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Production of Absorbent Material by Modifying Unconventional Polysaccharides

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ABSTRACT:

Production of absorbent materials by grafting polysaccharides with ethylenically unsaturated monomers is a well established process as the products, thus produced become biodegradable. A novel absorbent hydrogel material based on tamarind kernel powder (TKP) has been prepared via graft copolymerization and crosslinking of acrylamide (AAm) and itaconic acid (IA) monomers using methylenebisacrylamide (MBA) as the crosslinking agent and potassium persulfate (KPS) as an initiator. Evidence of grafting was obtained by comparison of FTIR spectra of the initial substrates and the modified product. A new absorption band at 1608 cm^{-1} in the FT – IR spectrum confirmed the presence of carboxylate group which resulted due to itaconic acid in the product. Absorbency of the products increased fairly after treatment with alkali at higher temperature. The final products thus obtained showed enhanced absorbency in normal water.

Keywords: TKP, Acrylamide, Itaconic acid, Grafting.

INTRODUCTION:

Natural polymers of high molecular weight have drawn much attention because of their various practical applications. They are very often tailored by modifications to develop functional properties such as solubility and enhanced absorbency. An extensive research work has been carried out on synthesized graft copolymer of polyacrylamide and polysaccharides to improve their properties [1,2]. Polysaccharide based absorbent hydrogels (SHs) have emerged as promising substitutes; they are nontoxic biopolymer, abundant in nature, usually available at low cost, and intrinsically biodegradable and biocompatible [3].

Tamarind kernel polysaccharide (TKP) is derived from the seeds of the tree Tamarindus indicia. Tamarind is a commercially important tree that grows abundantly in the dry tracts of central and south Indian states and also in other south East Asian countries [4]. Tamarind seed is a byproduct of the tamarind pulp industries [5]. Tamarind kernel polysaccharide (TKP) is found to be extensively used as a sizing material in the textile industry as well as in the food industry. It can also be used as an adhesive in bookbinding, cardboard manufacture and plywood industry, and in sizing and weighting compositions in the leather industry[6]. The sizing properties of TKP are due to the presence of a polysaccharide (called jellose). The jellose is also much used in confectionery, especially in the United States, and some European countries. Use of white TKP in three food products, jelly, fortified bread and biscuit has also been also detailed [7]. It is a branched polysaccharide with a main chain of -d-(1,4)linked glucopyranosyl units and it can spread in water easily and change to mucilaginous liquid when heated up, as an acid and thermal resistant solution.

Highly swelling polymers, i.e., superabsorbent hydrogels, are hydrophilic, three-dimensional networks that can absorb water in amounts from 10% up to thousands of times their dry weight. They are widely used in various applications such as hygienic products, foods, cosmetics, and agriculture. This accounts for the increase in the worldwide production of superabsorbent polymers (SAPs) from 6000 tons in 1983 to 450000 tons in 1996. Nowadays, the worldwide production of SAPs is more than one million tons in year. Hence, the synthesis and characterization of superabsorbent hydrogels is the main goal of several research groups in the

World [8].The present paper discusses work on application of tamarind kernel polysaccharides as a base material for synthesis of super absorbent polymer as an unconventional natural source of carbohydrate polymer.

MATERIALS AND METHODS

A. MATERIALS:

Itaconic acid, acrylamide, potassium per sulfate, ethanol were supplied by S.D. Fine Chemical Pvt. Ltd. TKP was supplied by Satguru Industries, Mumbai and other chemicals used were of laboratory grade. Itaconic acid was partially neutralized with sodium hydroxide before using in reaction.

B. METHODS:

Grafting: The reaction was carried out in a round bottom flask equipped with overhead stirrer and a nitrogen inlet. To control the reaction temperature, the flask was placed in a thermostat water bath. Grafted TKP (AM-g-TKP) copolymer was prepared by using solution polymerization reaction by dissolving TKP and monomers (mixture of acrylamide and itaconic acid) of 10 gm in 1:1ratio in 100 ml of water in presence of a cross-linker (MBA) of the reaction mixture and redox initiating system potassium persulfate (KPS) and N,N,N’,N’- tetramethylethylenediamine (TMEDA) in required amount. Polymerization reaction was carried out at 30^0C for 120 min. Insoluble product so formed was washed with distilled water to remove the unreacted monomer, oligomers, cross-linking agent, the initiator, the soluble and extractable polymer and other impurities. Then the product was washed with ethanol to remove water and then dried in oven at 50^0C to reach a constant weight.

