Preparation of Superabsorbents by Gamma-Ray Radiation

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Synopsis

Superabsorbent polymers were prepared using acrylonitrile grafted to corn starch employing low levels of gamma ray radiation as initiator. Various grafting parameters have been studied at these low dosages. Absorbency values for the final products are reported. Use of the above superabsorbent as a desiccant has been evaluated. The product will find application where dispersions of low viscosity and high water absorbencies are desired.

INTRODUCTION

Extensive research work on the preparation and properties of starch-based superabsorbents have been reported.[1-9] Most workers have used the well-known ceric ion initiation system of grafting for the preparation of superabsorbent. Although radiation is an effective initiator for grafting of various monomers onto cellulose and other polymers, very little work[10,11] employing this technique has been reported.

The present work describes (i) graft polymerization of acrylonitrile (AN) onto gelatinized starch by simultaneous Cobalt-60 initiation at low radiation dosages and saponification of the resulting graft copolymers to give water absorbents, (ii) characterization of the graft copolymers, and (iii) evaluation of the properties of the saponified products.

EXPERIMENTAL

Ten grams (dry weight) of corn starch (M/s. Anil Starch) were gelatinized in 100 mL of distilled water at 85°–90°C for 30 min and cooled to room temperature. Ten grams of freshly distilled AN (S.d. Fine Chemicals) were added to the gelatinized starch and mixed thoroughly. The samples were then irradiated to five different dosages of gamma ray radiation ranging from 0.1 to 0.5 Mrad at ambient temperature from a Cobalt-60 source at a dose rate of 0.2 Mrad/h. The Cobalt-60 source was supplied by Bhabha Atomic Research Centre, Bombay. During irradiation the temperature rose to about 47°C and no attempt was made to control the rise in temperature. After irradiation the irradiated product was washed with water followed by methanol. The crude products were air-dried and weighed. The water-soluble fraction was removed from the crude product by extraction with water at 90°C for 2.5 h. The dried

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residue was further extracted with dimethylformamide (DMF) overnight at room temperature, washed free of DMF with ethanol and water, and air-dried. The percentage grafting was obtained by estimating nitrogen in the pure copolymer. The percentage add-on which is the ratio by weight of the isolated polyacrylonitrile (PAN) to the weight of purified copolymer was calculated by acid hydrolysis method[1]. The acid hydrolysis of 1% slurry of the grafted copolymer was carried out for 4 h instead of 2 h.

The saponification of purified grafted copolymer was according to the method of Fanta et al.[12] For every gram of purified grafted sample 9.0 mL of 0.7N KOH was used. The suspension of the purified starch-g-polyacrylonitrile (starch-g-PAN) in KOH was taken in an Erlenmeyer flask which was heated in a water bath for 5–10 min till it assumed the reddish brown color and the flask was loosely stoppered and placed in an oven at 95–100°C for 3 h. Samples for the study of desiccant property were prepared as per method.[6] Ten grams (dry wt) of corn starch were gelatinized and grafted as described above using total radiation dose of 0.3 Mrad. After irradiation the entire aqueous mass was steam-distilled to remove excess of AN and KOH pellets were directly added (ratio of KOH to AN approx. 0.8 mol : 1 mol). After completion of the reaction, the product was neutralized with glacial acetic acid to bring down the pH to 8.0 and precipitated with 450 mL of methanol. This was further disintegrated to granular form in a laboratory blender and dried in vacuum at 40°C.

The procedure adopted for the determination of molecular weight of polyacrylonitrile (PAN) was according to the method described in Ref. 1.

The hydrolysis time was increased to 4 h instead of 2 h to facilitate total dissolution of PAN samples in dimethylformamide (DMF). The number average molecular weight of PAN was calculated from the Mark–Houwink equation using Onyon's constants.[13] Viscosity of 1% slurry of the saponified product was determined by a Brookefield viscometer (Model RV). The method[12] adopted by Fanta and co-workers was used for absorbency tests. The desiccant property of the superabsorbent product was compared with $CaCl_2$ and silica gel. A known quantity of cotton wool sample (53% moisture) was placed in desiccators containing the above three desiccants. Periodically, cotton wool samples were weighed to find the weight loss.

