Gamma-Radiation Induced Grafting of Acrylonitrile onto Guar Gum: Influence of Reaction Conditions on the Properties of the Grafted and Saponified Products

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SYNOPSIS

In the gamma-radiation induced grafting of acrylonitrile onto guar gum, the influence of different concentrations of the monomer acrylonitrile on the PAN add-on, the number average molecular weight of the PAN side chains, and the grafting frequency of the PAN side chains are reported. At 0.3 Mrad dosage, the PAN add-on were 32.4, 48.5, and 66.2% and the number average molecular weight of the PAN side chains were 59,700, 132,200, and 238,900, respectively, at three different reaction conditions. The frequency of grafting also showed considerable variation at 0.2 Mrad dosage, for all three sets of samples. The viscosity of the aqueous dispersions of the saponified samples at different concentrations are also reported. The water absorbency of the saponified samples were evaluated and the values were around 250 g/g. The fall in viscosity of the aqueous dispersions on storage were also evaluated. The observed fall in viscosity was lower in the case of the product with higher PAN content. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Guar gum is a naturally occurring plant-derived polysaccharide of great commercial importance. It is a branched polymer with β-D-mannopyranosyl units linked (1 → 4) with single members α-D-galactopyranosyl units as side branches.[1] This polymer as such or in the form of various derivatives finds extensive applications in the field of textiles, paper, foods, oil well drilling etc. Many modification treatments have been attempted on guar gum to prepare superabsorbents.[2-3] In a recent communication Lokhande et al.[4] have discussed the preparation and properties of guar gum-*g*-polyacrylonitrile obtained using gamma radiation as initiator, employing a simultaneous irradiation technique. They have also discussed the properties of the absorbent products derived from the above grafted copolymers. The object of the present investigation, which deals with the gamma-radiation induced grafting of acrylonitrile onto guar gum, is to study: the influence of reaction conditions on the various grafting parameters especially on the molecular weight, the grafting frequency of the polyacrylonitrile (PAN) side chains of the grafted products, and the properties of the saponified products of the above grafted copolymers.

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EXPERIMENTAL

Materials

Edible grade guar gum powder (M/s. Hazrat & Co.) was used for the grafting experiments. The irradiation was carried out with a Cobalt-60 source at a dose rate of 0.126 Mrads/h. The Cobalt-60 source was supplied by Bhabha Atomic Research Centre, Bombay.

Preparation of Grafted Products

Twenty grams (dry weight) of guar gum and the required quantity of acrylonitrile (AN) (S. d. Fine Chemicals Ltd.) were dispersed in 400 mL of distilled

water at ambient temperature (30°C) in a laboratory blender. The samples were irradiated to different dosages of radiation ranging from 0.2–0.6 Mrads at ambient temperature (30°C) from a Cobalt-60 source at a dose rate of 0.126 Mrads/h. During irradiation no attempt was made to control the rise in temperature, which was around 50°C. Employing the above conditions of irradiation, three sets of samples were prepared by varying the concentration of monomer only and keeping the rest of the conditions the same. After irradiation, the crude grafted product was washed with water to remove the unreacted AN. The crude product was air dried at room temperature. The air-dried sample was extracted with water at 100°C, maintaining a material to liquor ratio of 1 : 100, until no further weight loss was noticed. This required about 3 h extraction time. After extraction, the water was evaporated under vacuum and the residue weighed. The above sample was extracted in dimethyl formamide (DMF) (S. d. Fine Chemicals Ltd.) with a material to liquor ratio of 1 : 50 for 24 h at room temperature (30°C), as no further weight loss was observed after about 12–15 h extraction. The DMF solubles were estimated after evaporating the DMF under vacuum. The grafting was confirmed by IR analysis.

