

Synthesis of Superabsorbent from Tamarind Kernel Polysaccharide (TKP)

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Abstract - The graft copolymerization of acrylamide (AM) on to tamarind kernel polysaccharide (TKP) using ammonium per sulfate (APS) as an initiator, N,N,N',N'-Tetramethylethylenediamine (TEMED) as an activator and N, N'-Methylene bis-acrylamide (MBS) as a crosslinker in aqueous media has been carried out to obtain a super absorbent. The effects of different parameters such as time, tamarind kernel polysaccharide: monomer ratio, initiator concentration, concentration of activator and concentration of crosslinker on graft copolymerization were studied, and the optimized values were found to be 90 min, 1:1.5 (w/w), 1% (with respect to TKP), 0.5 ml and 0.5% respectively. The product so formed was saponified with 0.1 N NaOH, dried and finely powdered sample was characterized using FT-IR, TGA, and SEM. Product showed maximum water absorbency of 290 g/g, and salt solution absorbency (NaCl) 40 g/g qualifying itself to be called as superabsorbent.

Key Words: Tamarind kernel polysaccharide (TKP), Graft copolymerization, Saponification, Superabsorbent polymer

1. INTRODUCTION

Superabsorbents hydrogel are loosely cross-linked network of hydrophilic polymers that can absorb and retain aqueous fluids up to thousands times of their own weight [10]. They are used in many fields such as medical, agriculture, horticulture, etc as gel actuator as well as drug-delivery systems [1], [7]. They are also used in communication cables, industrial absorbents, artificial snow for winter sports, toys, and cosmetics, etc [15], [11].

Recently 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 [12] Polysaccharide based superabsorbent hydrogels (SHs) have emerged as promising substitutes, they are nontoxic biopolymer, abundant in nature, usually available at low cost, and intrinsically biodegradable and biocompatible [5].

Tamarind kernel polysaccharide [TKP] is derived from the seeds of the tree *Tamarindus indica*. Tamarind is a commercially important tree that grows abundantly in the dry tracts of central and south Indian state and also in other south East Asian countries [6]. Tamarind seed is a byproduct of the tamarind pulp industries [11]. Tamarind kernel powder (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 [9]. 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 [3], [2].

The seed contains xyloglucans, which are used extensively as food thickener and gelling agent [6]. Tamarinds kernel is a xyloglucans, which has β (1-4) linked D- glucose backbone that is partially substituted at the O-6 position of its glucopyranosyl residue with at O-2 position [11] TKP is water soluble, but its individual molecule tend not to fully hydrate and hence supramolecular aggregates remain even in very dilute solution [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.

2. MATERIAL AND METHOD

2.1 Material

TKP was supplied by Satguru Industries, Mumbai and all other chemicals used were of laboratory grade. Acrylamide (AM), cross-linker (MBA) potassium per sulfate, N, N, N', N'-tetramethylethylenediamine (TMEDA) and other chemicals were supplied by S.D.Fine Chemical Pvt. Ltd.

2.2 Method

2.2.1 Physical characterization of TKP: Swelling power

The estimation of swelling power was carried out using the method reported by Subramanian and coworkers [13]. TKP (0.6 g) was dissolved in 30 ml of distilled water. The mixture was then centrifuged (using CRU- 5000 centrifuge) at 5000 rpm for 15 min. The supernatant liquid was carefully removed and the swollen TKP sediment was weighed. Swelling power (g/g) was calculated as the ratio of the weight of the wet sediment to the initial weight of the dry TKP.

2.2.2 Preparation of acrylamide grafted TKP (AM-g-TKP)

Acrylamide grafted TKP (AM-g-TKP) copolymer was prepared by using solution polymerization reaction by dissolving TKP and acrylamide 10 gm (1:1.5) in approximately 100 ml of water in presence of a cross-linker (MBA) 0.5% of the reaction mixture and redox initiating system ammonium persulfate (APS) 1% on weight of TKP and N,N,N',N'- tetramethylethylenediamine (TMEDA) 0.25 ml. Polymerization reaction was carried out at 300C for 75 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 and dried in oven at 600C to reach a constant weight.

A series of experiments were carried out to optimize the reaction in terms of swelling capacity by varying different parameter such as time, TKP: acrylamide ratio, concentration of initiator and concentration of crosslinker.

