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PREPARATION OF GRAFT COPOLYMER MAIZE-STARCH-G-ACRYLONITRILE AND ITS SAPONIFICATION

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Graft copolymer of acrylonitrile onto maize-starch using ceric ammonium nitrate as a catalyst has been prepared. The effect of monomer, backbone and catalyst concentration on rate of conversion of monomer (Rp), rate of graft copolymerization (Rg), grafting efficiency (GE) and grafting rate (GR) have been discussed. The absorption of water by saponified product of graft copolymer is determined. The effect of sodium chloride on saponified product is also discussed.

Key words: Graft copolymer, Maize-strach, Catalyst

Introduction

The modification of natural and synthetic copolymer has been gaining interest both from the practical and fundamental point of view. Casein (Khan *et al* 1994; Khan and Khalil 1995; Mohan *et al* 1984; Mohan *et al* 1983 and Mohan *et al* 1983) and gelatin (Anne and Radhakrishnan 1985) have been usually used for finishing both artificial and natural leather. Casein does not give smooth finishing on leather but becomes brittle. On grafting casein with any vinyl monomer (like acrylamide, acrylates) gives better results. Similarly starch is one of the important natural polymer and has wide uses. Modification of starch by grafting vinyl monomers unit onto its backbone has been discussed earlier (Patel *et al* 1985; Fanta *et al* 1966; Gugliemelli and Swarsan 1973 and Fanta *et al* 1982). Acrylonitrile is one of the important vinyl monomer which on grafting with starch gives useful product. This product on saponification with alcoholic alkali gives polymeric material which can absorb water more than two hundred times of this material. Several studies have been conducted on grafting of acrylonitrile (AN) onto starch (Gugliemelli and Swarsan 1973; Gugliemelli *et al* 1968 and Mohan *et al* 1989) but its kinetic study needs to be discussed in detail. The present study describes the grafting of AN onto starch under various experimental conditions by changing concentration of initiator, monomer and starch. The aim of the study is to find out the effects of monomer initiator and backbone of grafting ratio (GR), grafting efficency (GE), rate of conversion of monomer (R_p), rate of homopolymerization of monomer (R_h), rate of graft polymerization of monomer (R_g) and absorbency. Maize starch has been used for this study.

Experimental

Material: Pure grade acrylonitrile was fractionally distilled in an atmosphere of nitrogen. The middle fraction was collected. Reagent grade ceric ammonium nitrate, analar grade butanol and maize starch (Maize Rafhan. PF/3402), GR grade of sodium chloride and KOH (Merck) were used without further purification.

Synthesis of graft copolymer (St-g-PAN). Required quantities of maize starch are shown in Tables 1 - 3. Water (95 ml) and butyl alcohol (8 ml) were refluxed for 5 h.Then butyl alcohol was distilled off with some quantity of water (total volume 45 ml). For grafting, known quantities of ceric ammonium nitrate and AN were added to refluxed material and heated at 50°C for 5 h. under nitrogen. The product was washed with alcohol and dried. Ungrafted PAN was removed by extracting with DMF. Removal of starch from the extracted St-g-PAN was carried out by hydrolysis with HCl (Fanta *et al* 1982).

Preparation of absorbing material. The extracted St-g- PAN obtained from different starch and AN ratios were saponified by heating (75°C) a mixture of St-g-PAN (4g), alcoholic solution of KOH (4g in 40 ml ethanol) and 10 ml water for 2 h. The saponified product was washed with water then ethanol to remove unreacted KOH and dried in vacuum desiccator.

Infrared spectrum of St-g-PAN was determined to ensure the attachment of growing polymer chain of PAN onto the backbone of starch from the appearance of characteristic absorption bands which were not present in the spectrum of starch. I R spectrum was recorded at 3400 (s), 2920 (w), 2240 (s) 1620 (m), 1440 (w), 1380 (m) and 1080-1020 (m) cm^{-1} which shows the association of growing polymer chain of PAN onto starch.

