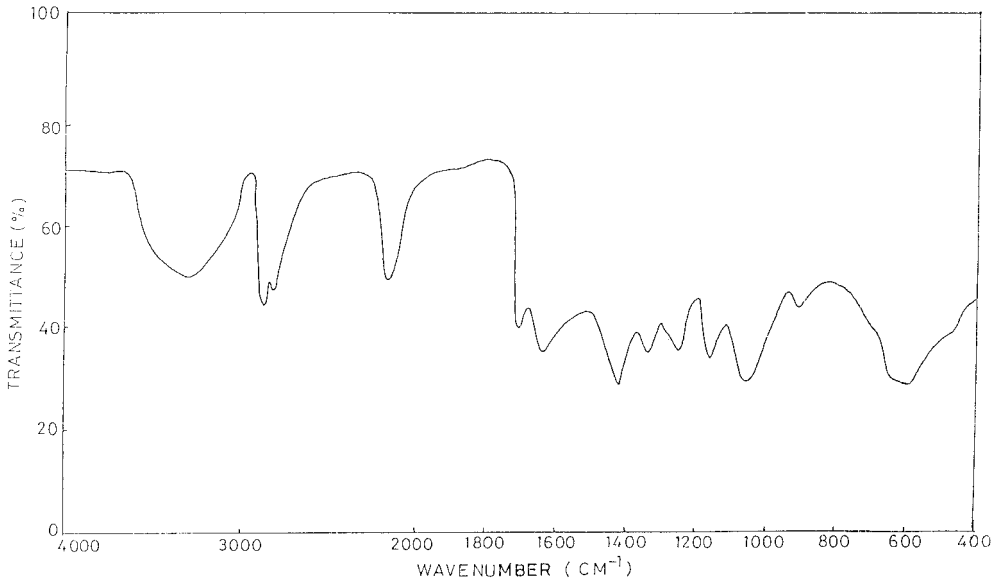


Figure 1 Infrared spectrum of chitosan reacted with 1,6-hexamethylene diisocyanate.

been extensively documented.[7,8] It has generally been accepted that the factors involved in the complex formation are the van der Waals interaction between the hydrophobic moiety of the guest molecules and the cyclodextrin cavity, hydrogen bonding between the polar functional groups molecules and the hydroxyl groups of cyclodextrin, release of high-energy water molecules from the cavity during the complex formation, etc. Since the mechanism of the inclusion complex formation is well defined, we did not made any attempt to study the interaction of cholesterol with the BCD-coupled chitosan. We presume that the factors governing the complex formation with BCD are