2.2.3 Saponification

The graft copolymer product was saponified by adding 0.50 g of AM-g-TKP to 50 ml of NaOH solution in 100 ml flask which was immersed in thermostated water bath and was fitted with magnetic stirrer and reflux condenser. The NaOH concentrations of 0.05, 0.1, and 0.15 N, saponification temperatures (60 °C, to 100 °C) and saponification time (60 – 120 min) were studied. After completion of reaction, the mixture was allowed to cool to room temperature. It was then washed with distilled water to be free from excess of NaOH and dried in oven at 60 °C to reach a constant weight.

3. CHEMICAL CHARACTERIZATION

3.1. Fourier-transform infrared spectroscopy (FTIR)

The IR spectra of original and AM-g-TKP samples were recorded using FTIR spectrophotometer (Shimadzu 8400s,

Japan) using ATR sampling technique by recording 45 scans in % T mode in the range of 4000 to 600 cm⁻¹.

3.2. Thermogravimetric analysis (TGA)

The thermograms of TKP and grafted co-polymer of TKP with Acrylamide samples was recorded using Shimadzu 60 H DTG using aluminum pan between temperature range 30-500 °C and under inert atmosphere of N₂ at a flow rate of 50ml/min.

3.3. Scanning electron microscopy (SEM)

Analysis of the morphology of dried and grafted sample was carried out using scanning electron microscope (JEOL, Japan).

4. WATER ABSORBENCY MEASUREMENT

The dry sample was weighed (0.2 g) and 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 [4]:

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

where in, M₁ and M₂ are weights of dry sample and of fully swollen hydrogel, respectively.

4.1. Swelling variation with Ph

The procedures for these experiments are same as those described in "Water absorption measurement" section. The pH dependence of hydrogel swelling was evaluated by considering certain amounts of the hydrogel samples (0.5 ± 0.001 g) in solutions (200 ml) with different pH. The various solutions were adjusted to the desired pH value by addition of dilute HCl or NaOH.

5. RESULT AND DISCUSSION

Results of characterization of TKP indicate that the swelling power of the TKP was 7.39 g/g.

5.1. Evidence of graft co-polymerization on TKP

The FTIR spectrum of Acrylamide grafted on to tamarind kernel polysaccharides (AM-g-TKP) (Fig.1) clearly indicates the peak for N-H stretching vibration at 3367 cm⁻¹ which confirms the introduction of NH₂ group after grafting of TKP with acrylamide. The other peak at 1656 cm⁻¹ confirmed the presence of CO group which otherwise was missing in ungrafted sample of TKP.

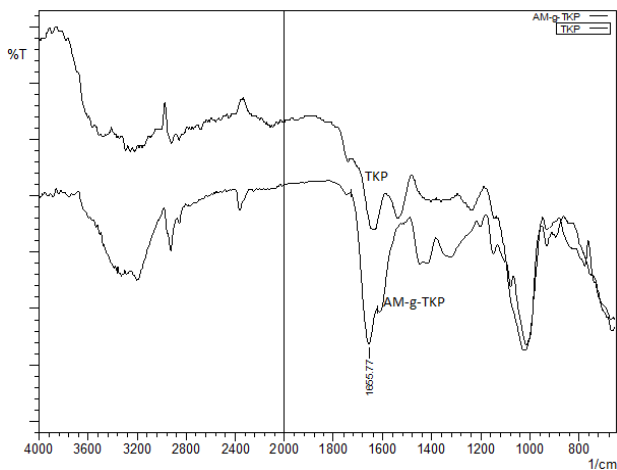


Fig -1: FTIR spectra of TKP and co-polymer with acrylamide (AM-g-TKP)

Fig. 2 shows the thermogram of TKP and grafted TKP. In the initial stages weight loss values of both the samples were 10.29 % and 3.90 % at 150 °C, respectively. Beyond this temperature, the drastic decomposition of the sample resulted in to significant weight loss which was 18.30 % for TKP and 17.02 % for AM-g-TKP copolymer at 300 °C. However, beyond 300 °C, the loss in weight was slowed down and finally at 500 °C, weight loss values observed were 78.44 % for TKP and 62.28 % for grafted TKP, respectively. This clearly indicates that the grafted TKP with AM showed relatively higher thermal stability as compared to that of ungrafted TKP. This could be attributed to the formation of crosslinked network as a result of graft co-polymerization of AM monomer on to a TKP backbone.

