Modification of natural polysaccharides via grafting and cross-linking and their applications

ABSTRACT

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Deepak Kumar

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Co-Supervisor

Dr. Pramendra Kumar

Assistant Professor
Department of Applied Chemistry
M.J.P. Rohilkhand University
Bareilly, 243006

Supervisor

Dr. Jyoti Pandey

Assistant Professor
Department of Applied Chemistry
School for Physical Sciences
Babasaheb Bhimrao Ambedkar University
Vidya Vihar, Rae Bareli Road,
LUCKNOW-226 025

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ABSTRACT

Polysaccharides are carbohydrate polymers in which monosaccharide [$(CH_2O)_n$] units are covalently joined by *O*-glycosidic bond in either a branched or linear configuration. Polysaccharides serve as stores of energy, as in glycogen (branched polysaccharide of glucose), and as a structural component of bacterial cell walls, as cellulose (linear polysaccharide of glucose). Natural polysaccharides have the properties of artificial counterparts and in addition being essentially biodegradable, renewable, non-toxic, and comparatively cheap. Their characteristics at the structural level are associated with their hydrogen-bonding ability, side-group reactivity with either primary or secondary linkages.

Polysaccharides have been extensively used in various fields owing to their remarkable chemical, biological and physical properties. Herein, the applications of polysaccharides are introduced, specifically in wound healing, targeted delivery, bio-sensing, conducting polymer, catalysis and agents with antimicrobial, antiviral, anticancer capabilities, in water treatment and many industries such as textile, paper, rubber, plastic and pharmaceutical industries etc. In spite of the significant chemical and physical properties of polysaccharide, biodegradability and short shelf life, are posing problems in the commercialization of the utility of polysaccharide. The grafting of synthetic monomer/polymers onto natural polysaccharides is a popular, significant and convenient route to modify the polysaccharide. There are two main grafting methods: one is the conventional method and another is microwave irradiation method. In conventional grafting process, an inert atmosphere is required along in the long reaction time whereas there is no need of inert atmosphere in microwave irradiation process and it can happen in seconds. Indeed, increasing interest in clean and green environmentally friendly chemistry has motivated the use of microwaves in the polysaccharide grafting modification for various applications. Microwave irradiation significantly reduces the use of toxic solvents, as well as the reaction time for almost all the grafting reactions of interest here, ensuring high yields, product selectivity and clean product formations.

The whole research work is divided into five chapters. The first chapter comprises the general introduction of polysaccharides and graft/crosslink copolymer preparation methods including Microwave irradiation and conventional methods. The exhaustive literature review on the topic and the objective of the present work

has been discussed. In the chapter the general characteristics and applications of graft/crosslink copolymer and the various instrumentation techniques are discussed for identification of prepared graft/crosslink materials.

In the second chapter, a binary grafted copolymer of Psyllium mucilage (Psy) with acrylic acid (AA) and acrylonitrile (An) has been successfully synthesized under microwave conditions for *in vitro* drug release study. The grafting was confirmed by FTIR spectroscopy, XRD, SEM, EDX, TGA analytical techniques and the intrinsic viscosity studies. The swelling behavior of grafted material has been studied in solutions of different pH and time. We have also prepared Psy-g-Poly (AA-co-An) based beads with the anti-cancer drug [(2-Chloro-3-(4-hydroxyphenylamino) naphthalene-1, 4-dione)]. The drug release behavior of Psy-g-Poly (AA-co-An) based beads has been determined in aqueous medium at different pH, where highest drug release was observed at pH 1.6. The drug release kinetics was analyzed using different models. This study demonstrates that the release of drug depends on the composition of beads and pH of release medium. Kinetics of drug release from beads is best fitted by zero order and first order model.

In the third chapter, we report herein the synthesis of novel antibacterial graft [Chit-g-Poly (AA-co-An)] and crosslink [Chit-cl-Poly (AA-co-An)] copolymer, consisting of acrylic acid (AA), acrylonitrile (An) and chitosan by using the microwave route, where it has been found that grafting and crosslinking copolymers have excellent antimicrobial properties. Studies of antibacterial activities of graft and crosslink samples were carried out against gram-positive [*Staphylococcus aureus (S. aureus*)], gram-negative [*Escherichia coli (E. coli)* and *Pseudomonas aeroginosa (P. aeroginosa*)] bacteria. The graft [Chit-g-Poly (AA-co-An)] and crosslink [Chit-cl-Poly (AA-co-An)] copolymers were characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron micrography (SEM), thermogravimetric analysis (TGA), X-ray diffraction (XRD) techniques to study structural characteristics of synthesized chitosan derivatives. The graft [Chit-g-Poly (AA-co-A)] copolymer shows excellent antibacterial activities against *E. coli*, *P. aeroginosa* and *S. aureus* 30, 31 and 26 mm zone inhibition, respectively meanwhile [Chit-cl-Poly (AA-co-A)] shows antibacterial activities against *E. coli*, *P. aeroginosa* and *S-aureus* 26, 36 and 21 mm zone inhibition respectively.

In the fourth chapter, the antimicrobial binary grafted chitosan film [chit-g-Poly (An-co-Am)] was prepared by grafting of acrylonitrile and acrylamide on to

chitosan via microwave initiated graft copolymerization. The grafting of acrylonitrile and acrylamide onto chitosan backbone was confirmed by FTIR, XRD, SEM and TGA/DTA/DTG analytical techniques. The binary grafted chitosan film possessed efficient antimicrobial activity against three tested strains, i.e. *Escherichia coli*, *Staphylococcus aureus* and *Pseudomonas aeruginosa*. The prepared binary grafted chitosan film was tested for packaging of apple and guava to prevent microbial infection and extend their shelf life. The biodegradability study of binary grafted chitosan film was also done and all the results were positive.

In the fifth chapter, Psyllium-g-Poly-(acrylamide-co-acrylonitrile) has been synthesized from psyllium under the N_2 atmosphere, in presence of ceric ammonium nitrate and ascorbic acid couple (CAN/AA) as initiator for adsorption of mercuric ions from synthetic solution of $HgCl_2$. The synthesized samples were optimized by varying synthetic parameters *viz.* monomer concentration, reaction time, temperature, initiator concentration etc. to obtain the maximum yield of grafted product as well as maximum adsorption of ionic mercury. The optimized sample has been characterized through FTIR spectroscopy, SEM analysis, X-Ray diffraction and thermal studies (TGA/DTA/DTG). The mercury adsorption was studied onto the optimized sample and found maximum at temperature (30°C), dose (30 mg), pH (6), time (60 min) and initial concentration of mercury with 100 ppm. Equilibrium isotherm data were analyzed through Langmuir and Freundlich isotherms. Langmuir model was more fitted (R^2=0.9976) which indicated the monolayer sorption. The kinetics of sorption of mercury (II) were also analysed using the first order (R^2= 0.9971), second order (R^2= 0.9887), pseudo-first order (R^2= 0.9971), pseudo-second-order (R^2= 0.9481), intra-particle diffusion (R^2= 0.9958) and Elovich equation (R^2=0.9624). Second order rate kinetics has best linearly fitting, which follows the chemisorption mechanism.