

SYNTHESIS OF COPOLYMERS OF “PAN and drumstick mucilage”

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Abstract :

The grafting of acrylonitrile (AN) onto drumstick mucilage was carried out in aqueous medium by ceric ammonium nitrate(CAN) initiator and under a nitrogen gas atmosphere to produce (PAN) grafted mucilage. The maximum percentage of grafting (%G) was ascertained to be 72% at the following optimum condition 25 °C reaction temperature, 2 hour reaction period. The formation of grafted copolymer was confirmed by using IR and XRD analytical technique.

Key words : Moringa olifera Pods ,Hydroquinone , methyl alcohol,etc

1. INTRODUCTION

Copolymers are prepared by polymerizing a monomer in the presence of a fully formed polymer of another monomer.”Grafting results into retention of desirable properties of base polymer and incorporation of favorable properties of grafted polymer”.

Incorporation of specific functional groups onto polymers influences the physical, chemical, thermal, mechanical and rheological properties of materials. Copolymerization is done to enhance the properties and the utility of a system in various applications.

Graft copolymerization is considered for designing wide variety of new materials. Hybridization of natural polymers is great interest because of their application to biomedical and biodegradable materials. The improvement of natural polymers by grafting other monomers has been finding a large interest in the scientific world and industry due to combinational properties of both natural and synthetic polymers.

The incorporation of polyacrylates into biopolymers and, specifically, the grafting of acrylic monomers onto starch and starch like biopolymers result in combined properties such as biocompatibility, non-toxicity, and higher bioadhesion, which would confer attractive characteristics on the newly prepared composite materials.

Grafting of acrylic monomers onto biopolymers is usually performed to prepare materials with high absorbency for water. Incorporation of vinyl monomers onto the backbone of natural polysaccharides helps in improving some original properties of

polysaccharides and also allows the product copolymers to show novel functionality. Natural polymers, mainly polysaccharides, can be the most desirable flocculants for various waste water treatments, if their shelf life increased. Grafting has been utilized as an important technique for modifying the properties of a polymer.

This project incorporates the results of the synthesis of graft copolymers of polyacrylonitrile (PAN) on to drumstick mucilage.

2. Chemical Structure of MORINGA

The whole pods are reported contain, an isothiocyanate and thicarbamates and O – [2'-hydroxy 3'-(2'' heptenyloxy)] – propylundecanoate and O-ethyl-4-[α -1-rhamnosyloxy)-benzyl] carbamate, methyl –p- hydroxybenzoate and β -sistosterol. The pods designated as drumstick polysaccharides, the investigation of which revealed the presence of galactose, dextrose, xylose and sodium, potassium, magnesium, calcium salts of glucuronic acid, contrary to the definition of mucilage, the presence of dextrose was exception.

Modification of the seed gums and mucilages by grafting on to it water-soluble vinyl monomers has been reported to result into retention of desirable properties and incorporation of favorable properties. Grafting results into retention of desirable properties of base polymer and incorporation of favorable properties of grafted polymer. Synthetic polymers though are more efficient but their non biodegradability acting as a poison to the environment. One great advantage thus gained is the consequent reduced biodegradability because of drastic change in the original regular structure of natural polymers. It is also observed that grafting of shear degradable polymers on to the rigid polysaccharide back bone provides fairly shear stable systems.

3. Materials and methods :

Description of Mucilage



Moringa oleifera (Pods and tree)

Drumstick are a rich source of the polysaccharide galactomannan. They are also a source of saponins such as diosgenin, yamogenin, gitogenin, tigogenin, and neotigogens. Other bioactive constituents of moringa include mucilage, volatile oils, and alkaloids such as choline and trigonelline.

Description of Other Chemicals Used: Acrylonitrile, Acetone, ethanol isopropyl alcohol, nitric acid, hydroquinone, ceric ammonium nitrate, nitrogen gas.

Techniques and Equipments Used

Fourier Transform- Infrared (FT-IR) Spectroscopy, Model Make: Bruker, Vector 22 are useful for qualitative identification of molecular compounds.

X-Ray Diffraction (XRD) Model Make: ISO Debyflux – 2002 (Rich and Scifert)

Methods: Isolation and Purification, Synthesis of Graft Copolymers, Grafting Parameters.

Isolation and Purification of Natural Polysaccharides: Drumstick mucilage was extracted from pods of *Moringa oliefera*. The pods cut in to pieces and soaked into distilled water overnight. The mucilaginous extract was filtered through muslin cloth. It was precipitated from the extract by addition of EtOH. The crude mucilage was collected, washed with acetone and dried by keeping in oven at 40°C for 24 hours.