Molecular Weight of the Grafted Side Chain

The grafted side chain from the purified grafted material was separated through acid hydrolysis with 1N HCl as described by Gugliemelli et al.[5] The hydrolysis was carried out for 4 h. The number average molecular weight of PAN was calculated from intrinsic viscosity (η) by using the equation of Banford et al.[6] The intrinsic viscosity in DMF at 25°C was estimated from the measured values of specific viscosity (η_{sp}) by the equation of Schulz and Sing.[7]

Alkaline Hydrolysis

The conversion of nitrile substituents of the grafted polyacrylonitrile side chains into a mixture of carboxamide and alkali metal carboxylate is effected in this step. Ten grams (dry weight) of purified grafted product was heated with 90 mL of 0.7N potassium hydroxide at 100°C for 2.5 h. The reaction mixture initially assumed a red-brown colour that gradually faded as the reaction went to completion. After the reaction, the mixture was cooled to room temperature and the pH of the mass was adjusted to 8.0 with glacial acetic acid. The mixture was then blended with 450 mL methanol and the solid separated by filtration. The solid was washed twice with methanol and allowed to air dry. The completion of the nitrile saponification was confirmed by infrared spectra.

Water Absorbency

The water absorbency of the saponified material was determined as per the method of Fanta et al.[8]

Viscosity of the Saponified Product

Different concentrations of aqueous dispersions of the saponified products were prepared and their viscosity determined by Brookefield Viscometer (Model RV).

Effect of Storage

Viscosity of 1% aqueous dispersions of the samples were measured for 9 days without adding any preservatives. The pH of all the samples was adjusted to 7.6.

RESULTS AND DISCUSSION

Table I presents the effect of different concentrations of the monomer AN on the grafting parameters, at different doses of gamma radiation ranging from 0.2–0.6 Mrad. It is seen that the PAN add-on increases with the increase in the monomer concentration, at all the dosages studied. It is also seen that in the case of set I samples, the percent add-on increases from 21.4–32.4 with the increase in the radiation dose from 0.2–0.3 Mrad. From 0.3 Mrad dosage onward, the add-on stabilises around 33%. But in the case of set II and III samples, the PAN add-on almost remains unchanged from 0.2–0.6 Mrad at around 49 and 65%, respectively. The percent water extract of grafted products of sets I, II, and III obtained at different radiation dosages are depicted in Figure 1. The water extract that reflects the ungrafted portion of the polysaccharide shows a decreasing trend with the increase in the radiation dosage in sets I and II. But very little change is observed in the set III samples. The DMF solubles indicate the extent of homopolymer formation during grafting process. An increasing trend is observed in DMF solubles from set I to set II samples probably because of a higher monomer concentration in set II. But surprisingly, the DMF solubles register low values for set III samples though the monomer con-

Table I Grafting Parameters at Different Radiation Doses

Dosage (Mrad)	Set I			Set II			Set III		
	Water Extract (%)	DMF Solubles (%)	PAN[a] (%)	Water Extract (%)	DMF Solubles (%)	PAN[a] (%)	Water Extract (%)	DMF Solubles (%)	PAN[a] (%)
0.2	4.32	0.46	21.4	7.17	0.90	48.3	2.62	0.85	65.3
0.3	3.13	0.75	32.4	6.92	0.89	48.5	3.11	0.26	66.2
0.4	2.57	0.44	34.0	3.78	0.70	50.0	2.59	0.29	63.7
0.5	3.19	0.33	32.2	4.72	0.60	47.8	3.46	0.59	66.4
0.6	—	—	—	3.78	0.70	49.2	3.00	0.39	65.2

[a] By acid hydrolysis.
Set I, M : L = 1 : 20. AGU : AN = 1 : 2; set II, M : L = 1 : 20, AGU : AN = 1 : 4, Set III, M : L = 1 : 20, AGU : AN = 1 : 8.

centration is much higher in this set. Table II presents the variation in the number average molecular weight of the grafted side chains with the change in the monomer concentration. An appreciable increase in the molecular weight of the grafted side chain is observed with the increase in the monomer concentration. The highest molecular weight of the PAN side chain is registered at 0.2 Mrad radiation dose at all the monomer concentrations and, with the subsequent increase in the radiation dose, a downward trend in the molecular weight was observed. In general, the data in Table II exhibits a decreasing trend in molecular weight of PAN and increasing trend in the frequency of grafting with increase in the radiation dosage in all three sets. From an overall consideration of various parameters like PAN add-on, molecular weight of the side chain, and the frequency of grafting, it may be observed that initially there is an increase in the number of shorter grafted side chains with the increase in the radiation dosage from 0.2–0.3 Mrad, though to different extents in the three different concentrations of the monomer considered. Similar observations have been made by Fanta et al.[9] in their work on the grafting of starch