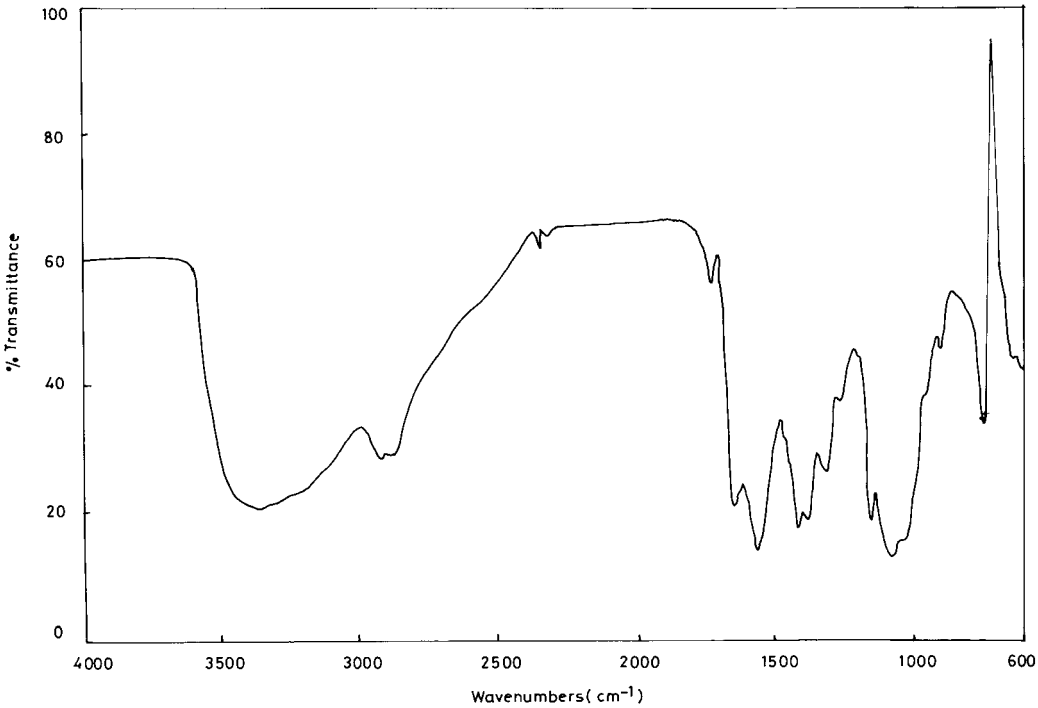


Figure 2 Infrared spectrum of chitosan.

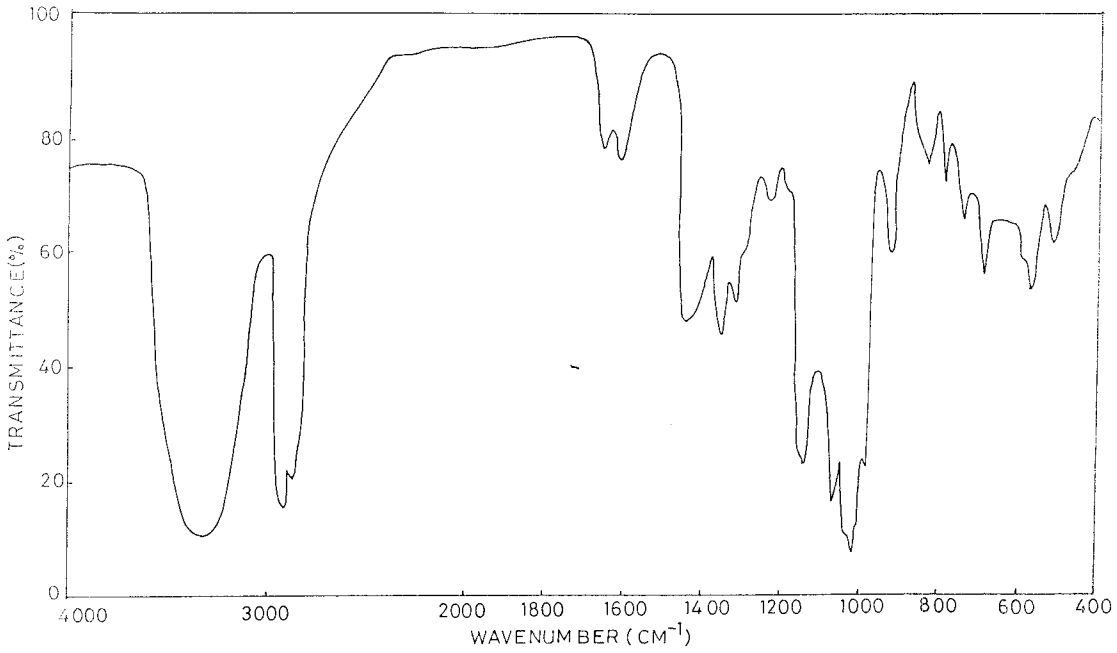


Figure 3 Infrared spectrum of BCD-coupled chitosan.

also responsible for the interaction of cholesterol with modified chitosan. BCD is known to form inclusion complexes with several organic compounds. However, its use as a complexing agent to selectively remove certain compounds from aqueous solutions is severally limited due to its inherent solubility in water. Converting BCD into an insoluble matrix without losing its complexing ability appears to be interesting. Insoluble cyclodextrins have been prepared as a packing for chro-

