

Synthesis of Chitosan grafted Vinyl Co-Polymeric Composites

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Abstract

Chitosan is a versatile biopolymer & to improve its performance, chemical modification has been carried out that lead to the formation of chitosan derivatives called grafted chitosan composites. In this work, three different chitosan grafted composites were prepared as sorbents for cationic dyes. Preparation was succeeded by a novel graft copolymerization method based on radical polymerization with vinyl monomer like N-isopropylacrylamide, methacrylic acid and acrylonitrile in order to address the large amount of swelling of the powdered form of the respective derivatives. The effect of initiator concentration, monomer concentration, time and temperature on %G and %GE were observed. The morphology of the grafted polymers was observed from the SEM picture. Evidence of grafting was obtained from comparison of SEM, XRD, and FTIR of the grafted and non-grafted chitosan as well as solubility characteristics of the composite products.

Keywords: chitosan; superabsorbent; N-isopropylacrylamide, methacrylic acid and acrylonitrile

1. Introduction

. Special attention has been given to polysaccharides such as chitosan, a natural amino polymer [4]. It is clear from the literature that the bio sorption of dyes using chitosan is one of the more frequently reported emerging methods for the removal of pollutants. Chitosan has been investigated by several researchers as a bio sorbent for the capture of dissolved dyes from aqueous solutions [5]. This natural polymer possesses several intrinsic characteristics that make it an effective bio sorbent for the removal of color. Its use as a bio sorbent is justified by two important advantages: firstly, its low cost compared to commercial activated carbon. Chitosan is derived by deacetylation of the naturally occurring biopolymer chitin which is the second most abundant polysaccharide in the world after cellulose [6-7].

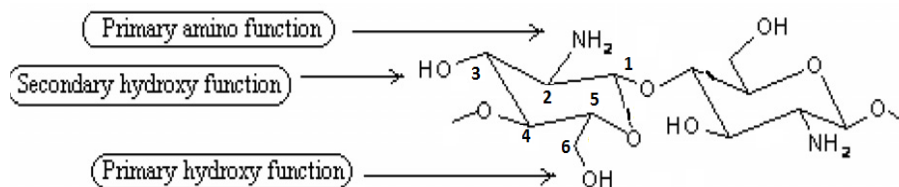
Chitosan is an amenable molecule and without disturbing degree of polymerization, one can chemically modify this acquiescent polymer, since it provides functional groups as primary amine (-NH₂ group of C₂) and

primary (-OH group of C₆) as well as a secondary (-OH group of C₃) hydroxyl groups in its monomers. Hence there are three main probable positions for chemical grafting. Detailed structure is shown in **Figure1**.

Chitosan based adsorbents have received a lot of attention for adsorption of dyes. Various modifications of this polysaccharide have been investigated to improve the adsorption properties as well as mechanical and physical characteristics of chitosan. In this Paper we discuss chitosan and its grafted derivatives for application in the removal of dyes from water. Modification of chitosan changes the original properties of this material so that it can be more suitable for adsorption of different types of dye. Many chitosan derivatives have been obtained through chemical and physical modifications of raw chitosan that include cross-linking, grafting and impregnation of the chitosan backbone [8-9]. A chemical modification opens ways to utilization of chitosan. The grafted composites have biocompatibility, biodegradability and non-carcinogenicity Keeping in view modified properties of chitosan grafted composite it was thought to study application of prepared composites. Almost all composite has excellent solvent absorptivity due to interstitial spaces and high lipophilicity. This property may be utilized for various technical application and drug delivery. The composite capture metal ions selectively and have affinity for few transition metals [10].