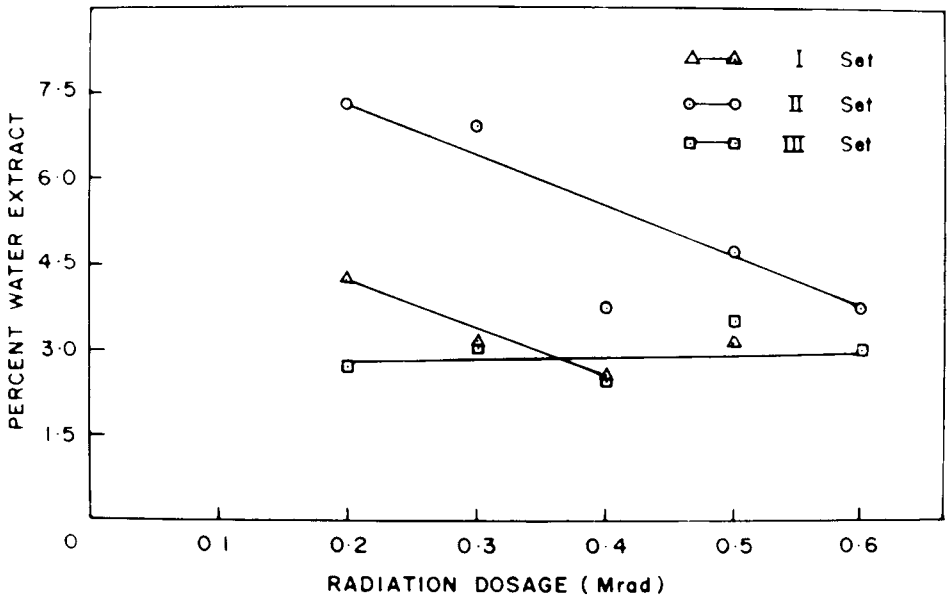

Figure 1 The percent water extract of grafted products obtained at different radiation dosages under different reaction conditions: set I, M : L = 1 : 20, AGU : AN = 1 : 2; set II, M : L = 1 : 20, AGU : AN = 1 : 4; set III, M : L = 1 : 20, AGU : AN = 1 : 8.

Table II PAN Side Chain Characteristics at Different Radiation Doses

	Set I			Set II			Set III		
Dosage (Mrad)	PAN[a] (%)	M_w	Frequency (AGU/graft)	PAN[a] (%)	M_w	Frequency (AGU/graft)	PAN[a] (%)	M_w	Frequency (AGU/graft)
0.2	21.4	77690	1761	48.3	150,900	997	65.3	240,100	788
0.3	32.4	59700	769	48.5	132,200	866	66.2	238,900	753
0.4	34.0	57250	686	50.0	139,000	858	63.7	197,000	693
0.5	32.2	51470	669	47.8	133,900	903	66.4	237,800	743
0.6	—	—	—	49.2	136,000	867	65.2	218,300	719

[a] By acid hydrolysis.

under high dilution. A comparison between the molecular weight of the side chains of the set II samples in Table II and the values of the molecular weight of the side chains, which were around 3.5×10^5 as reported by Lokhande et al.,[4] show the effect of the variation of material:liquor ratio on the molecular weight of the PAN side chains. It is observed that lower material to liquor ratio favours longer grafted side chains. The above observation agrees with the observations of Fanta et al.[9] Under the same liquor ratio, the higher concentration of the monomer probably favours a rapid initial buildup of PAN side chains that in turn might hinder the movement of the monomer to other active sites on the carbohydrate backbone thus favouring the addition of the monomer to the growing end of the PAN rather than to another active site on the backbone polymer. Whereas, under the lower monomer concentration conditions, the lower ratio of propagation probably results in more termination reactions thus keeping the molecular weight of the PAN chains low. At the same time, shorter PAN chains probably pose lesser hindrance to the movement of the monomer thus creating an easier access to the other active sites, initiating newer chains at more places along the backbone.

