

# Characterization and Solution Properties of a Partially Hydrolyzed Graft Copolymer of Polyacrylamide and Dextran

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**ABSTRACT:** Graft copolymers of dextran (Dx) and polyacrylamide (PAM) were synthesized through the grafting of PAM chains onto a Dx backbone with a ceric-ion-induced solution polymerization technique. By the variation of the amount of the initiator (ceric ammonium nitrate), four different grades of graft copolymers were synthesized. The partial alkaline hydrolysis of Dx-g-PAM was carried out in an alkaline medium. Three grades of partially hydrolyzed products were synthesized through the variation of the amount of alkali. These hydrolyzed graft

copolymers were characterized with elemental analysis, infrared spectroscopy, neutralization equivalent measurements, a rheological technique, scanning electron microscopy, thermal analysis, viscometry, and X-ray diffraction. The flocculation efficiency and viscosifying characteristics of the graft copolymers were enhanced upon their alkaline hydrolysis. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 1297–1303, 2008

**Key words:** graft copolymers; rheology; viscosity

## INTRODUCTION

Dextran [Dx or C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>]<sub>n</sub>] is a polysaccharide consisting of glucose<sup>1</sup> monomers linked mainly (95%) by  $\alpha$ -D-(1,6)-linked units and linked a little (5%) by  $\alpha$ -D-(1,3)-linked branch units. It is produced from sugar beet sucrose, which is fermented by bacterium *leuconostoc mesenteroids* (B512F). Dx is a water-soluble, biodegradable, and versatile polysaccharide used extensively in the wastewater treatment (flocculation), pharmaceutical, photographic, cosmetic, and agricultural industries. Of all polysaccharides, Dx is most readily available on a large scale in a wide variety of molecular weights.

Among polymeric flocculants, synthetic polymers can be tailor-made through the control of the molecular weight, molecular weight distribution, structure of the polymers, and nature and percentage of the ionic groups. Thus, synthetic polymers are very efficient flocculants. Natural polymers, mainly polysaccharides, are biodegradable, low-cost, fairly shear-stable, and easily obtained. The biodegradability of natural polymers reduces the storage life as well as performance. It is thus evident that all polymers,

whether natural or synthetic, have one or another disadvantage.

Many attempts have been made to combine the best properties of both natural and synthetic polymers through the grafting of synthetic polymers onto the backbone of natural polymers.<sup>2</sup> One great advantage thus gained is the subsequently reduced biodegradability because of the drastic change in the original regular structure of the natural polymer as well as the increased synthetic polymer content in the product. It has also been observed that the grafting of shear degradable polymers onto the rigid backbone of polysaccharides provides fairly shear-stable systems.

In our laboratory, many graft copolymers have been synthesized through the grafting of polyacrylamide (PAM) chains onto amylopectin, carboxyl methylcellulose, glycogen, guar gum, sodium alginate, starch, and xanthan gum.<sup>3–8</sup> It has been observed that graft copolymers having fewer and longer chains are more efficient as drag-reducing agent as well as flocculating agents. This is due to the highly branched structure of the graft copolymer, which leads to better approachability of the dangling grafted chains to the contaminants per Singh's model.<sup>9</sup>

It has been observed in some cases that partially hydrolyzed PAM shows better flocculating behavior than PAM itself. Partially hydrolyzed poly(vinyl alcohol) (PVA)-g-PAM has shown similar behavior. These polymers are generally prepared by an alkali

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**TABLE I**  
Synthetic Details of the Graft Copolymers

Polymer	Parameter X	Parameter Y	Intrinsic viscosity (dL/g)
Dx-g-PAM1	0.0306	7.645	6.55
Dx-g-PAM2	0.0204	7.899	6.92
Dx-g-PAM3	0.0153	8.808	7.21
Dx-g-PAM4	0.0122	7.792	7.03

Parameter X = Acrylamide (mol)/CAN (mol  $\times 10^{-5}$ ); parameter Y = Acrylamide (mol)  $\times$  Conversion efficiency; Conversion efficiency = (Weight of the graft copolymer - Weight of polysaccharide)/Weight of acrylamide.

treatment. With hydrolysis, PAM acquires a polyelectrolyte character. As a result, the viscosity of the polymer solution increases because of coil expansion. This enhances the flocculation characteristics.

Graft copolymers of Dx and PAM (Dx-g-PAM1 to Dx-g-PAM4) were synthesized with solution polymerization induced by ceric ammonium nitrate (CAN)/nitric acid. The hydrolysis of the graft copolymers was carried out with an alkali (NaOH). The hydrolyzed grades are called Hyd1 Dx-g-PAM3 to Hyd3 Dx-g-PAM3. In this article, we report the characterization of hydrolyzed and unhydrolyzed graft copolymers of Dx and PAM by elemental analysis, IR spectroscopy, neutralization equivalent (NE) measurements, a rheological technique, scanning electron microscopy (SEM), thermal analysis, viscometry, and X-ray diffraction (XRD).

## EXPERIMENTAL

### Materials

Dx was procured from Sigma Chemicals (St. Louis, MO). Acrylamide was procured from E. Merck (Darmstadt, Germany). CAN was obtained from Loba Chemie (Mumbai, India). Acetone and hydroquinone were supplied by S.D. Fine Chemicals (Bombay, India). Sodium hydroxide and nitric acid were obtained from E. Merck (Mumbai, India).