2. Material and Method-

Chitosan has acetamide groups at the C-2 positions instead of hydroxyl groups. So it is a nitrogen (amido/amino) containing polysaccharide, with repeating units of 2-acetamido amino-2-deoxy-(1,4)- β -D-glucopyranose (Fig.3). In addition to its unique polysaccharide architecture, the presence of a little amino groups(5-15%) in chitin ^[58] is highly advantageous for providing distinctive biological functions and for conducting modification reactions^[59]. Chitosan is the N-deacetylated derivative of chitin, though this N-deacetylation is almost never complete^[60]. Actually, the names chitin and chitosan correspond to a family of polymers varying in the acetyl content structural repeating units of chitin (DD= 5-15%) and its deacetylated product, chitosan (DD \geq 40%)..Therefore, the degree of acetylation (DA) determines whether the biopolymer is chitin or chitosan. Chitosan is the term used for the considerably deacetylated chitin that is soluble in dilute acetic acid (degree of deacetylation, DD 70%).^[61-63]



1. (-NH₂)Primary amino group of C₂
2. (-OH)Secondary hydroxy group of C₃
3. (-OH) Primary hydroxy group of C₆

Chitosan is an amenable molecule. Without disturbing Degree of Polymerization of chitosan, one can chemically modify this acquiescent polymer, since it provides functional groups as primary amine and primary as well as a secondary hydroxyl groups in its monomers. Hence there are three main probable positions for chemical grafting. Detailed structure as shown in fig.3 The important examples of modified chitosans that hold prominent places in research are listed.

3. Synthesis of N-isopropylacrylamide-graft-Chitosan Composite :

3.1 Experimental:

Materials :

Chitosan (from Sigma Aldrich Mol wt. 22742 Da and degree of deacetylation of 75%) NIPAAm (Wako Pure Chemical Co. Ltd., Osaka, Japan) was further purified by recrystallization. Switzerland), *N, N*-methylenebisacrylamide (NMBA; Sigma Chemical Co., St. Louis, MO) as a cross-linker, and *N,N,N,N*-tetramethylethylenediamine (TEMED; Fluka Chemical Co.) as an accelerator were used as received. Ammonium persulphate (APS) (Wako Pure Chemical Co. Ltd.) as an initiator was further purified by recrystallization.

3.1.1. Preparation of Poly Nisopropylacrylamide :

Nisopropylacrylamide was synthesized by radical polymerization in dioxane solution initiated with azoisobutyronitrile (AIBN). A 30 mg of AIBN, dissolved in a small amount of dioxane, was added to 25 mL of an oxygen-free solution of NIPAM (20 wt%) in dioxane. After 20 h polymerization at 70°C, the mixture was cooled and the solvent was evaporated within a fume hood. The residue was dissolved with tetrahydrofuran (THF) and

precipitated with n-hexane. The crude polymer was further purified by 3-fold precipitation with diethylether from a methanolic solution and then vacuum dried at 60°C^[6].

Preparation of Composite:

Purified Chitosan (1.5g) was suspended in 60 mL of aqueous PNIPAM (0.3 g) solution. To the suspension 15 mL of citric acid solution (1 mol/L) was added with stirring. The mixture was vigorously shaken for more than 30 min to make sure that chitosan was dissolved completely. The solution was thoroughly degassed via vacuum extraction. After degassing, Glutaraldehyde solution (2.8 wt %, 10 mL) was added slowly to the polymer solution with shaking. The mixture was agitated for another 5 min and then kept at room temperature without shaking.

3.1.2 Grafting parameters:

% Grafting efficiency (%Gr) are Grafting parameters of grafting copolymerization reaction.

$$\% \text{Gr} = \frac{W_3}{W_2} \times 100$$

Where, W₂, and W₃ are weight of the total product (i.e. copolymer and homopolymer), and pure graft copolymer (after solvent extraction), respectively.

3.2 Synthesis of Chitosan-graft-polymethylmethacrylate composite:

Materials:

Chitosan (from Sigma Aldrich Mol wt. 22742 Da and degree of deacetylation of 75%), Ceric Ammonium Nitrate and Methylmethacrylate (Merck, Germany) were used as such.

3.2.1. Synthesis of Grafted copolymerized Composite:

A 5% w/v solution of Chitosan was prepared in 5 % aqueous acetic acid. The reaction was carried out at 70° C in nitrogen atmosphere. A solution of 0.3M Ceric Ammonium Nitrate(CAN) in 30 ml of 1N nitric acid was added followed by a known amount of MMA drop by drop with continuous stirring. After a specified time, the reaction was stopped and the product was precipitated using sodium hydroxide solution with vigorous stirring. The

precipitate was washed with distilled water several times and filtered. The homopolymer was extracted from the grafted product using acetone as solvent in a soxhlet extractor until a constant weight was obtained^[7].

