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hossam maghraby

شبكة المعلومات الجامعية

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التوثيق الالكتروني والميكروفيلم

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صفحات بالرسالة
لم ترد بالأصل

MODIFICATION OF SOME NATURAL POLYMERS BY GRAFTING WITH VINYL MONOMERS

THESIS

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BY

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APPROVAL SHEET FOR SUBMISSION

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Contents

AIM OF THE WORK

Chitin is the second most abundant natural polymer found in nature after cellulose, about one hundred billion tons is naturally produced per year. But still chitin is an idle biomass (It isn't have been used as its production value). Chitin is intractable, and insoluble in most of the common organic and inorganic solvents. So, in order to make a use for this chitin, we modify it to the more soluble chitosan (after >50% hydrolysis).

Chitosan is a functional material due to its high nitrogen content (6.89%) and has excellent properties such as ***biocompatibility, biodegradability, non-toxicity, and adsorption properties***.

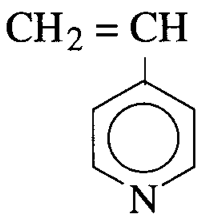
In this work, **Modification** of chitosan is carried out by grafting technique using three different vinyl monomers 4-vinylpyridine, vinyl acetate and *N*-acryloyl-*N'*-cyanoacetylhydrazine. The grafting process was investigated under homogeneous and heterogeneous conditions. Evidences of grafting and characterization of the grafted samples by elemental analysis, IR, NMR X-ray and Surface morphology (SEM) were studied. Also, the parameters of grafting were studied systematically.

Moreover, some applications for the grafted samples were studied namely:

- *Gelling tendency and Hydrophilicity.*
- *Swelling properties.*
- *Metal up-take.*
- *Dyeability.*
- *Thermal stability.*
- *Antifungal activity.*

SUMMARY

In the present work, chitosan is grafted with three different vinyl monomers namely 4-vinylpyridine, vinyl acetate or Acryloylcyano-acetohydrazide (ACAH).



4 -vinyl pyridine (VP)

$CH_2 = CH-OCOCH_3$

vinyl acetate (VAc)

$CH_2 = CH-CO\text{-}NH\text{-}NH\text{-}COCH_2CN$

Acryloylcyanoacetohydrazide (ACAH)

Polyvinyl pyridine could be grafted onto chitosan up to 130 % under homogeneous conditions (in 5 % acetic acid) and up to 96 % in the heterogeneous conditions (as suspension in water). The grafting efficiency in homogeneous conditions is higher than that in heterogeneous conditions for all the investigated parameters. It was possible to control the extent of grafting by varying the reaction parameters namely, monomer concentration, initiator concentration, temperature and time. The grafted samples are insoluble in common solvents, however are soluble in hot diluted acids, therefore one can exclude crosslinking reaction between the chains but an increased hydrogen bonding making the solubility more difficult. Dye uptake of the grafted samples was studied using acidic and basic dyes. It has been shown that the acid dye uptake is much higher than that for the basic dye which is due to the basic character of chitosan and the presence of vinyl

pyridine in the graft copolymer. The dye fastness is also much higher for the acidic than that of the basic dye and this is due to the chemisorption of the acidic dye onto the basic chitosan graft copolymer. SEM microscopy showed that grafting occurs probably on the surface, this could be a consequence of the high crystallinity of chitosan. The swelling behavior of chitosan and its grafted copolymers showed that water uptake increases with increasing the grafting content. Moreover, the swelling in acidic medium is higher than in basic medium and the swelling in the latter medium is higher than that in neutral medium. This property could be useful for further practical biomedical applications, particularly for drug release applications. Further increase in the swelling capacity was achieved upon quaternization of chitosan / polyvinyl pyridine copolymer with dimethyl sulfate in basic medium. Quaternization with three moles of dimethyl sulfate led to the preparation of soluble graft copolymer with a film forming ability, the antibacterial properties of this system shows that increasing G% leads to higher inhibition values for bacteria and fungi. The thermal stability of the graft copolymer did not show deterioration compared to the original Chitosan.

Polyvinyl acetate could be grafted onto chitosan up to 360 % under homogeneous conditions, and up to 180 % in heterogeneous conditions, thus the homogeneous conditions are more favorable. It was possible to control the extent of grafting by varying the reaction conditions namely, monomer concentration, initiator concentration, temperature, and time. The grafted samples swelled in ethanol-acetic acid mixture and in water better than the unmodified chitosan. Acid hydrolysis for polyvinyl acetate/chitosan copolymer led to the preparation of polyvinyl alcohol/chitosan copolymer with a better swelling character than the PVAc/chitosan copolymers. An enhancement of the dye uptake of the grafted copolymers was observed, especially for the acidic dyes due to the cationic character of chitosan. The thermal characteristic of the graft copolymer did not suffer from the grafting process; on the contrary there was a slight improvement of the thermal resistance.

Poly (ACAH) could be grafted onto chitosan up to 92 % under homogeneous conditions. Parameters of the grafting reaction namely, monomer concentration, initiator concentration, temperature, and time were studied systematically. The grafted samples were insoluble in aqueous acetic acid. The grafted samples had a better swelling character than the original chitosan. An enhancement of the dye uptake of the grafted copolymers was observed, especially for the acidic dyes due to the cationic character of chitosan. The thermal characteristic of the graft copolymer did not suffer from the grafting process; on the contrary there was a slight improvement of the thermal resistance.

Finally, the above grafted copolymers showed antimicrobial activity with three examined microorganisms

Rhizoctonia solani, Sclerotium rolfsii and macrconidia of *Fusarium solani* at 27°C

Chitosan, the grafted chitosan and the complexes of chitosan graft copolymers are strong anti-fungicidal agents and can be used as fungicidal agents to be used either directly in the soil or as in seed treatment. The seed treatment with fungicides is essential because a large number of disease causing fungi are carried on and/or in the seed and when the seed germinates, these fungi become active and cause either seed or seedling mortality or produce diseases at a later stage.

CHAPTER I

LITRATURE SURVEY

Chapter I
Introduction
Chitin and Chitosan

Occurrence of chitin: Chitin is a naturally abundant mucopolysaccharide, and the supporting material of crustaceans (such as crab, shrimp and cuttlefish), insects, etc., and is well known to consist of 2-acetamido-2-deoxy-β-D-glucose through a β (1-4) linkage as shown below. It is a highly insoluble material resembling cellulose in its solubility and low chemical reactivity. It may be regarded as cellulose with hydroxyl at position C-2 replaced by an acetamido group. Like cellulose, it functions naturally as a structural polysaccharide. It is a white, hard, inelastic, nitrogenous polysaccharide (the most abundant natural amino polysaccharide and second to cellulose in nature) and estimated to be produced annually almost as much as 10 billion tons [1-3].

Extraction of chitin:

In the production of chitin, calcium carbonate is first dissolved by stirring the shells in dilute hydrochloric acid at ambient temperature (demineralization). Proteins are then extracted from the decalcified shells by treating them with dilute aqueous sodium hydroxide (deproteinization); crude chitin is then obtained. Protein, calcium chloride, and carotenoid pigments obtained in the production process as side products may be used further.