

## GRAFTING OF ACRYLONITRILE ONTO RICE STARCH-SUPER ABSORBENT POLYMER

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Grafting of acrylonitrile (AN) onto rice starch was accomplished using ceric ammonium nitrate (CAN) as catalyst. The effect of monomer, backbone, catalyst concentration on rate of conversion of monomer ( $R_p$ ), rate of graft copolymerization ( $R_g$ ), grafting efficiency (GE), grafting ratio (GR) is discussed. The absorption of water obtained from different sources by saponified product of graft copolymer was determined. The increment in absorbancy ( $\text{g H}_2\text{O g}^{-1}$ ) is due to the formation of carboxyl anions ( $-\text{COO}^-$ ) in the polymer network which develops strong electrostatic forces. The effect of aqueous sodium chloride on saponified product is also discussed.

**Key words:** Water absorbancy, Graftcopolymer, Grafting efficiency, Rice starch.

### Introduction

Starches find wide application in synthetic chemistry, survey of the literature provides so many references about the modification graft copolymer of acrylates are claimed to be used as sizing agents for hydrophobic yarns whilst poly (Oxyalkalene) ether grafted copolymers with carboxymethyl starch as thickeners, adhesives etc in the food, textile and paper industries (Brockway *et al* 1962; Radley 1976) Grafts of styrene with hydroxyethyl starch or amylose give thermoplastic resins of high impact strength whereas starch - acrylamide grafts are used as electrolyte-holding media in dry cells (Radley 1976). Nowadays graft copolymers of polyacrylic acid and potato starch is used in detergent composition to act as anti-deposition agents as well as in mud drilling liquids for oil wells. Beside these uses of graft copolymers grafts of acrylonitrile with different kinds of starches are introduced in the preparation of such products which retain water molecules 100-1000 times by weight (Fanta *et al* 1982; Gugliemelli and Swan San 1973. Saponification of the graft copolymer gives a product which can absorb 110-175g  $\text{H}_2\text{O g}^{-1}$ . It has a potential use in agriculture as well as in the preparation of baby diapers sanitary pads, portable urinals etc. This paper deals with grafting of acrylonitrile (AN) onto the backbone of rice starch and its saponification.

### Experimental

**Materials.** Acrylonitrile (BDH) was dried ( $\text{Na}_2\text{SO}_4$ ) distilled at  $76^\circ\text{C}$ . Reagent grade ceric ammonium nitrate (CAN), Analar grade butanol, laboratory grade DMF, Bacto Rice powder

(Difco Labs. USA), G. R. grade sodium chloride, potassium chloride and KOH (Merck) were used without further purification.

**Synthesis of graft copolymer (Starch-g-PAN).** Grafting of PAN onto the backbone of rice starch was carried out by using the method given elsewhere. Synthesis of (starch-g PAN) is a two step process. In the first step active centres are created onto the backbone of starch and in the second step, reaction with monomer in the presence of CAN is carried out. Required quantity of rice starch, water (100 ml) and butyl alcohol (10 ml) was refluxed for 5h. Then butyl alcohol with some quantity of water (total volume 50 ml) was distilled off. For grafting AN onto starch, the refluxed material was heated at  $50^\circ\text{C}$  for 6 h with known quantity of AN and CAN under nitrogen. The resulting product was washed with methanol and dried under vacuum. Ungrafted monomer was removed with DMF from the product samples. Extraction showed that a little amount of PAN remained ungrafted (See Tables).

**Saponification of graft copolymer.** To graft copolymer (2-4g), add (4- 10ml) water, (18-40 ml) ethyl alcohol and 4g KOH and heat at  $75^\circ\text{C}$  for 2h. The saponified product was washed with water and ethanol to remove unreacted KOH, dried and kept in vacuum desiccator.

Infrared spectrum of graft copolymer was used for identification of grafting of PAN onto starch by noting the appearance of characteristic absorption bands which were found absent in the spectrum of starch (Figs 1, 2).

Nitrogen estimation of product sample was also carried out to ensure the attachment of growing polymer chain of PAN onto the backbone of starch.

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Water absorbancy of saponified material was determined in deionized water, distilled water, tap water and aqueous dilute solutions of NaCl and KCl at room temperature.