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA)

TABLE I
Grafting of AN to Gelatinized Starch by γ -Irradiation

Sample no.	Dosage (Mrad)	Wt.[a] of crude (g)	Wt.[a] after water extraction (g)	Wt.[a] after DMF extraction (g)
1	0.1	15.50	—	14.01
2	0.2	14.79	14.12	13.12
3	0.3	16.74	16.40	15.73
4	0.4	18.63	—	16.02
5	0.5	18.23	17.84	17.50

[a]Samples were air-dried (8% moisture).

TABLE II
Changes in Grafting Parameters Due to Radiation Dosage

Sample no.	Dosage (Mrad)	% Add-on[a]		Molecular weight PAN ($\times 10^5$)	Frequency of grafting (AGU/graft)
		A	B		
1	0.1	36.19	31.15	2.98	4066
2	0.2	44.48	41.89	3.08	2640
3	0.3	44.70	42.52	2.82	2360
4	0.4	43.61	41.34	3.38	2970
5	0.5	47.00	44.62	2.82	2170

[a]A = from nitrogen analysis; B = from wt loss on acid hydrolysis.

TABLE III
Properties of Final Product

Sample no.	Dosage (Mrad)	Viscosity[a] (Brookefield)	Absorbency (g/g)
1	0.1	5350	374
2	0.2	5600	345
3	0.3	6200	427
4	0.4	5300	368
5	0.5	3200	460

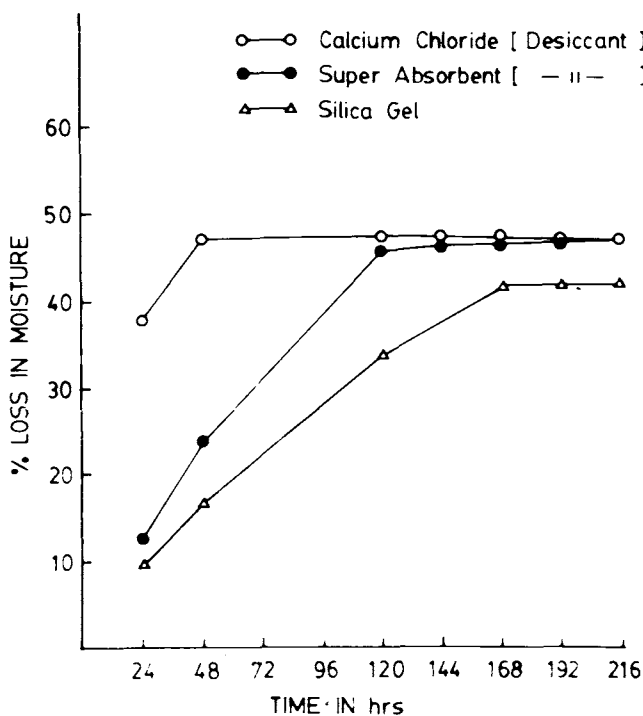[a]Spindle no. 4: rpm 20 at room temperature.

Fig. 1.   Loss in moisture as a function of time.

were carried out on Mettler Thermo Balance TAHE 20. About 10 mg of the
purified sample were heated in a quartz crucible, to 680°C at the rate of
10°C/min. The studies were carried out in air for DTA. Alumina was used as
a reference. The primary thermogram was automatically recorded. From the
primary thermogram the decomposition temperatures for 10–100% weight loss
were calculated. Initial decomposition temperature (idt) and integral proce-
dural decomposition temperature (ipdt)[14] were also calculated.