Some of the important properties like viscosity of 1% aqueous dispersion, water absorbency, and percent water solubles of the saponified products of sets I, II, and III are presented in Table III. The viscosity of the aqueous dispersions of the samples of sets II and III are significantly higher than those of the set I samples, probably because of higher PAN add-on and higher molecular weight of the side chains in the former. The higher PAN add-on at the same time has not brought about any appreciable improvement in the viscosity over the aqueous dispersion of the ungrafted guar gum. This is probably due to the degradative effect of the gamma radiation on the polysaccharide backbone as observed by many workers.[4,10,11] Figure 2 depicts the relationship between the viscosity of 1% aqueous dispersions of the saponified products of sets I, II, and III, obtained at different radiation dosages. Up to a dosage of 0.3 Mrad, the product with higher PAN add-on seems to show higher viscosity. But from 0.3 Mrad dosage

Table III Properties of the Saponified Products

	Set I			Set II			Set III		
Dosage (Mrad)	Viscosity[a] (cps)	Water Absorbency (g/g)	Water Solubles (%)	Viscosity[a] (cps)	Water Absorbency (g/g)	Water Solubles (%)	Viscosity[a] (cps)	Water Absorbency (g/g)	Water Solubles (%)
0.2	700	250	—	2400	262	21.9	3200	319	23.5
0.3	304	332	42.2	2700	275	16.1	2900	317	—
0.4	260	271	39.2	—	229	29.3	—	—	29.4
0.5	610	164	37.3	4650	169	19.6	2000	195	19.0
0.6	—	—	—	3500	201	13.6	2000	253	14.7

[a] Brookefield, speed 20 rpm and spindle No. 2.

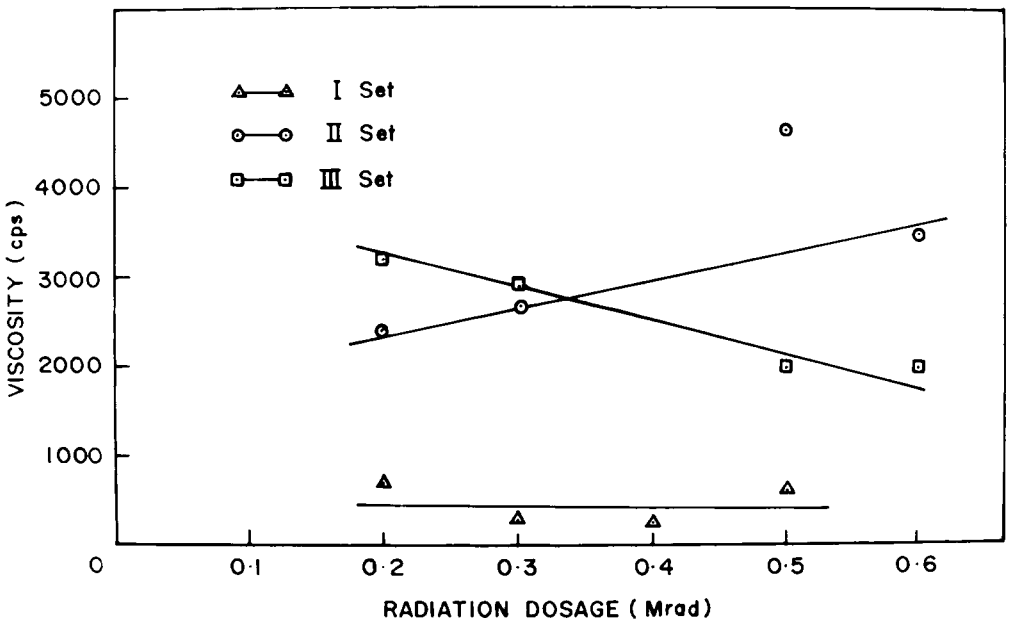

Figure 2 Relationship between the viscosity of 1% aqueous dispersions of the saponified grafted products obtained at different radiation dosages under different reaction conditions: set I, M : L = 1 : 20, AGU : AN = 1 : 2; set II, M : L = 1 : 20, AGU : AN = 1 : 4; set III, M : L = 1 : 20, AGU : AN = 1 : 8.