## Results and Discussion

The results for the synthesis of rice starch-g - PAN are summarized in Table 1-3. The graft copolymers were identified by elemental analysis, solubility and I. R spectral studies. The analysis of prepared samples of PAN showed 26.25% nitrogen whereas 14 samples of the product contained 18.51% 25.33% nitrogen. This variation in percentage of nitrogen may be due to the branching of growing polymer chain of PAN onto the backbone of starch. Further the contents of product sample were different and not in order. This difference and decrease in percentage of nitrogen evidences the formation of graft copolymer. Polyacrylonitrile dissolves in cold/hot DMF whereas the product gets swollen in DMF with high uptake. This also supports the above statement. IR Spectra of starch and one of the product sample are shown in Figs 1-2. The strong absorption band at

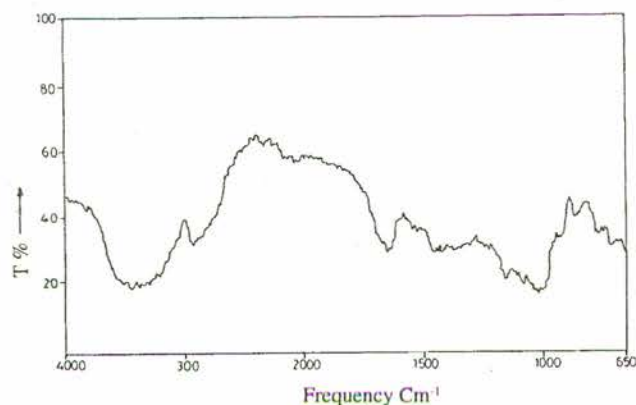


Fig 1. IR spectrum of rice starch (Bacto rice powder, Dif Co. Labs. USA).

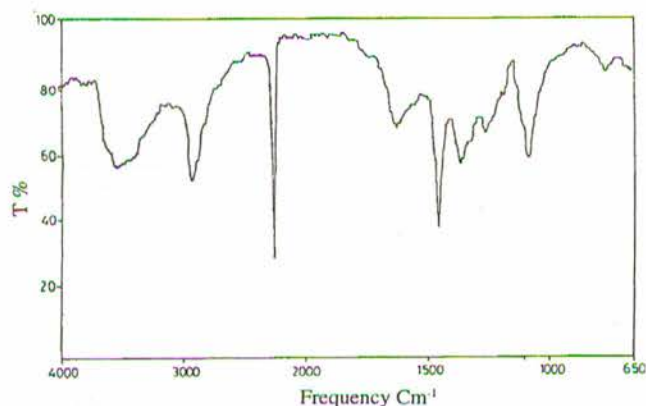


Fig 2. I R Spectrum of rice starch-g-AN.

2235  $\text{cm}^{-1}$  for nitrogen is quite distinct while the band at 3400  $\text{cm}^{-1}$  shows the appearance of -OH groups.

The total conversion of monomer, grafting efficiency (GE), grafting ratio (GR), rate of graft copolymerization (Rg), rate of polymerization of monomer (Rp) and rate of homopolymerization (Rh) are calculated by using the following simple relations.

$$\begin{aligned} \text{Total conversion \%} &= \frac{\text{Total weight of vinyl polymer formed}}{\text{Weight of vinyl monomer used}} \times 100 \\ \text{GE} &= \frac{\text{Weight of vinyl monomer in graft}}{\text{Total weight of vinyl polymer formed}} \times 100 \\ \text{GR} &= \frac{\text{Weight of vinyl polymer in graft}}{\text{Weight of backbone}} \times 100 \\ \text{Rg} &= \frac{\text{Grafted monomer } \mu \text{ in mole}}{\text{Time (in second)}} \\ \text{Rp} &= \frac{\text{Total conversion of monomer (in mole)}}{\text{Time (in second)}} \\ \text{Rh} &= \text{Rp} - \text{Rg} \end{aligned}$$

The influence of monomer concentration on the grafting of AN onto rice starch is given in Table 1. An increase in monomer concentration is found to increase Rg, Rp and GR whereas GE decreases at highest concentration of monomer (16.2g). The increase in these values might be due to the higher availability of the monomers molecules in the vicinity of starch macro-radicals. The more growing polymer chains of AN are available which combine onto the activated sites of starch resulting more grafting. The same thing happens in the grafting of AN onto maize starch. Grafting of acrylamide (Khan *et al* 1994), MMA (Khan and Khalil 1995) vinyl acetate (Khan *et al* 1999) on casein are other few examples in which the same effect was observed. The contents of nitrogen of product samples are on higher side. It might be due to the attachment of bigger growing polymer chains onto backbone. The rate of conversion of acrylonitrile is greater than the rate of grafting since at the early stage of reaction homopolymerisation of AN also takes place as shown in Table 1. The monomer propagation species are utilized in the homopolymerization of AN which directly influence the grafting efficiency (Expt. No.1).