Water Absorbency: The dry sample of starch (0.2 g) was immersed in water for 24 h to reach absorption equilibrium. The fully swollen hydrogel was separated from the unabsorbed water with a 65-mesh screen and thereafter, the hydrogel was weighed. The relative water absorbency was calculated as follows.

$$\text{Water absorbency}\left(\frac{g}{g}\right) = \frac{M_2 - M_1}{M_1}$$

Wherein, M_1 and M_2 are weights of dry sample and of fully swollen hydrogel, respectively.

Saponification: Saponification was carried out by taking 1 g of dried sample in 100 ml of 0.1 N NaOH solution and keeping it at 80^0C for 90 min. It was then cooled to room temperature and washed with water till pH 7 was obtained. It was dried, ground and stored in air tight packets. Its swelling capacity was tested in the same way as described earlier.

FTIR Analysis: The IR spectra of original and various samples were recorded using FTIR spectrophotometer (Shimadzu 8400s, Japan) using ATR sampling technique by recording 45 scan in %T mode in the range of 4000–650cm^{-1}.

RESULTS AND DISCUSSION

Tamarind kernel polysaccharide has been utilized for producing absorbent materials as per the reaction system mentioned earlier. For the initial reaction, following parameters were chosen; TKP to monomer ratio 1:1, 99:1 of acrylamide to itaconic acid ratio, 2 h time, initiator concentration 1% on the weight of TKP and crosslinker MBA concentration 0.05% of the reaction mixture.

Evidence of grafting of monomers onto TKP backbone

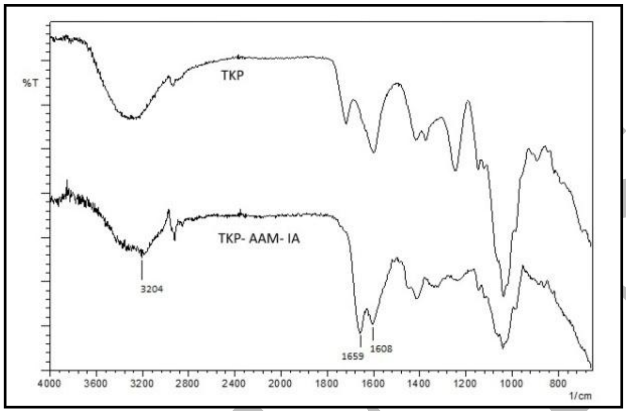

Figure 1 : FT-IR analysis of unmodified and modified TKP

It has been already said that the itaconic acid has been neutralized prior to utilizing it in the reaction. The incorporation of carboxylate groups in the product is visible in FT-IR analysis. Clearly visible band at 1608 cm^{-1} is proving the presence of carboxylate group in the product. In the FTIR graph, peak for N-H stretching vibration at 3204 cm^{-1} and 1659 cm^{-1} for N-H bending vibration confirming the introduction of $–NH_2$ group onto TKP backbone.

Table1: Effect of different parameters of reaction on water absorbency.

Sr. No.	TKP: Monomer (AAm & IA) Ratio(w/w)	Time (min)	AAm: IA	Initiator Concn. (%)	Conc. of Cross linker (%)	Polymer Yield (%)	Water Absorbency of AM-g-TKP in (g/g)	
							Unsaponified	Saponified
1.	1:1	120	100:0	1	0.05	50	33	68
2.	1:1	120	99:1	1	0.05	50	31	65
3.	1:1	120	98:2	1	0.05	48	32	61
4.	1:1	120	97:3	1	0.05	48	32	62
5.	1:1	120	96:4	1	0.05	37	28	52
6.	1:1	120	95:5	1	0.05	20	21	42
7.	1:0.5	120	97:3	1	0.05	20	18	35
8.	1:1	120	97:3	1	0.05	48	32	62
9.	1:1.5	120	97:3	1	0.05	59	38	92
10.	1:1.5	90	97:3	1	0.05	35	32	52
11.	1:1.5	120	97:3	1	0.05	59	38	92
12.	1:1.5	150	97:3	1	0.05	59	40	93
13.	1:1.5	120	97:3	0.5	0.05	53	32	71
14.	1:1.5	120	97:3	1	0.05	59	38	92
15.	1:1.5	120	97:3	1.5	0.05	58	36	86

16.	1:1.5	120	97:3	1	0.05	59	38	92
17.	1:1.5	120	97:3	1	0.1	70	48	141
18.	1:1.5	120	97:3	1	0.15	71	32	115