Purification: The mucilage was deproteinized by sodium complexing .5% (w/v) aqueous solution of crude mucilage was prepared by continuous stirring with water for 12h at 60°C and precipitating with saturated sodium hydroxide solution. The complex was separated by centrifugation and taken in 1M acetic acid stirred for 8h, centrifuged and precipitated with methanol. It was washed with 70, 80, 90 and 95% methanol. The precipitate was finally dried by keeping in oven at 40°C for 24 hours.

Synthesis of Graft Copolymer of *Moringa oliefera* with Acrylonitrile were prepared (Ds-g-PAN): 0.5 gram of mucilage was dissolved in distilled water (150mL) in an Erlenmeyer flask. The flask was then sealed with septum stopper and nitrogen gas was flushed into the solution through hypodermic needle for 20 minutes. Then the required amount of acrylonitrile was added into the solution through the stopper by hypodermic syringe with constant stirring using magnetic stirrer. The solution was stirred for 30 minutes while being bubbled with nitrogen. The required amount of ceric ion solution (in 1N HNO₃) was injected through the stopper by hypodermic syringe. The nitrogen flushing was continued for another 20 minutes; then the needles were

taken out, and the flask was further sealed with teflon tape. The reaction temperature was maintained at requisite temperature. The reaction mixture was stirred occasionally; the reaction was continued for required time and then terminated by injecting 0.5 mL of saturated aqueous hydroquinone solution.

The reaction product was precipitated in excess of isopropanol and filtered through sintered glass filter. The precipitate was again slurried in acetone followed by filtration and finally the precipitate was dried in vacuum oven at 40°C. The homopolymer was extracted from the grafted product using acetone as solvent in a soxhlet extractor until a constant weight was obtained.

Influence of Reaction Parameters

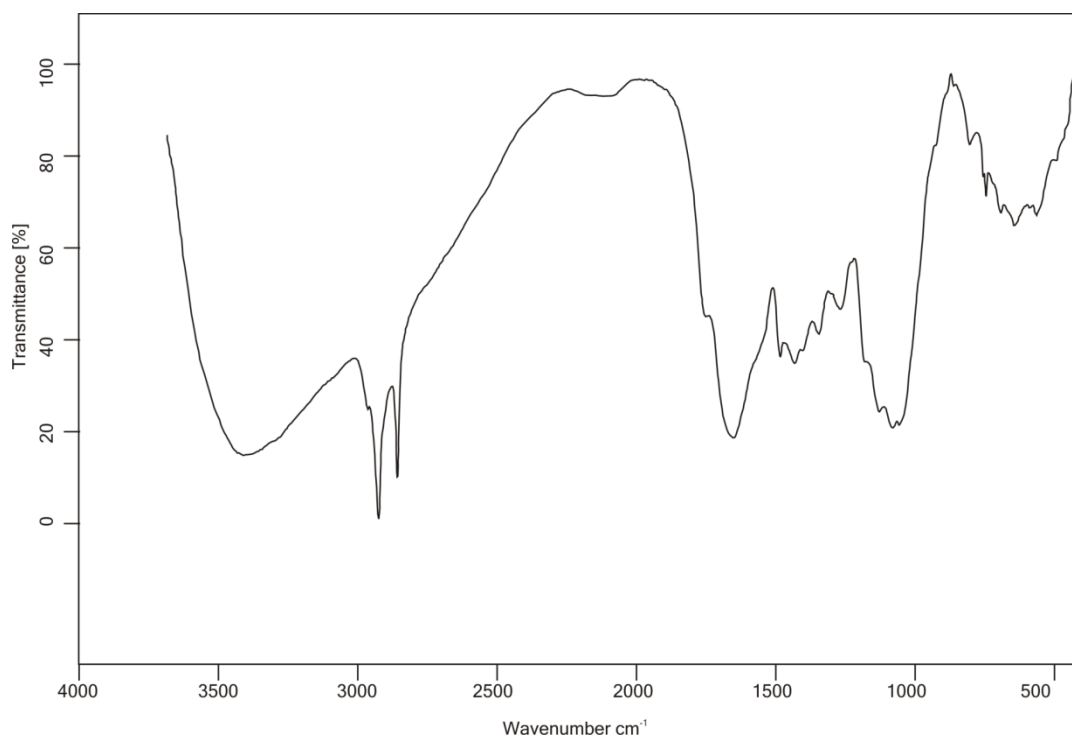
Effect of Initiator (CAN) Concentration: On increasing the concentration of initiator i.e., (CAN) from 0.5×10^{-3} moles to 1.5×10^{-3} moles, PG increased due to increase in the free radicals on polysaccharide chain. With further increase in (CAN) concentration, up to 2.50×10^{-3} moles, (PG) decreased. The falling of (PG) at higher (CAN) concentration is a well-known phenomenon and ascribed to the increasing participation of the ceric ion in the termination of the growing grafted chains.