RESULTS AND DISCUSSION

Various grafting parameters are shown in Table I. Table II gives the values
of the purified grafted product. A substantial increase in grafting percentage
from 36.19% at 0.1 Mrad to 44.48% at 0.2 Mrad is observed. Thereafter, no
significant increase is observed up to 0.4 Mrad but at 0.5 Mrad a value of
47.00% is obtained. The values of the number average molecular weight for the
PAN side chains are found practically to be independent of total dose of
radiation. Similar observations have been made by Min and Inagaki.[15] In fact,
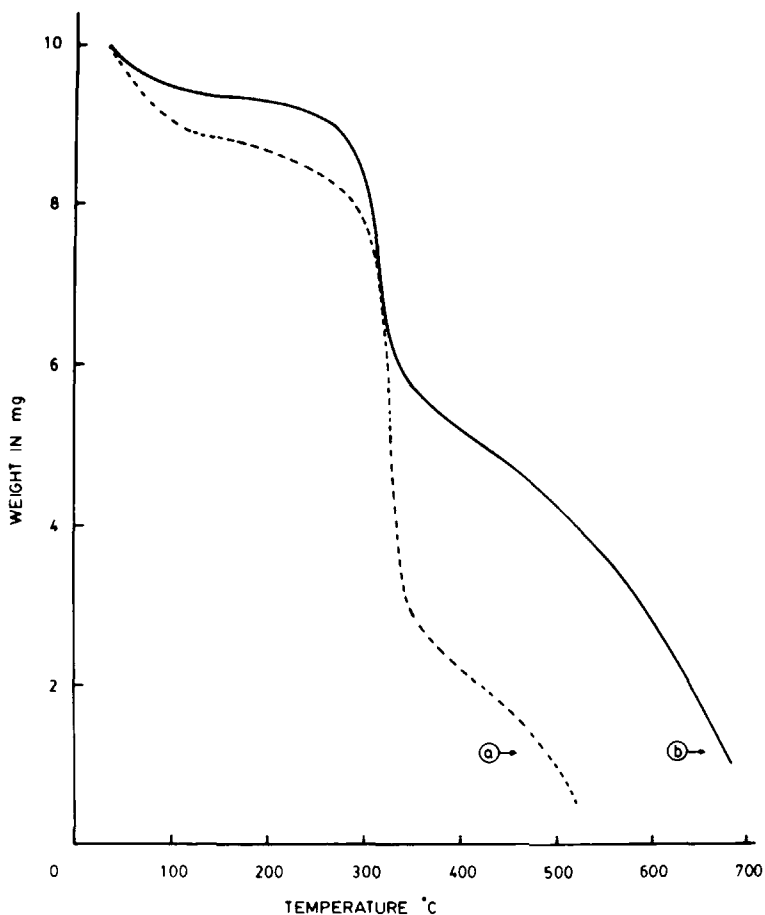the molecular weight of PAN side chains average around 3×10^5 at all

Fig. 2.   TGA graph: ⓐ starch, ⓑ grafted starch (44%).

dosages. From the values of molecular weight of PAN side chains and the % grafting it can be readily inferred that the number of side chains having nearly the same length increases from 0.1 to 0.2 Mrad. From 0.2 to 0.4 Mrad no significant change is observed. Again it registers an increase at 0.5 Mrad. The values for frequency of grafting (Table II) also support the above observations.

The values of absorbency and viscosity of the dispersions of the final product prepared from the extracted starch-g-PAN are shown in Table III. The absorbency values are fairly good and comparable with those reported for various products prepared by chemical initiation methods.[11,16] It also appears that the PAN add-on and the increased frequency of grafting are directly related to the absorbent properties of the products. The viscosity values of the dispersions of the final product are lower than the reported values of around 17,000 cps for the products prepared through ceric ion initiation.