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Table 1

Effect of monomer concentration on grafting of AN onto maize-starch*

Sample No.	AN (g)	Total conversion of AN		Elemental analysis	Grafted AN	GR %	GE %	Rate of polymerization x10^7 mole Sec^{-1}			Absorbency gH_2O/g
		g	%	%N	(g)			Rp	Rg	Rh	
1.	9.7	4.22	43.5	18.8	4.02	2233	95.3	36.862	35.115	1.747	125
2.	12.1	4.62	38.2	19.9	4.30	2389	93.1	40.356	37.561	2.795	126
3.	15.7	4.72	30.0	20.17	4.62	2567	97.9	41.230	40.356	0.874	130
4.	20.2	5.02	24.9	21.01	4.81	2672	95.8	43.850	42.016	1.834	151

*Amount of starch n feed, 0.18g; time of grafting, 5h; CAN, 0.37g; temp, 50 ° C

Table 2

Effect of backbone concentration on grafting of AN onto maize-starch*

Sample No.	Starch (g)	Total conversion of AN		Elemental analysis	Grafted AN	GR %	GE %	Rate of polymerization x10^7 mole Sec^{-1}			Absorbency gH_2O/g
		(g)	%	%N	(g)			Rp	Rg	Rh	
5.	0.18	4.72	30.0	20.17	4.62	2567	97.9	41.230	40.356	0.0874	130
6	0.20	4.91	31.3	21.57	4.61	2305	93.9	42.889	40.269	0.262	135
7.	0.25	5.20	33.1	22.13	4.90	1960	94.2	45.423	42.802	0.262	110
8.	0.36	6.41	39.1	19.05	5.20	1444	84.7	53.634	45423	0.821	175

*Amount of AN in feed,15.7g; time of grafting, 5h; CAN, 0.37g; temp, 50 ° C

Table 3

Effect of ceric ammonium nitrate (CAN) concentration on grafting of AN onto maize-starch*

Sample No.	CAN (g)	Total conversion of AN		Elemental analysis	Grafted AN	GR %	GE %	Rate of polymerization x10^7 mole Sec^{-1}			Absorbency gH_2O/g
		(g)	%	%N	(g)			Rp	Rg	Rh	
9.	0.1	1.45	9.2	21.01	1.38	6.90	95.2	12.056	12.666	0.0611	115
10.	0.2	4.90	31.3	21.57	4.61	2305	93.9	42.889	40.269	0.0262	135
11.	0.37	5.60	35.7	22.13	4.92	2410	87.9	48.917	42.977	0.594	135
12.	0.45	6.50	41.4	22.30	5.87	2935	90.3	56.778	51.275	0.550	130

*Amount of AN in feed,15.7g; starch in feed,0.2g; time of grafting, 5h; CAN, 0.37g; temp, 50 ° C

Results and Discussion

Data regarding the graft copolymerization of acrylonitrile (AN) onto starch (amylose/amylopectin) using ceric amonium nitrate (CAN) as initiator at 50°C are illustrated in Table 1-3. The graft copolymer was identified by elemental analysis, solubility and I R spectral studies. The elemental analysis of the twelve samples of graft compolymer was carried out for nitrogen. The twelve samples of the product contain 18.8-22.13% nitrogen whereas polyacrylonitrile contains 26.2% nitrogen. Further the percentage of nitrogen of each sample product is different. The difference and decrease in percentage of nitrogen indicate the attachment of starch molecules with the growing polymer chain of polyacrylonitrile. PAN is soluble in cold/hot DMF whereas the product does not dissolve in DMF. It also provides information about the attachment of starch molecules with polymer chain of PAN and supports the results of elemental analysis that the product is graft copolymer. I R spectrum of the product was also recorded. The prominent absorption bands at 2240 cm^{-1} (-C=N) and 3400 cm^{-1} (-OH) show the association of growing polymer chains of PAN onto starch resulting of graft copolymer St-g-PAN.

The grafting ratio (GR) and grafting efficiency (GE) were calculated by using the following sample ralations:

$$\text{Grafting ratio (GR) \%} = \frac{\text{Weight of vinyl polymer graft}}{\text{weight of backbone}} \times 100$$

$$\text{Grafting efficiency(GE)\%} = \frac{\text{Weight of vinyl polymer in graft}}{\text{total weight of vinyl polymer formed}} \times 100$$

Table 1 includes the results of the effect of monomer concentration on the graft copolymerization of AN onto starch. It is observed from the table that with an increase of AN concentration, the rates of conversion of monomer (Rp), graft copolymer (Rg), grafting ratio (GR) increases whereas GE decreases. Further, the rate of homopolymerization(R_h) does not increase or decrease progressively with the increases in concentration of monomer. Increase in the values of Rp, Rg and GR with increase in monomer concentration might be due to higher availability of AN molecuels in the vicinity of activated sites of starch. The more growing polymer chains of AN are available which attack onto the activated sites of starch, resulting more grafting. The rate of conversion of acrylonitrile is greater than the rate of grafting since at the early stage of reaction homopolymerization of AN also takes place though it is on the lower side. The monomer propagative species are utilized in the homopolymerization of AN which directly influences the grafting efficiency (GE).