Effect of Monomer Concentration: The best (PG) was obtained for 0.02 moles of (AN). The increase of (PG) till .02 moles was expected with increase in (PAN) concentration due to the availability of (PAN) monomer with respect to polysaccharide macroradicals, leading to larger possibility of grafting. When more than .02 moles of (AN) was taken in the reaction medium the formation of homopolymers i.e. (PAN) hinderd the rates of penetration of monomer molecules to the polysaccharide free radicals, resulting in decrease in (PG).

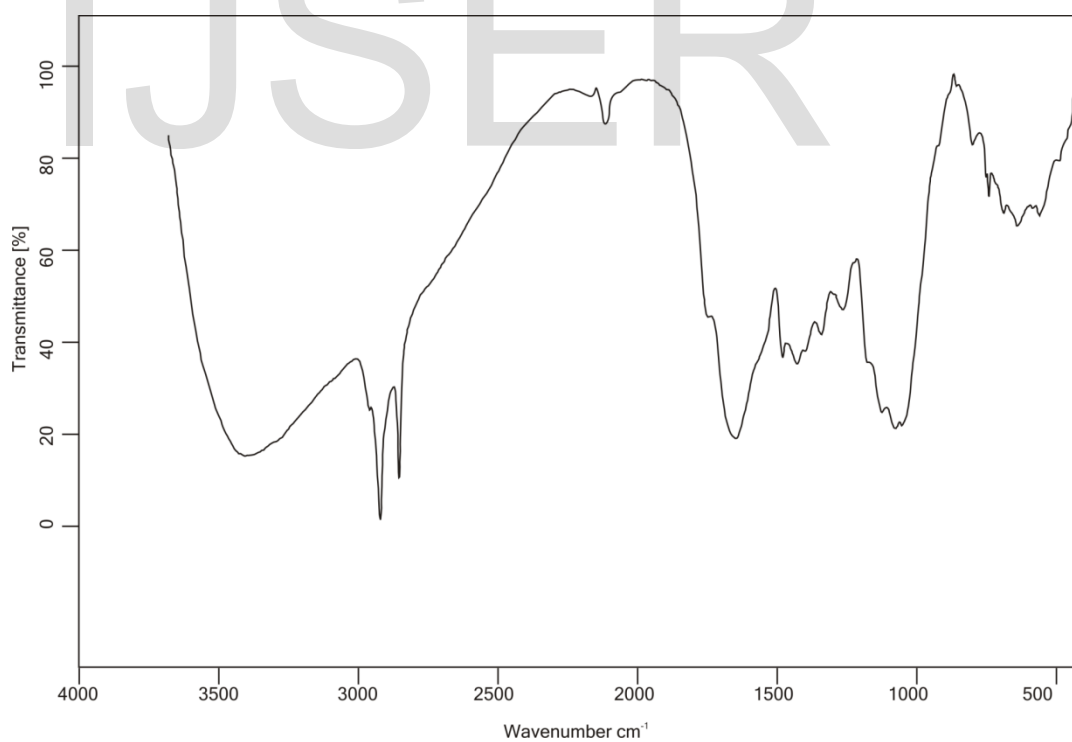
Effect of Time: The percentage grafting efficiency increased with increase in the reaction time. This agrees with the earlier observation with free radical initiated polymerization.

Effect of Reaction Temperature: Reaction temperature is an important reaction condition in the graft copolymerization. The effect of temperature on percentage grafting and grafting efficiency is shown in figure 4.4. (PG) and %GE both increased on varying the reaction temperature from 20 to 40° C and started decreasing on further increase in temperature upto 50°C. The decreased (PG) observed with increase in temperature at 50°C might be attributed to faster rate of termination and more homopolymerization at higher temperature.