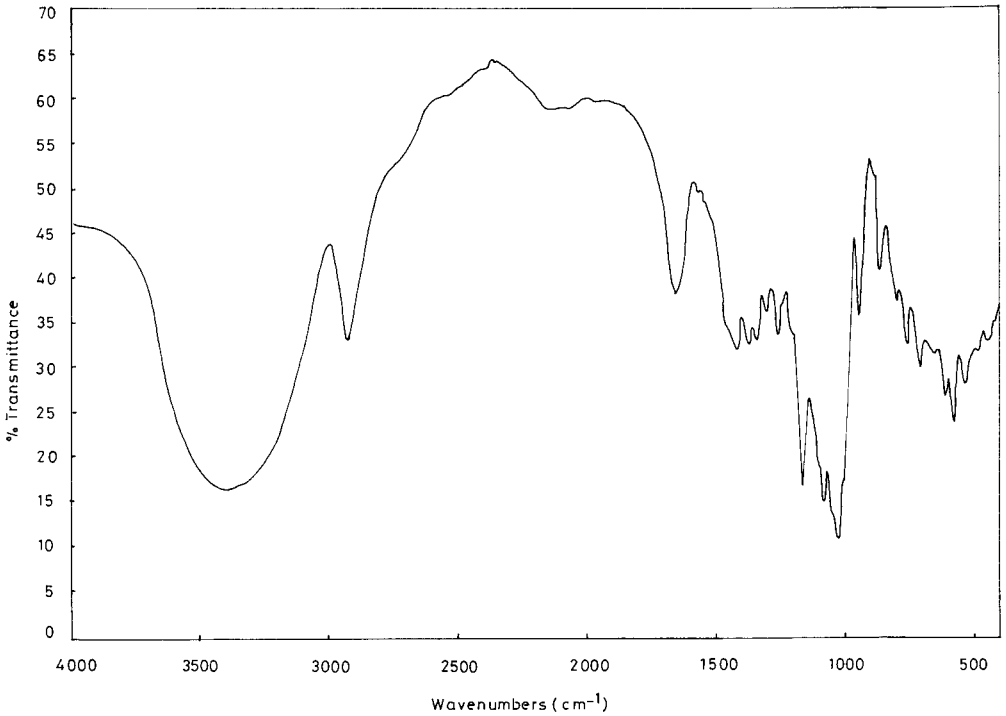
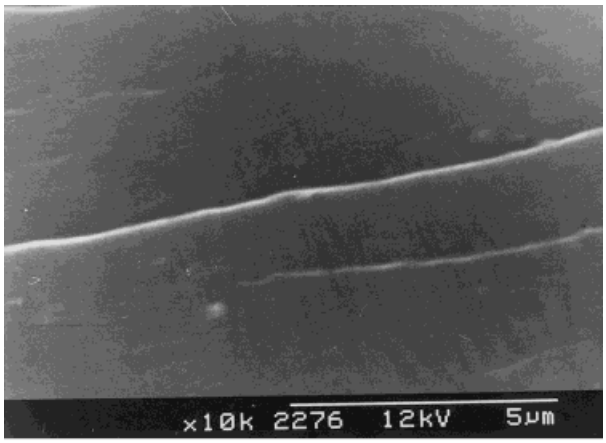
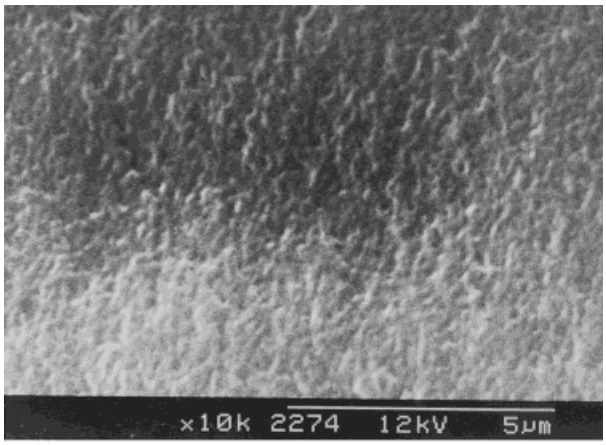


Figure 4 Infrared spectrum of BCD.

matographic applications.[11] The possibility of using crosslinked BCD as a sorbent has also been discussed.[12] However, the combination of BCD and chitosan, which are known for their ability to form complexes with a variety of other appropriate compounds, with a view to develop novel sorbent matrices has not been reported. The present study pointed out the feasibility of converting naturally occurring entities like chitosan into useful sorbents which may have far-reaching clinical applications.



(a)



(b)

Figure 5 (a) SEM micrograph of chitosan; (b) SEM micrograph of BCD-coupled chitosan.

Table I Interaction of Cholesterol with BCD-Coupled Chitosan

Material	Amount of Cholesterol Removed from the Solution (%)
Chitosan	Not detected
BCD-coupled chitosan	20.68 ± 0.02

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