It has been seen from the experiments (Table 1) that with increase in itaconic acid concentration the absorbency of the product remains almost constant till 3%. However, beyond this concentration, the absorbency starts reducing and it is observed during experiments, beyond 10% of concentration of itaconic acid, the gel does not form. Therefore, for the rest of the reaction, 3% of total monomer concentration was taken. When the ratio of starch to monomer was varied, it was found that with increase in monomer concentration the absorbency increased significantly. This is expected as with increase in monomers, number of hydrophilic groups increase. However, in order to keep the product's biodegradable nature the ratio of TKP to monomer was not increased beyond 1:1.5. In the next set of experiments, reactions were carried out for 90 min, 120 min and 150 min separately. It has been seen that after 120 min of reaction, no further increase in polymer yield was seen and so was reflected in the absorbency of the product. Optimized concentration of initiator was found to be 1% on the weight of TKP. Increase in concentration of crosslinking agent in the reaction upto 0.1% (w/w) of total weight of monomers and TKP, increased the water absorbency. This may be attributed to the fact that addition of crosslinking agent increase the interpolymeric chain bonding and thus more water is retained within the three dimensional structure of polymer. This augmentation in absorbency may be also due to the fact that the cross linking agent make the homopolymers of the monomers also retain water along with the grafted biopolymers by crosslinking them together. Further increase in MBA concentration made the hydrogels quite brittle and thus although the polymer yield increased to some extent, the absorbency reduced significantly. Hence, optimized conditions of reaction were selected as TKP to monomer ratio 1:1.5, 97:3 of acrylamide: itaconic acid ratio, 2 h time, initiator concentration 1% on the weight of TKP and crosslinker MBA concentration 0.1% of the reaction mixture.

Table 2: Effects of various parameters of saponification

Sr. No.	Effect of NaOH Conc. (N)	Time (min)	Temp (^{0}C).	Water Absorbency of (g/g) Saponified Samples
A	0.1	60	80	106
B	0.1	80	80	141
C	0.1	120	80	92
A	0.1	80	60	112
B	0.1	80	80	141
C	0.1	80	100	96
A	0.05	80	80	92
B	0.10	80	80	141
C	0.15	80	80	78

It has been seen that after saponification absorbency increases. On saponification, –COOH groups convert into –COONa groups whereas –CONH$_2$ groups are converted into first –COOH groups and then –COONa groups. The amounts of these hydrophilic groups in turn govern the extent of water absorbency of the product. The optimum parameters for saponification were found to be 0.1 N NaOH solution, 80^{0}C and 80 min.

CONCLUSION

The aim of this research was to produce a biomaterial based absorbent material using TKP as a backbone and also utilizing itaconic acid for two reasons;

1. To introduce anionic groups on to product,
2. The biodegradability of itaconic acid which can make the product more ecofriendly.

The results show that TKP can be successfully utilized for producing biopolymer based absorbent product which can retain upto 141 g/g of normal water.

REFERENCES

1. D. A. DaSilva, R. C. M. De Paula, and J. P. A. Feitosa, "Graft Copolymerization of Acrylamide onto Cashew Gum". European Polymer Journal. 2007, 43: 2620–2629.
2. R. P. Singh, B. R. Nayak, D. R. Biswal, T. Tripathy, and K. Banik, "Biobased polymeric flocculants for industrial effluent treatment". Mater Res Innovations, 2003,7:331-340.
3. K. Park, W. S. W. Shalaby and H. Park, "Biodegradable hydrogels for drug delivery". Technomic Publishing. 1993, 35–66.
4. R. M. Marathe, U. S .Annapure, R. S. Singhal and P. R. Kulkarni, "Gelling behavior of polyose from tamarind kernel polysaccharide". Food Hydrocolloides 2002, 16: 423-426
5. S. Pal, G. Sen, S. Mishra, R. K. Dey and U. Jha, "Carboxymethyl tamarind: Synthesis, characterization and its application as novel drug-delivery agent" J. Appl. Polym. Sci. 2008, 110: 392-396
6. S. J. Patil, and B. S. Nadagouder, "Handbook of Herbs and Spices" Woodhead Publishing, 1997, 27-28.
7. S. Bhattacharya, S. Bal and R, K. Mukherjee, "Functional and nutritional properties of (Tamarindus indica) kernal protein". Food chemistry, 1994, 49: 1-9.
8. M. Sadeghi, "Synthesis of a biocopolymer Carrageenan-g-poly(AAm-co-IA)/ Montmorilonite superabsorbent Hydrogel composite". Brazilian Journal of Chemical Engineering 2012, 29: 295 – 305