Table 2 illustrates the results of the effect of backbone concentration on the graft copolymerization of AN onto starch. These results indicate that Rp, Rg, Rh, increase whereas GR and GE decrease as starch concentration increases. The increase in concentration of starch produce large number of grafting sites along the backbone resulting in the increase of Rp, Rg, Rh. 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 utilize the grafting sites of starch partially and some unbound starch propagating species are left behind which cause mutual termination between backbone propagating species (Mohan *et al* 1989). Further at the initial stages, the homopolymerization of vinyl monomer causes the drop in GE values.

Table 3 shows the results of effect of catalyst concentration (Ce^{+4} ions) on the graft copolymerization of AN on the starch. These results indicate that GR, Rp, Rg, Rh increase with the increasing concentration of ceric ammonium nitrate. It is due to more available active species produced by different concentration of ceric ammonium nitrate in the system. Decrease in the value of GE might be due to non availability of sufficient grafting sites on starch for coupling of propagative growing polymer chain and starch.

Amongst twelve samples of graft copolymer, water absorbency of saponified material range is 110-175gH_2O/g. The water absorbency mostly depends upon the amount of grafted PAN onto starch. The maximum absorbency (175g H_2O/g) is observed for sample No.8 which is synthesised by reacting 0.36g starch, 15.7g AN and 0.37g CAN. When graft copolymer St-g-PAN is saponified, yellowish polymeric material is obtained. Saponification of graft copolymer in alcoholic potassium hydroxide converts the nitrile substituents (-C=N) of PAN to a mixture of alkali metal carboxylate and carboxamide and affords a polymer that exists in water as a highly swollen but largely in soluble gel (Fanta *et al* 1982). The absorbency of different concentration of aqueous solution of sodium chloride is also tested. The absorbency is found to be decreasing with increasing concentration of NaCl.

Concentration of NaCl%	Absorbency gH_2O/g
0.00	175
0.25	95
0.50	60
1.00	40
2.00	34

Sodium chloride is absorbed on the surface of the saponified polymer and closes the pores which decreases the absorbency.

References

Anne G, Radhakrishan G, 1985 Graft copolymerization of ethyl acrylate on gelatin in water-acetic acid medium. *Eur Polymer J* **21** (12) 1081-3.

Fanta G F, Burr R C, Doane W M 1982 Saponified strach-g-polyacrylonitrile. Variable in the Ce^{+4} initiation of graft copolymerization. *J Appld Polymer Sci* **27** 2731-2737.

Fanta G F, Burr R C, Russell C R and Rist C E (1966)Graft copolymer of strach I. Copolymerization of gelatinized wheat strach with acrylonitrile. *J Appld Polymer Sci* **10** 929-937.

Fata G F, Burr R C, Russell C R, Rist C E (1969) *J Appld Polymer Sci* **13** 133.

Gugliemelli L A, Swansan C L (1973) Acrylonitrile grafting onto starch *J Polymer Sci.* Polymer Chem Ed **11** 2451.

Guglimelli L A, Weaver M O, Russell C R (1968) New method for isolation of starch vinyl graft copolymer *Polymer Letters* **6** 599-602.

Khan A Rasheed,Khalil Ahmed , Yousufzai A H K 1994 Synthesis of graft copolymer of casein with acrylamide. *Pak J Sci Ind Res* **37** 92.

Khan A Rasheed, Khalil Ahmed 1995 Studies of graft copolymerizationof MMA on casein. *Pak J Sci Ind Res* **38** 292.

Kimura S, Imoto M (1960) *Macromol Chem* **42** 140.

Mohan D, Radhakrishnan Ganga and Rajadurai S (1983) Synthesis of casein-g-poly (MA) *J Macromol Sci Cham* A 20(2) p.201-212.

Mohan D, Radhakrishnan G, Rajadural S, Nagabushanam T and Joseph T 1984 Studies of graft copolymerization of acrylate monomers onto casein. *J Appl Polymer Sci* **29** 329-339.

Mohan D, Radhakrishnan Ganga, Rajadurai S Venkata Rao K and Cameron G G (1989) *J Appld Polymer Sci* **27** 2123.

Mohan D, Radhakrishnan Ganga and Rajadurai (1983) J. *Polymder Sci Polymer Chemistry* Edition **21** 3041.

Patel A R, Patel K C and Patel R D, *Die Angewandte Macromole Kulare Chemie* **135** 11 20.

Toylor N W and Bagley E B (1974) *J Appld Polymer Sci* **18** 2747.

Weaver M O, Montgomery R R, Miller L D Sohns V E, Fanta G F and Doane W M (1977) *Staerke* **29** 413.