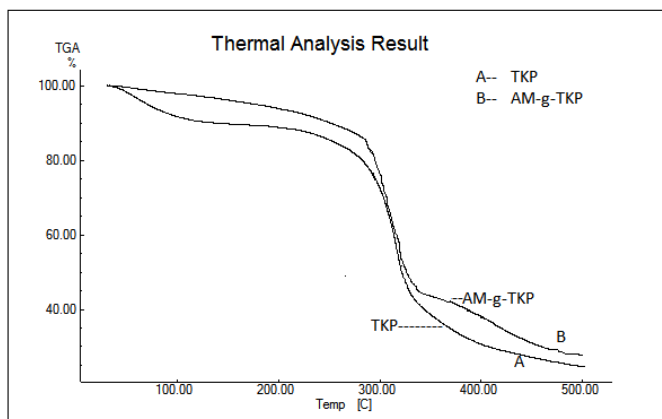


Fig. 2 Thermogravimetric analysis of TKP and AM-g- TKP

SEM micrographs (Figs. 3 a and b) of modified TKP i.e AM-g-TKP clearly show surface modification such as presence of cavity which is otherwise absent in TKP indicating influence of grafting of Acrylamide on to TKP.

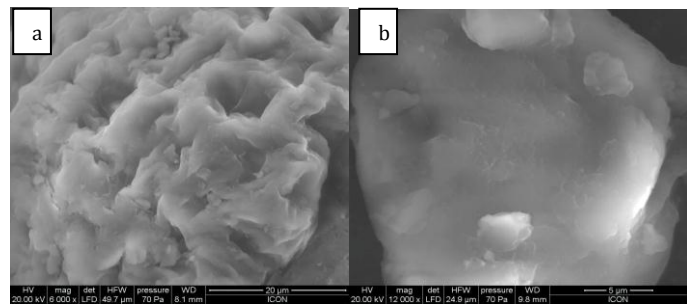


Fig -3 :SEM a) AM-g-TKP Copolymer, b) TKP polymer

Results in Table 1 show the effect of various parameters of reaction on water absorbency of the final product. The optimized conditions for highest absorbency were 75 min, initiator concentration 1% with respect to TKP and 0.25 ml TEMED. TKP: monomer mixture concentration was 1:1.5 (w/w), and crosslinker was 0.5%. Either side of these optimized conditions, product showed the decrease in water absorbency, which may be attributed to reduced extent of crosslinking due to not so favorable conditions for reactions.

Table -1: Effect of different parameters on graft co-polymerization yield and water absorbency of AM-g-TKP copolymer

Sr. No	TKP: AM Ratio (w/w)	Crosslinker Conc.(%)	Initiator Conc. (%)	Time (min)	Polymer Yield (%)	Water Absorbency of AM-g-TKP in (g/g)	
						Unsaponified	Saponified
1 Effect of Time							
A	1:1	0.5	1	60	60	50	180
B	1:1	0.5	1	75	90	80	220
C	1:1	0.5	1	90	90	85	290
D	1:1	0.5	1	120	90	85	290
2 Effect of Initiator Concentration							
A	1:1	0.5	0.5	90	65	60	185
B	1:1	0.5	1	90	90	85	290
C	1:1	0.5	1.5	90	85	70	210
3 Effect of Crosslinker							
A	1:1	0.25	1	90	70	50	180
B	1:1	0.5	1	90	90	85	290
C	1:1	1.0	1	90	90	60	210
4 Effect of TKP: AM							
A	1:0.5	0.5	1	90	48	50	180
B	1:1	0.5	1	90	75	70	210
C	1:1.5	0.5	1	90	90	85	290
D	1: 2	0.5	1	90	83	78	260

Saponified copolymer showed increased water absorbency [14]. In case of AM-g-TKP, the -CONH₂ groups are converted in to -COOH and -COONa groups during saponification. The effect of various parameters of saponification and on conversion of -CONH₂ to -COOH and -COONa is seen from the results in Table 2. The optimized parameters observed were temperature 80 °C, time 90 min and NaOH concentration 0.1 N corresponding to maximum absorbency. With increasing temperature, time and NaOH concentration

beyond optimized limits the product shows decreased water absorbency. This may be due to degradation of polymer network because of over hydrolysis. The amount and variety of hydrophilic groups such as $-\text{CONH}_2$, $-\text{COONa}$ and $-\text{COOH}$ will govern the absorbency of superabsorbents. The enhanced absorbency behavior may be attributed to the collaborative absorbency effect of $-\text{CONH}_2$, $-\text{COONa}$ and $-\text{COOH}$ groups which is superior to that of individual category of $-\text{CONH}_2$, $-\text{COONa}$ and $-\text{COOH}$ groups [14].