Grafting parameters:

% Grafting efficiency (%Gr) are Grafting parameters of grafting copolymerization reaction.

$$\% \text{Gr} = \frac{W_3}{W_2} \times 100$$

Where, W₂, and W₃ are weight of the total product (i.e., copolymer and homopolymer), and pure graft copolymer (after solvent extraction), respectively.

3.3 Synthesis of Chitosan-graft-Polyacrylonitrile:

3.3.1 Materials:

Chitosan (from Sigma Aldrich Mol wt. 22742 Da and (degree of deacetylation of 75%), Ceric ammonium nitrate (CAN) was purchased from Merck (Darmstadt, Germany) and was used without purification. It was used as freshly prepared solution in 1N HNO₃. Acrylonitrile (AN; Merck) was used after distillation to remove the inhibitor. All other chemicals were of analytical grade.

3.3.2 Synthesis of Grafted copolymerized Composite:

A CAN solution was prepared by dissolving 1.5 g ceric ammonium nitrate in 50 mL of 1N HNO₃. Generally, 1.0 g of this stock solution (0.10M) was used in reaction. The chitosan solution was prepared in a 50-mL two neck flask equipped with magnetic stirrer, gas inlet, and reflux condenser. Chitosan was dissolved in degassed distilled water containing 1 wt % of acetic acid. The total volume of the aqueous solution was 25 mL in all experiments. To control the reaction temperature, the flask was placed in a water bath preset at the desired temperature. AN (1. g) was added to the flask and the mixture was heated at a given temperature and stirred for 5 min. Then a given volume of the initiator solution was added to the mixture. The mixture was continuously stirred at the desired temperature until completion of the reaction (2 h). The product was then precipitated by neutralization using 1N NaOH solution. The product was thoroughly washed with methanol and dried at 50°C for

1 h. To separate the polyacrylonitrile (PAN) homopolymer, 0.50 g of the crude product was poured in 50 mL of dimethylformamide (DMF) and stirred gently at 30°C for 24 h. After centrifugation and decanting the supernatant (PAN in DMF), the chitosan- g-polyacrylonitrile was precipitated in methanol, thoroughly washed with methanol, and dried at 50°C to reach a constant weight [8].

3.4 Grafting parameters:

% Grafting efficiency (%Gr) are Grafting parameters of grafting copolymerization reaction.

$$\% \text{Gr} = \frac{W_3}{W_2} \times 100$$

Where, W₂, and W₃ are weight of the total product (i.e., copolymer and homopolymer), and pure graft copolymer (after solvent extraction), respectively.

3.5 Characterization of Composites

The structural parameter for chitosan grafted composites was further investigated by using FT-IR, DSC, XRD and SEM. The growing interest in chemical modification of chitosan to improve their solubility and applications requires structural analysis of chemically modified form of chitosan. Degree of deacetylation is one of the most important chemical parameters which affects physicochemical properties of chitosan. The degree of deacetylation of chitosan sample used for this work was 75%, which was confirmed by FTIR studies. The spectrum of pure chitosan was used for comparing composites prepared by grafting with various vinyl monomers. In DSC technique amount of heat required to increase temperature of sample and references were measured as a function of temperature. Both sample and reference were maintained at nearly same temperature throughout experiment. The glass transition temperature (T_g) of graft polymer was measured by DSC. The change in the chitosan structure after graft polymerization was investigated by X-ray diffraction studies. Chitosan showed crystalline peaks at around 2θ=20°, 30° and 35°. Characteristic reflection at 2θ =20° corresponds to Orthorhombic crystal structure of chitosan. The surface morphology and cross section morphology of chitosan and chitosan grafted composites were characterized by Scanning Electron Microscopy (SEM). The surface morphology of chitosan was studied by using SEM to measure porosity and partial size of chitosan. The structure of pure chitosan was smooth and uneven.