onward, the samples of set III, despite having higher PAN add-on and higher molecular weight of PAN side chains, register lower viscosity as compared to the corresponding samples of set II. This trend prevails up to the 0.6 Mrad dosage studied. The gel viscosity as measured by Brookefield viscometer is

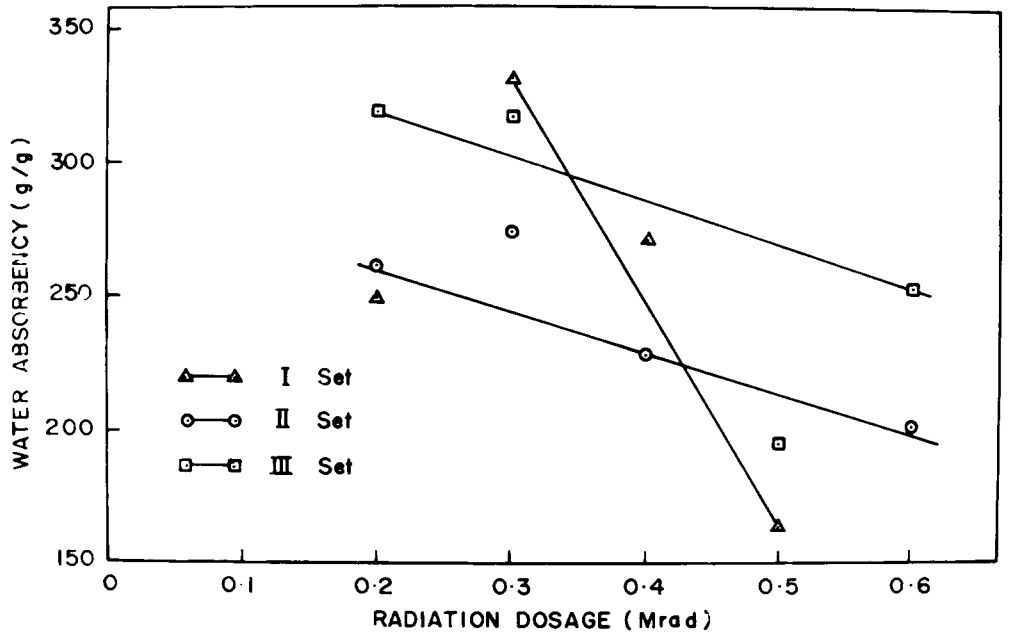

Figure 3 Water absorbency of saponified grafted products obtained at different radiation dosages under different reaction conditions: set I, M : L = 1 : 20, AGU : AN = 1 : 2; set II, M : L = 1 : 20, AGU : AN = 1 : 4; set III, M : L = 1 : 20, AGU : AN = 1 : 8.

Table IV Water Absorbency Index of Saponified Products

Dosage (Mrad)	Set I	Set II	Set III
0.2	—	48.44×10^{-3}	82.86×10^{-3}
0.3	42.13×10^{-3}	56.00×10^{-3}	87.91×10^{-3}
0.4	49.56×10^{-3}	58.28×10^{-3}	91.92×10^{-3}
0.5	48.13×10^{-3}	52.93×10^{-3}	89.36×10^{-3}
0.6	—	56.75×10^{-3}	90.68×10^{-3}

Water Absorbency Index = %PAN × (1/frequency of grafting).