This may be the result of degradative effect of gamma radiation on starch backbone as reported by Taga and Inagaki[17] and Min and Inagaki[15] or due to the high water solubles in the final product. But our value of 25% water solubles for the sample (product 3, Table III) as estimated by the method given in Ref. 12 is comparable to that of the product obtained through chemical initiation. Hence, if the degradative effect due to radiation can be
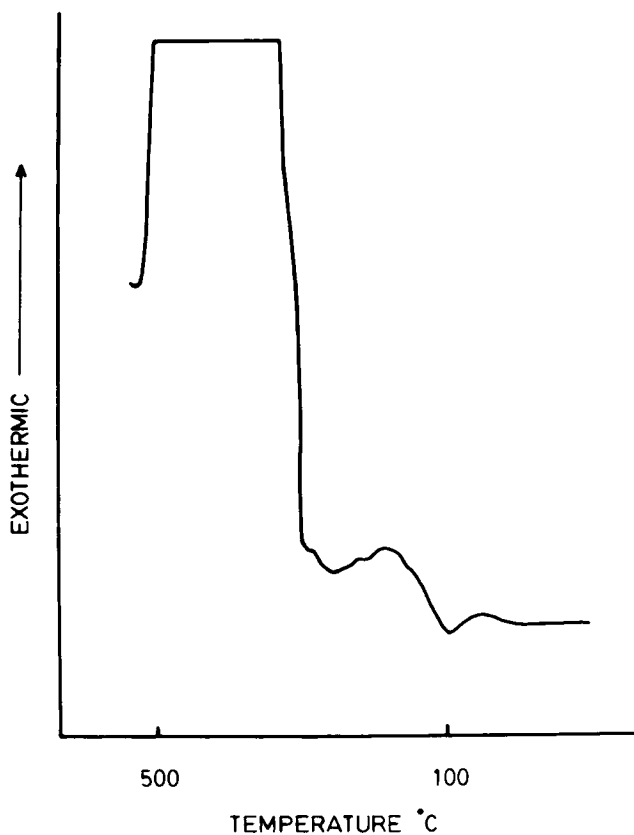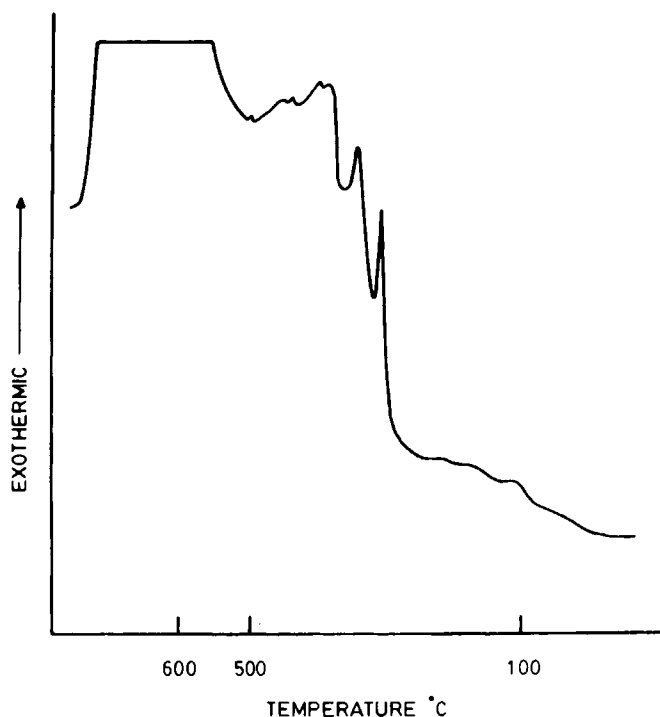

Fig. 3. DTA graph of starch.

Fig. 4.   DTA graph of grafted starch (44%).

minimized, there is a good scope for improving both the viscosity as well as the absorbency of the product.

In the evaluation of superabsorbent as desiccant, moist cotton samples were used instead of dry samples so as to obtain enhanced differences in the weight of cotton wool. The ratio of cotton wool to desiccant was 1 : 10 in the case of superabsorbent and $CaCl_2$ and 1 : 25 in the case of silica gel. Identical

TABLE IV
TGA Data Showing Loss in Weight of Samples at Different Temperatures[a]

Sample no.	Loss in weight (%)	Temperature (°C)	
		Control	Grafted (cold DMF extracted)
1	10	100	270
2	20	305	305
3	30	315	315
4	40	325	335
5	50	325	425
6	60	335	515
7	70	345	580
8	80	375	630
9	90	460	665
10	100	520	680

[a] Note: ipdt values: control 314.6; grafted (44%) 460.4.

desiccators were used in all the cases. Figure 1 clearly reveals the superiority of superabsorbent over silica gel as a desiccant.

Figures 2, 3, and 4 bring out the thermal stability of the control and purified grafted samples. Table IV shows the decomposition temperatures of both control and purified grafted starch at various stages. It is obvious that the thermal stability of the purified grafted sample is superior to that of control at all stages of its degradation cycle. The above fact is further confirmed by way of increased ipdt values of grafted samples. The thermograms also reveal that the peak shift in the endo and exo region of the grafted samples as compared to the control coincides with the changes in the TGA degradative profiles.

The study points out the potential use of low level of gamma ray irradiation as initiator for the production of low viscosity and high absorbent polymers.

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