4. Swelling study of Composites

A composite sample (0.10 g) was put into a weighed tea bag and immersed in 100 ml distilled water and allowed to soak for 2 h at room temperature. The equilibrated swollen composite was allowed to drain by removing the tea bag from water and hanging until no drop drained (20 min). The bag was then weighed to determine the weight of the swollen composite. The absorbency (equilibrium swelling) was calculated using the following equation [14];

$$\text{Material Equilibrium Swelling Ratio} = \frac{\text{weight of dry composite material before swelling}}{\text{Weight of equilibrated composite}} \quad (1)$$

So, swelling ratio (absorbency) was calculated as grams of water per gram of resin (g/g). The accuracy of the measurements was $\pm 3\%$. Buffer solution of pH 3, 5, 9 and 11 was prepared by using respective buffer tablets. Dry weight of composite were measured and inserted into respective buffer solution and then weight of composite was measured after 2 hours at room tem and swelling ratio of following composite's solution are observed. The swelling study revealed that the composites were having variable swelling behavior in different pH solutions contributed to effect on swelling. This indicated that the composites phase transition was well affected pH environment which make it favorable for metal and dyes extraction properties **Figure 7** [15].

5. Thermodynamic Parameters

Spontaneity of a process can be determined by thermodynamic parameters such as enthalpy change (ΔH°), free energy change (ΔG°) and entropy change (ΔS°). A spontaneous process will show a decrease in ΔG° and ΔH° values with increasing temperature [18]. The temperatures used in the thermodynamic study were 300 and 310 K. The thermodynamic parameters were calculated based on the following equations:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (3)$$

6. Result and discussion

The objective of the present work was to modify chitosan with selected vinyl monomers through free radical graft copolymerization for the development of synthetic natural polymer hybrid materials with defined structures, compositions and tailor-made properties. An elaborate physico-chemical, thermo-analytical and morphological evaluation of the copolymers has been done using FTIR, DSC, XRD and mechanical property evaluation, swelling

studies, scanning electron microscopic studies etc. As Chitosan is second most abundant polysaccharide in on earth which give green route for metal extraction. The study throws some light on the prospects of synthetic protocols that can be adopted to realize chitosan-g-vinyl polymers with controlled extent of grafting and nature of graft. Their characterization was ensured by spectral, chemical, swelling studies, thermal studies, X-ray diffraction. As a general conclusion, the objective of the study to synthesize natural–synthetic hybrid materials with tailor-made properties has been achieved through the copolymerisation of chitosan with the selected vinyl monomers like acrylic acid , acrylamide .N-isopropylacrylamide, methacrylic acid and -polyacrylonitrile.

7. Conclusion

Chitosan based adsorbents have received a lot of attention for adsorption of dyes. Various modifications of this polysaccharide have been investigated to improve the adsorption properties as well as mechanical and physical characteristics of chitosan. Modification of chitosan changes the original properties of this material so that it can be more suitable for adsorption of different types of dye. In the present investigation chitosan grafted composites, namely, (Chitosan-g-poly (acrylic acid–co-acrylamide), Chitosan graft polyacrylamide, Chitosan graft polyacrylic acid, Chitosan–graft N-isopropylacryl amide, chitosan graft poly (methacrylic acid) and Chitosan-graft-Polyacrylonitrile were prepared by homogeneous grafting by free radical mechanisms. The composites showed higher swelling ratio at pH 5 and Chitosan-g-poly (acrylicacid-co-acrylamide) showed maximum swelling than other composites at acidic pH. Chitosan graft poly (methacrylic acid) composite showed higher sorption capacities than other all composites selectively for Methylene blue and Malachite green at acidic pH. Adsorption studies of Chitosan graft poly (methacrylic acid) for Methylene blue and Malachite green showed endothermic behavior. The previous findings indicated that a feasible solution to the drawback of the high degree of swelling of chitosan-g-poly (acrylicacid-co-acrylamide) derivatives was devised by other chitosan composites. But all those chitosan grafted composites can show metal extraction behavior which could be new horizon in field of green chemistry. In particular, Chitosan graft poly (methacrylic acid) has all of the sorption characteristics of effective application in large-scale implementations for cationic dye removal from aqueous solutions.

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