a result of a complex interaction of the physical state of the gel particles, its aggregation, its geometry of packing etc. Assuming that the extent of degradation is similar in the case of set II and III samples at different dosages, the above anomaly can probably be attributed to the physical state of the saponified grafted guar gum particles. The difference in the PAN add-on, the molecular weight of the PAN side chains, and the frequency of grafted side chains between the set II and III might be contributing to the difference in the physical state of the two gels. The water absorbency of the samples, in general, average around 250 g/g. These values are comparable to those reported for starch-based superabsorbents.[12,13] Though no definite relationship is seen between the water absorbency and the various grafting parameters like PAN add-on and the molecular weight of the grafted side chains, an upward trend in the average value of the water absorbency is nonetheless discernable from set I to set III. A comparison of water absorbency of the saponified grafted products of sets I, II, and III obtained at various radiation dosages is presented in Figure 3. A higher water absorbency is observed for all the samples of set III as compared to the corresponding samples of set II. This may perhaps be attributed to the higher PAN add-on in the case of set III samples. But a reverse trend is observed in the case of the samples of set I and set II in spite of the fact that the samples of set II have a higher PAN add-on as compared to the samples of set I. This may be attributed to the fact that water absorbency in such systems may not be a function of PAN add-on alone, but it may also depend upon the number of graft-chains (frequency) attached to the backbone polymer chains. Hence, in the present investigation a new Water Absorbency Index (WAI) has been proposed to explain the above anomaly. The new WAI has been defined as the product of PAN% and Frequency.$^{-1}$ Table IV gives the values of the WAI for the samples of sets I, II, and III. The WAI shows an increasing trend in the water absorbency from set I to set III. It is also interesting to note that in general, the products obtained employing higher dosages of radiation shows lower water absorbency. This might be attributed to the degradative effect of gamma radiation on

Table V Viscosity of 1% Aqueous Dispersion of Saponified Products

Concentration (%)	Viscosity[a] (cps) Dosages (Mrad) 0.2	0.4	0.6
Set I			
4.0	41,000	45,000	8,000
3.5	24,000	15,600	11,750
3.0	17,000	10,750	22,250
2.5	11,500	5,200	15,250
2.0	5,050	2,400	10,250
1.5	2,000	775	6,500
1.0	700	260	2,330
Set II			
4.0	54,000	26,000	28,000
3.5	44,000	31,400	33,250
3.0	40,000	16,000	28,500
2.5	18,000	12,000	21,250
2.0	12,000	7,700	13,625
1.5	6,750	3,300	7,500
1.0	4,100	980	3,500
Set III			
4.0	51,000	14,000	48,000
3.5	46,000	21,000	26,500
3.0	37,000	15,650	25,250
2.5	26,000	9,250	17,000
2.0	17,000	4,950	10,250
1.5	6,750	2,350	6,050
1.0	3,200	700	2,000

[a] All measurements at 20 rpm using appropriate spindle numbers.

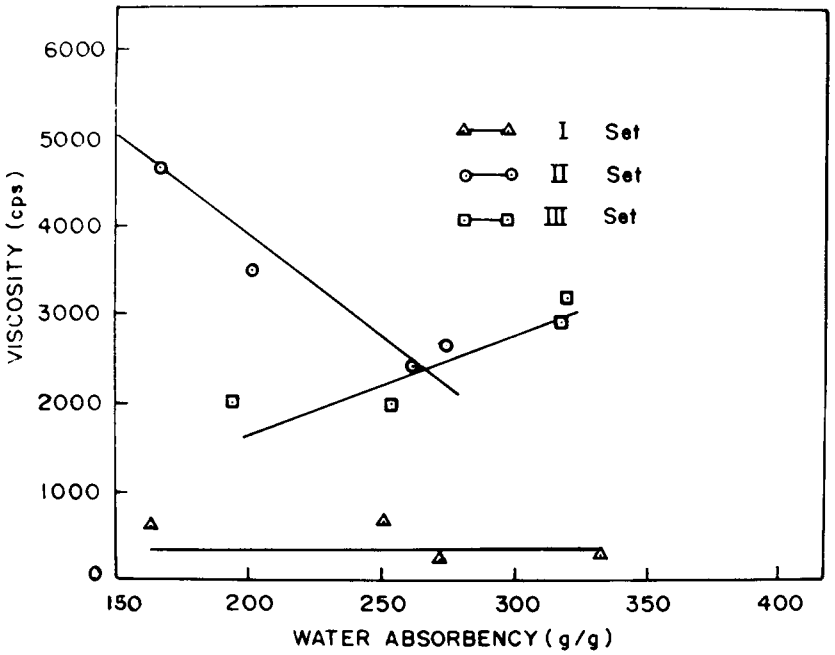

Figure 4 Relationship between the water absorbency and the viscosity of 1% aqueous dispersions of the saponified grafted products obtained at different radiation dosages under different reaction conditions: set I, M : L = 1 : 20, AGU : AN = 1 : 2; set II, M : L = 1 : 20, AGU : AN = 1 : 4; set III, M : L = 1 : 20, AGU : AN = 1 : 8.