Characterization of Graft Copolymers by IR: The FTIR spectra of pure mucilage and (Ds-g-PAN) (PG = 70%). The FTIR spectra of purified Moringa shows characteristic peaks of -OH between 3404-3150 cm⁻¹, ether linkage at 1455-1400 cm⁻¹, -CH stretching between 2918 -2850 cm⁻¹, -C-O stretching ether at 1059 cm⁻¹, -C=O stretching in aldehyde at 1632 cm⁻¹, thioamide stretching 1245.66 cm⁻¹ and -CH₃ at 2923 cm⁻¹. In the grafted sample of (Ds-g-PAN), the characteristic absorption at 2219 cm⁻¹ of indicates grafting of (PAN) with drumstick. The O-H stretching frequency in the grafted product is broader as compared to that in spectrum of drumstick mucilage. This is due to unequal hydrogen bonding in the grafted product again attributing to the fact that grafting has occurred.



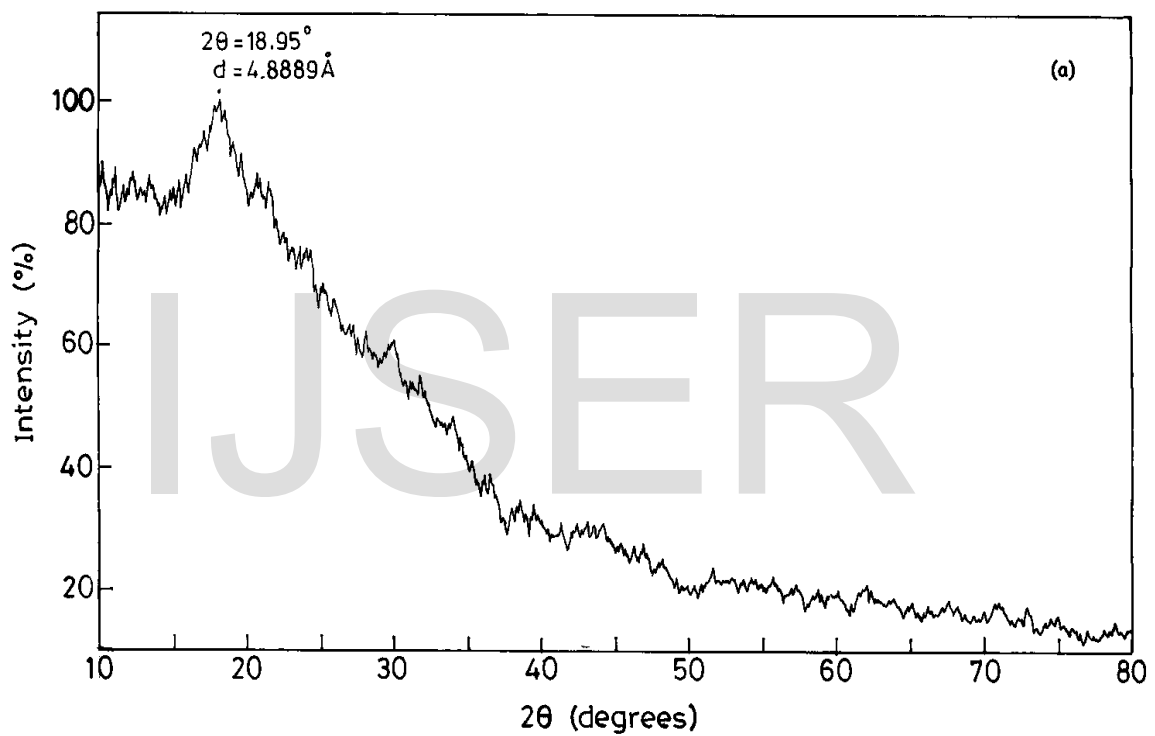
IR Spectrum of Drumstic mucilage



IR Spectrum of (Ds-g-PAN)

X-Ray Diffraction Analysis: XRD pattern of (Ds-g-PAN) supported grafting and revealed that pure mucilage is partially crystalline in nature, whereas after grafting, peaks for the crystalline areas appear near 2θ ; 19.89° , 23.24° and 57.99° , indicating the increased crystallinity on grafting due to grafted PAN chains on to the pure mucilage molecules .

XRD of drumstick mucilage



4. RESULTS AND DISCUSSION

The results of synthesis of polyacrylonitrile-grafted copolymers of drumstick mucilage. (Ds-g-PAN) was synthesized by grafting acrylonitrile (AN) onto purified drumstick mucilage by radical polymerization method in aqueous system using ceric ion/nitric acid redox initiator.

5. CONCLUSION

The following conclusions were drawn from present study “**Synthesis of Copolymers of (PAN) and Moringa olifera mucilage** “ The conclusions drawn proved that the objectives set before the study has been achieved to an appreciable extent. The variation in monomer concentration, initiator concentration, reaction time and temperature affected the percent grafting and grafting efficiency of the polysaccharides.

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