Table 2 includes the results of the effect of concentration of backbone on GE, GR, N, Rg, Rp and Rh. These results indicate that only GR decreases with the concentration of starch whereas the value of Rg, Rp, GR, and N do not increase or decrease progressively. The decrease in grafting ratio might be due to the absolute decrease in the monomer to starch concentration ratio (monomer/backbone). The number of grafting sites on the backbone of starch is more than the number of growing polymer chains which utilizes the grafting sites of starch partially and some unbound starch propagating species are left behind which cause mutual termination

between starch propagating species (Mohan *et al* 1989). The increase in concentration of starch, produce large number of grafting sites along backbone resulting an increase of grafting efficiency. But at certain concentration of starch probably required quantity of active centres could not be formed or utilized for coupling the growing polymer chains of monomer. In addition, gel effect may cause swelling of starch which assists in the diffusion of monomer molecules to the growing polymer chains but active centres on the starch do not favour grafting reactions at this concentration (Khan

and Khalil 1995; Mohan *et al* 1989). It is because as the concentration of starch increases the values of above mentioned parameters get increased showing that swelling of starch definitely help in the diffusion of monomer to the growing polymer chains and active centres on the starch thereby favour grafting reactions. The values of GE (Expt.9, 10) supports this view.

Table 3 summarizes the observations obtained from the effect of catalyst concentration ( $Ce^{++}$  ions on grafting of AN on starch. These results show that with an increases in

**Table 1**

Effect of monomer concentration on graft copolymerization of acrylonitrile onto rice starch using ceric ammonium nitrate as catalyst.

S.No.	AN (g)	Total conversion of AN		Elemental analysis %N	Grafted AN (g)	GR %	GE %	Rate of polymerization $\times 10^6$ mole $sec^{-1}$		
		(g)	%					Rp	Rg	Rh
1.	5.67	3.5	61.7	18.51	3.4	944.4	97.1	3.0573	2.9700	0.0873
2.	8.10	3.7	45.7	23.00	3.6	1000.0	97.3	3.2320	3.1446	0.0874
3.	9.72	3.8	39.1	22.85	3.7	1027.8	97.4	3.3193	3.2320	0.0873
4.	12.15	4.1	33.7	21.70	4.0	1111.1	97.6	3.5814	3.4941	0.0873
5.	16.20	5.4	33.3	20.79	5.1	1416.7	94.4	4.7170	4.4549	0.2621

Starch, 0.36g; CAN, 0.25g; temp, 50-55°C; time, 6h.

**Table 2**

Effect of backbone concentration of graft copolymerization of acrylonitrile onto rice starch using ceric ammonium nitrate as catalyst.

S.No.	AN (g)	Total conversion of AN		Elemental analysis %N	Grafted AN (g)	GR %	GE %	Rate of polymerization $\times 10^6$ mole $sec^{-1}$		
		(g)	%					Rp	Rg	Rh
6	0.10	2.0	12.3	21.09	1.96	1960.0	98.0	1.7470	1.7121	0.0349
7.	0.20	4.0	24.7	23.13	3.92	1960.0	98.0	3.4941	3.4242	0.0699
8.	0.36	5.4	33.3	20.79	5.10	1416.6	94.4	4.7170	4.4549	0.0699
9.	0.40	3.8	23.4	24.57	3.72	930.0	97.9	3.3193	3.2495	0.0698
10.	0.5	4.0	24.7	20.26	3.90	780.0	97.5	3.4941	3.4067	0.0874

AN, 16.2g; CAN, 0.25g; temp, 50-55°C; time, 6h.

**Table 3**

Effect of catalyst on copolymerization of acrylonitrile onto rice starch using ceric ammonium nitrate as catalyst.

S.No.	AN (g)	Total conversion of AN		Elemental analysis %N	Grafted AN (g)	GR %	GE %	Rate of polymerization $\times 10^6$ mole $sec^{-1}$		
		(g)	%					Rp	Rg	Rh
11.	0.25	4.4	27.2	20.79	4.04	1122.2	91.8	3.8435	3.529	0.3145
12.	0.30	4.65	28.7	23.96	4.6	1277.8	98.9	4.0618	4.0182	0.0436
13.	0.35	4.70	29.0	24.26	4.65	1291.7	98.9	4.1055	4.06184	0.0437
14.	0.40	5.03	31.0	25.33	4.95	1375.0	98.4	4.3938	4.3239	0.0699

AN, 16.2g; starch, 0.36g; temp, 50-60°C; time, 6h.