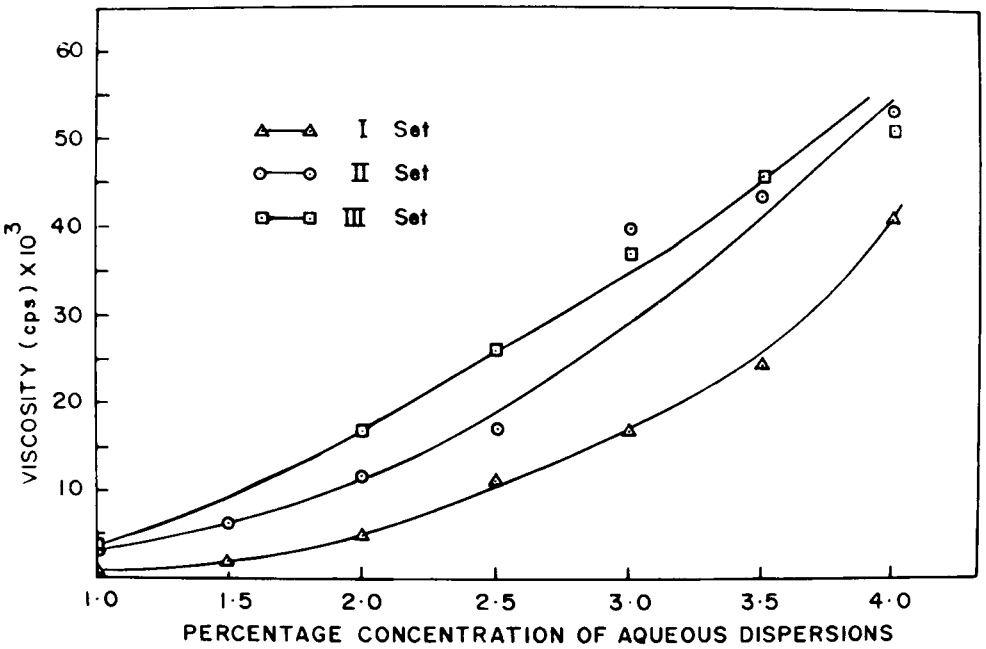

Figure 5 Change in viscosity with the concentration of aqueous dispersion of the saponified grafted product obtained at 0.2 Mrad under different reaction conditions: set I, M : L = 1 : 20, AGU : AN = 1 : 2; set II, M : L = 1 : 20, AGU : AN = 1 : 4; set III, M : L = 1 : 20, AGU : AN = 1 : 8.

