MODIFICATION OF SODIUM SALT OF PARTIALLY CARBOXYMETHYLATED TAMARIND KERNEL POWDER THROUGH GRAFTING WITH ACRYLONITRILE: SYNTHESIS, CHARACTERIZATION AND SWELLING BEHAVIOR


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Abstract  A graft copolymer of polyacrylonitrile (PAN) with sodium salt of partially carboxymethylated tamarind kernel powder (Na-PCMTKP, DS = 0.15) was synthesized by using ceric ammonium nitrate (CAN) as a redox initiator in an aqueous medium. The optimum reaction conditions for affording maximum percentage of grafting were established by successively varying reaction conditions such as concentrations of nitric acid, CAN, monomer (AN) as well as reaction time, temperature and amount of substrate. The influence of these reaction conditions on the grafting yields was discussed. The kinetic scheme of free radical graft copolymerization was proposed and the experimental results were found to agree very well with the proposed kinetic scheme. The graft copolymer (Na-PCMTKP-g-PAN, percentage of grafting $G = 413.76\%$ and percentage of grafting efficiency $GE = 96.48\%$) sample synthesized under the established optimized reaction conditions was hydrolyzed by 0.7 mol·L$^{-1}$ NaOH solution at 90–95 °C to yield the superabsorbent hydrogel, H-Na-PCMTKP-g-PAN. The swelling behavior of the hydrogel was studied by carrying out its absorbency measurements in low conductivity water, 0.15 mol·L$^{-1}$ salt (NaCl, CaCl$_2$ and AlCl$_3$) solutions and simulated urine (SU) solution at different timings. FTIR, TGA and SEM techniques were used to characterize the products.

Keywords: Sodium salt of partially carboxymethylated tamarind kernel powder; Acrylonitrile; Graft copolymerization; Superabsorbent hydrogels; Swelling behavior.

INTRODUCTION

The chemical modification of natural, renewable polymers by grafting has received considerable attention in recent years as it functionalizes the natural, biopolymers to their potential, imparting desirable properties onto them without affecting the architecture of the polymer backbone[1]. Among commonly used types of hydrogels, natural based and especially polysaccharides based superabsorbent hydrogels exhibit potential applications in many fields such as hygienic products, agriculture and horticulture, pharmaceutics and medical applications[2, 3]. Graft copolymerization of vinyl monomers onto polysaccharides followed by crosslinking of their chains is regarded as an efficient method for the synthesis of polysaccharide based superabsorbent hydrogels[4–10].

Tamarind kernel powder (TKP), a food grade natural polysaccharide and one of the cheapest gums, is derived from the seeds of Tamarindus indica Linn; a common and most important tree of India and South East Asia. The polysaccharide is composed of D-galactose, D-xylose and D-glucose in the molar ratio of 1:2:3[11]. It consists of a main chain of $\beta$-D-(1→4) linked glucopyranosyl units, and a side chain consisting of a single xylopyranosyl unit is attached to every second, third and fourth D-glucopyranosyl units through an $\alpha$-D-(1→6)

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linkage. One D-galactopyranosyl unit is attached to one of the xylopyranosyl units through a β-D-(1→2) linkage. TKP has potential commercial applications in textile, explosives, plywood and food industries. Even though TKP finds wide range of industrial applications, it also suffers from some drawbacks like biodegradability\(^{12}\), which limits its uses considerably. These drawbacks can be improved through the grafting of vinyl monomers onto it. However, due to the low solubility of TKP in cold water, poor solution clarity as well as the desire for products with modified or special properties, we have used carboxymethylated derivative of tamarind kernel powder i.e. sodium salt of partially carboxymethylated tamarind kernel powder (Na-PCMTKP) in the present work for its further modification via grafting. Recently, graft copolymerization of acrylamide\(^{13}\) as well as acrylonitrile\(^{14}\) onto TKP using CAN as a redox initiator has been reported. The synthesis of carboxymethyl tamarind-g-acrylamide and its application as a novel polymeric flocculant has also been reported\(^{15}\).

The comprehensive literature survey reveals that there is no published report regarding the modification of sodium salt of partially carboxymethylated tamarind kernel powder (Na-PCMTKP) by following the grafting technique. Recently, therefore, as a part of our research programme we have successfully carried out modification of Na-PCMTKP (DS = 0.15) by graft copolymerization with acrylonitrile (AN), methyl acrylate (MA), methacrylate (MMA) and butyl acrylate (BA) using ceric ammonium nitrate (CAN) as a redox initiator. However, in the present work we report the evaluation of the optimal reaction conditions for affording maximum percentage of grafting of AN onto Na-PCMTKP (DS = 0.15) and the saponification of the optimally synthesized graft copolymer (Na-PCMTKP-g-PAN, G = 413.76%) to form a superabsorbent hydrogel, H-Na-PCMTKP-g-PAN. The swelling behavior of the hydrogel has also been studied in low conductivity water as well as in different saline solutions.

EXPERIMENTAL

Materials
Sodium salt of partially carboxymethylated tamarind kernel powder (Na-PCMTKP, DS = 0.15) was kindly supplied by Encore Natural Pvt. Ltd., Naroda, Ahmedabad (Gujarat, India). AN (Samir Tech. Pvt. Ltd., Baroda, Gujarat, India) was distilled out at atmospheric pressure, and the middle fraction was collected and used. CAN of reagent grade and analar grade nitric acid (both Qualigens India Ltd.) were used as received. Fresh solutions of the initiator were used, prepared by dissolving the required amount of CAN in nitric acid. Sodium hydroxide, calcium chloride and magnesium sulphate (all Samir Tech. Pvt. Ltd., Baroda, Gujarat, India) were used as received. Sodium chloride and urea (both Maruti Chemicals Corporation, Anand, Gujarat, India) as well as aluminum chloride (Loba Chemie, Mumbai, India) of analytical reagent grade were used as received. All other reagents and solvents used in the present work were of reagent grade. Nitrogen gas was purified by passing through fresh pyrogallol solution. Low conductivity water was used for the preparation of solutions as well as for polymerization reactions.

Graft Copolymerization
A 500 mL three-necked flask equipped with mechanical stirrer, a reflux condenser and a glass inlet system was immersed in a constant temperature bath for grafting reactions. In a typical reaction, varying amount of (0.5 to 3 g) of Na-PCMTKP (DS = 0.15) was dissolved in low conductivity water (100 mL) with constant stirring and bubbling a slow stream of nitrogen for 1 h at desired temperature (15 °C to 55 °C). Freshly prepared 10 mL solution of CAN (2.5 × 10\(^{-3}\) mol-L\(^{-1}\) to 80 × 10\(^{-3}\) mol-L\(^{-1}\)) in nitric acid (nil to 1.0 mol-L\(^{-1}\)) was added and stirred for 20 min. Nitrogen gas was continuously passed through the reaction solution and freshly distilled AN (0.037–0.370 mol-L\(^{-1}\)) was added. The grafting reactions were carried out for varying time intervals (0.5–10 h). After completion of the reaction, the mixture was immediately poured into excess of methanol to coagulate the crude graft copolymer. The crude graft copolymer product was filtered, repeatedly washed with nitric acid as well as 95% methanol and finally washed with pure methanol. The crude graft copolymer thus obtained was dried under vacuum at 40 °C. The homopolymer (PAN) was separated from the crude graft copolymer by extraction with dimethyl formamide for 48 h. After complete removal of the homopolymer, the pure graft copolymer was dried at 40 °C under vacuum to a constant weight.