**Table 4**  
Effect of different sources of water on absorbancy of saponified product (Rice starch-g-AN).

Sample No.	Deionized water g H <sub>2</sub> O g <sup>-1</sup>	Distilled water g H <sub>2</sub> O g <sup>-1</sup>	Tap water g H <sub>2</sub> O g <sup>-1</sup>
1.	157	147	92
2.	212	208	91
3.	222	200	116
4.	180	150	114
5.	190	150	74
6.	248	236	120
7.	168	152	112
8.	190	150	74
9.	185	155	96
10.	136	148	102
11.	146	136	91
12.	180	170	120
13.	154	93	84
14.	150	140	102

concentration of catalyst, the values of GR, GE, Rp, Rg, and N get increased. It is due to more available active species produced by different concentration of catalyst in the system.

Fourteen product samples of graft copolymers were saponified in the presence of alcoholic potassium hydroxide. The absorbancy of product samples were determined in deionized water, distilled water, tap water and aqueous solution of NaCl and KCl and shown in Table 4 and 5. Amongst 14 samples of graft copolymer, water absorbancy of saponified material in deionized water ranges 150-248 gH<sub>2</sub>O g<sup>-1</sup> whereas water absorbancy in distilled water and tap water ranges respectively as 93-236 and 84-120 gH<sub>2</sub>O g<sup>-1</sup>. On the other hand absorbancy in aqueous NaCl and KCl respectively is observed as 26-86 gH<sub>2</sub>O g<sup>-1</sup>. The maximum absorbancy is observed in deionized water whereas it is lowest in aqueous solution of NaCl and KCl. Further it also depends upon the amount of grafted PAN onto starch. On saponification of the graft polymer with alcoholic KOH, the nitrile (-C=N) substituents of PAN convert into a mixture of alkali metal carboxylate and carboxamide. It results in the formation of carboxylic anions (COO<sup>-</sup>) in the polymer network which produce strong electrostatic forces. These forces help in expanding the polymer network and make the product highly swollen but largely insoluble gel. This strong electrostatic network is also affected by dissolved CO<sub>2</sub> in distilled water by the presence of Na<sup>+</sup> or K<sup>+</sup> (cations) in tap water (other soluble salt also) and aqueous solutions of NaCl and KCl. It seems that the net work

**Table 5**  
Effect of aqueous solution of NaCl and KCl saponified product (Rice starch-g-AN).

Sample No.	Effect of aqueous NaCl on absorbancy g H <sub>2</sub> O g <sup>-1</sup> at different concentrations.			
	1%	5%	0.25%	0.125%
1.	36	44	58	76
2.	50	55	76	86
3.	41	59	80	86
4.	43	46	72	86
5.	39	54	67	76
6.	26	49	50	45
7.	52	56	74	80
8.	39	54	67	76
9.	46	47	52	56
10.	33	43	49	52
11.	27	29	40	45
12.	39	54	67	76
13.	26	49	50	45
14.	30	52	56	61

Sample No.	Effect of aqueous KCl on absorbancy g H <sub>2</sub> O g <sup>-1</sup> at different concentrations.			
	1%	5%	0.25%	0.125%
1.	26	39	48	90
2.	57	78	89	112
3.	42	62	77	105
4.	42	47	79	102
5.	47	57	72	78
6.	26	49	50	45
7.	53	58	67	88
8.	47	52	72	78
9.	50	67	96	108
10.	30	40	48	70
11.	43	48	56	82
12.	47	52	72	78
13.	26	49	50	45
14.	30	51	52	58

becomes to narrow and does not accept excess of water. It might be due to the adsorption of various ions including Na<sup>+</sup> and K<sup>+</sup> cations on the surface of saponified polymer. Table 5 shows the results of absorbancy of different concentration of aqueous solution of NaCl and KCl. The absorbancy was found to be decreasing with increasing concentration of NaCl and KCl. These observations support above mentioned assumption that the adsorption of NaCl and KCl on the surface of the saponified polymer closes the pores which results in decrease in absorbancy. Similar results were also obtained when saponified maize starch-g-AN was kept in aqueous NaCl (0.25-2%), the absorbancy dropped from 175

to 34g H<sub>2</sub>O g<sup>-1</sup> and in the studies of hydrogels based on PVA-acrylic acid using methylene-bis-acrylamide as crosslinking agent.

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