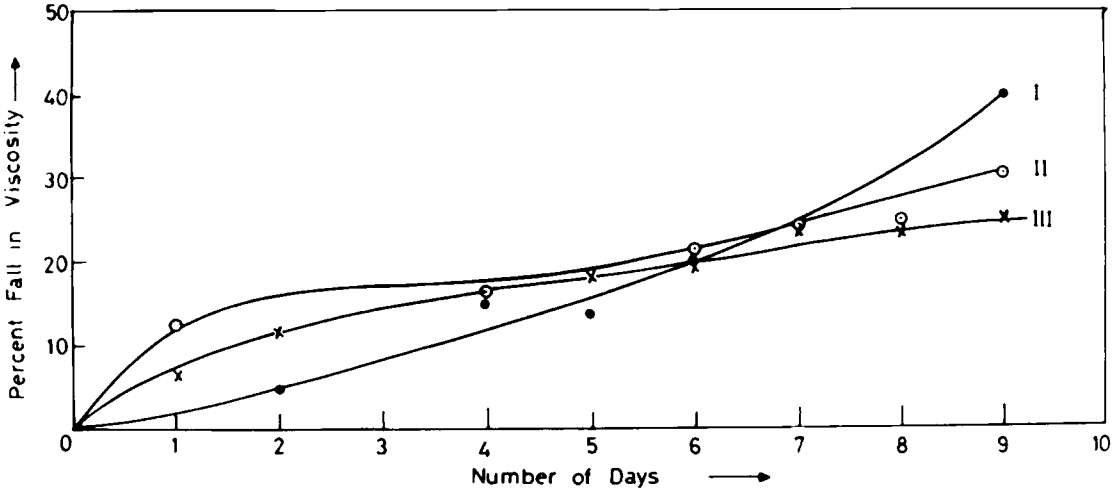

Figure 6 Change in viscosity on storage of 1% aqueous dispersions of the saponified grafted product obtained at 0.3 Mrad under different reaction conditions: set I, M : L = 1 : 20, AGU : AN = 1 : 2; set II, M : L = 1 : 20, AGU : AN = 1 : 4; set III, M : L = 1 : 20, AGU : AN = 1 : 8.

the carbohydrate backbone of the superabsorbent polymer.

The relation between the water absorbency and the viscosity of 1% aqueous dispersion of the corresponding saponified samples of sets I, II, and III are depicted in Figure 4. The water absorbency and the viscosity seem to be independent of each other as far as set I samples are concerned. In the case of set II samples, the water absorbency and the viscosity seem to be inversely proportional to each other. But in the case of set III samples, both the parameters are directly related to each other. On the whole, Figure 4 data once again seem to indicate that the Brookefield viscosity of a gel of the above type is influenced by various parameters and cannot be predicted by any single parameter. The percentage water solubles of the saponified product as shown in Table III show a decreasing trend from set I to set III. The lower water solubles and the higher viscosity of the aqueous dispersions of samples of sets II and III as compared to the samples of set I are indicative of a higher degree of cross linking between the PAN and the backbone polymer. A similar cross-linking effect was observed by Fanta et al.[14] Table V gives the viscosity profile of the aqueous dispersions of the samples at different concentrations, ranging from 1–4%. In general, a drop in the viscosity is observed with the decrease in the concentration of the dispersion. At the same time, it may be noted that considerable variation exists in the rate of fall of viscosity among the samples (Fig. 5), which depicts the change in viscosity with the change in the concentration of aqueous dispersion of the product obtained at 0.2 Mrad dosage under all the three conditions. Set I samples exhibited a rapid drop in the viscosity with the decreasing concentration of the dispersions as compared to the samples of sets II and III. Figure 6 depicts the change in the viscosity of 1% aqueous dispersion of the saponified material obtained from the grafted products of sets I, II, and III at 0.3 Mrad dosage in storage. A maximum drop of 40% in the viscosity is observed for the product I and the lowest drop of about 25% is registered for the product III, at the end of 9 days of observations. The product II records a fall of about 30% for the same period. The rate of degradation, though slow, initially product I with a PAN add-on of about 32% exhibited a continuous degradation registering the maximum fall in viscosity at the end of day 9. In the case of product II with a PAN add-on of 48%, though the initial fall in the viscosity is higher, it soon slows down considerably and registers a fall in viscosity of about 30% at the end of day 9. Product III, with a PAN add-on of about 66%, exhibits a higher fall initially, as compared to product I, subsequently the fall slows down considerably and registers the lowest fall in viscosity at the end of the day 9. As the microbial degradation is mainly responsible for the observed fall in viscosity and the PAN is a known inhibitor of the microbial growth, it is most probably the higher PAN add-on that slows down the fall in viscosity.

CONCLUSIONS

The results of the present study show that the frequency of the grafted side chains and their molecular weights are dependent on the reactant concentration. It also shows that at higher dilution, more short PAN side-chains are grafted. The viscosity of the aqueous dispersions of the various products indicate a positive correlation with the PAN add-on. Though not a definite trend, at the same time the results indicate a positive leaning of the water absorbency of the saponified products with the PAN add-on of the grafted products. The aqueous dispersions of the saponified products with higher PAN add-on exhibit a lower drop in the viscosity on storage. On the whole, the present study provides some means of controlling the structure and properties of the guar gum based superabsorbents.

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