Table-2: Effect of various parameters on water absorbency of saponified AM-g-TKP Graft copolymer

Sr. No.	Effect of NaOH Conc. (N)	Time (min)	Temp (°C).	Water Absorbency of AM-g-TKP in (g/g)
				Saponified
1 Effect of Time				
A	0.1	60	80	210
B	0.1	80	80	290
C	0.1	120	80	180
2 Effect of Temp.				
A	0.1	80	60	220
B	0.1	80	80	290
C	0.1	80	100	190
3 Effect of NaOH Conc.				
A	0.05	80	80	180
B	0.10	80	80	290
C	0.15	80	80	150

5.2. Variation in swelling with pH

It is recognized that the swelling behavior of superabsorbent is significantly influenced by factors such as salt solution and pH. To investigate the sensitivity of the hydrogel to pH, the hydrogel was studied at various pH ranging from 1.0 to 10.0 (Fig. 4). No additional ions (through buffer solution) were added to the medium for setting the pH, in order to avoid possible effect of ionic strength on the absorption of a superabsorbent. Therefore, stock solution of NaOH (pH 13.0) and HCl (pH 1.0) were diluted with distilled water to reach desired basic and acidic pH, respectively. Fig. 5 indicates that the maximum water absorbency is observed in distilled water (at pH 7). Although it may also happen in very acidic or basic pH, but the ionic strength of the medium at extreme pH causes decrease in water absorption of entangled network. Furthermore, due to the moderate change of ionic strength of the medium at the pH close to 7, the water absorbency of hydrogel decreased more slowly relative to higher pH. Absorbency in salt solution (0.1 N NaCl) was also studied and it was found to be 40 g/g. It is to be noted that maximum osmotic pressure is developed when hydrogels are placed in water and hence the maximum swelling is achieved giving very high degree of water absorbency.

However, when the polymer is in salt solution (e.g., NaCl), extent of the development of osmotic pressure is much lower than that in case of water which is due to the external solution which contains Na^+ and Cl^- ion. Therefore extent of swelling is also drastically reduced [10].

In general the superabsorbents are expected to be absorbing the water more than 100 times (or >1000%) that of their own weight [11], [15]. Our product showed maximum water absorbency of 290 g/g, and salt (NaCl) solution absorbency 40 g/g qualifying itself to be called as superabsorbent.

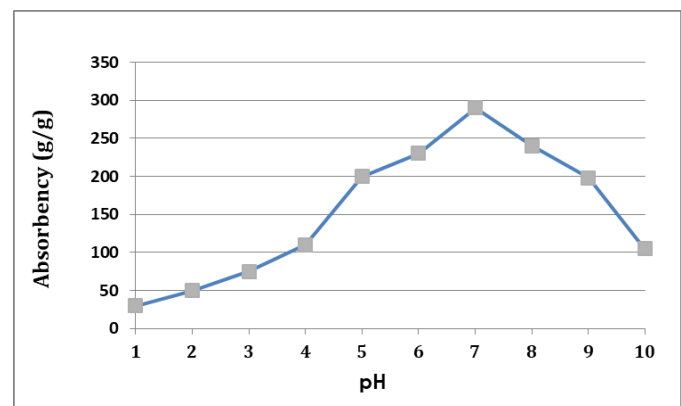


Fig -4: Effect of pH on absorbency of AM-g-TKP Copolymer

6. CONCLUSION

A new superabsorbent hydrogel is prepared by grafting AM on to a TKP using APS/TEMEDA as initiating system followed by saponification. This convenient preparative method conducted under normal atmospheric condition. Also this promotes the new biomaterial in textile, biomedical/pharmaceutical technology and moisture maintenance material in agriculture/horticulture as superabsorbent widely used in this fields

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