### Synthesis of the graft copolymers

Grafting reactions were carried out by the Ce(IV)/HNO<sub>3</sub>-induced solution polymerization technique to synthesize the graft copolymers (Dx-g-PAM1 to Dx-g-PAM4). The details of the synthetic procedure are

given elsewhere.<sup>10,11</sup> The graft copolymers were treated with a mixture of formamide and acetic acid (1 : 1 v/v) to remove the homopolymers.<sup>12</sup> The details of the synthetic parameters of the graft copolymers are summarized in Table I.

### Alkaline hydrolysis of the graft copolymers

Three grades of hydrolyzed products were synthesized with Dx-g-PAM3, which was the best performing graft copolymer in terms of flocculation efficiency. The synthetic procedure for these hydrolyzed graft copolymers is described elsewhere.<sup>10</sup> The details of the alkaline hydrolysis parameters are summarized in Table II.

### Characterization

#### Elemental analysis

The elemental analysis of all the hydrolyzed and unhydrolyzed graft copolymers (Dx-g-PAM3) was performed with a series II CHNS/O 2400 analyzer (Shelton, CT). The estimated analysis of three elements (carbon, hydrogen, and nitrogen) was undertaken. The results are shown in Table III.

#### IR spectroscopy

A PerkinElmer (Shelton, CT) 630 IR spectrophotometer was used to record the IR spectra within the range of 4000–400 cm<sup>-1</sup>. The IR spectra of hydrolyzed (Hyd2 Dx-g-PAM3) and unhydrolyzed graft copolymers (Dx-g-PAM3) were recorded in the solid state with a KBr pellet method.

#### Intrinsic viscosity measurements

Viscosity measurements of aqueous solutions of hydrolyzed (Hyd1 Dx-g-PAM3 to Hyd3 Dx-g-PAM3) and unhydrolyzed graft copolymers (Dx-g-PAM3) were carried out with the help of an Ubbelohde viscometer (PISCO, Kolkata, India) (P/2741) at 25  $\pm$  0.1°C.

#### NE measurements

NE is the equivalent of the acid as determined by titration with a standard base.<sup>12</sup> NE of an acid can be

**TABLE II**  
Synthetic Details of the Alkaline Hydrolysis of the Graft Copolymers

Polymer	Volume of 1N NaOH (cc)	Reaction temperature (°C)	Reaction time (h)	Intrinsic viscosity (dL/g)	NE
Hyd1 Dx-g-PAM3	8	50	1	52.3	370.4
Hyd2 Dx-g-PAM3	10	50	1	56.6	312.5
Hyd3 Dx-g-PAM3	12	50	1	54.5	333.3

**TABLE III**  
**Elemental Analysis of the Hydrolyzed Graft Copolymers**

Polymer	Carbon (%)	Hydrogen (%)	Nitrogen (%)
Dx	39.67	6.81	0.08
Dx-g-PAM3	44.28	7.01	14.71
Hyd1 Dx-g-PAM3	37.13	6.16	8.27
Hyd2 Dx-g-PAM3	38.40	6.61	9.34
Hyd3 Dx-g-PAM3	37.02	5.97	8.32

determined in the following way: Let  $x$  grams of a sample of an unknown acid require  $y$  milliliters of  $z$   $N$  NaOH for complete neutralization. Because each 1000 mL of the base contains  $z$  equivalents and the number of equivalents of base required equals the number of equivalents of acid present, the equivalent weight of the acid will be equal to  $(x \times 1000)/(y \times z)$ . NE measurements for three grades of hydrolyzed Dx-g-PAM3 are shown in Table II.

#### Rheological measurements

The rheological measurements of aqueous solutions of hydrolyzed (Hyd2 Dx-g-PAM3) and unhydrolyzed graft copolymers (Dx-g-PAM3) were carried out with an Advanced AR-1000 controlled-stress rheometer (Mumbai, India). A 2° cone with a diameter of 4 cm and with a truncation of 46  $\mu\text{m}$  was used for the measurements.

#### SEM

For this study, the hydrolyzed (Hyd2 Dx-g-PAM3) and unhydrolyzed graft copolymers (Dx-g-PAM3) were used in the form of small granules. A Cam Scan series 2 (Cambridge Scanning Co., Cambridge, United Kingdom) was used for the study.

#### Thermal analysis

The differential thermogravimetry (DTG) analysis of the graft copolymer (Dx-g-PAM3) and hydrolyzed graft copolymer (Hyd2 Dx-g-PAM3) was carried out with a Pyris Diamond TG/DTA SII instrument (PerkinElmer). DTG analysis of the samples was performed up to a temperature of 500°C, starting at 50°C, in an atmosphere of nitrogen. The heating rate was uniform in all cases (10°/min).

#### XRD

Hydrolyzed (Hyd2 Dx-g-PAM3) and unhydrolyzed Dx-g-PAM3 polymers were subjected to XRD analysis. The powdered polymer sample was packed into a hole 2 mm in diameter in a small container made of Perspex [poly(methyl methacrylate)] about 1.5 mm thick. This piece was mounted on the specimen

holder with pressure-sensitive tape so that the X-ray beam would pass through the hole. A PW 1840 diffractometer and a PW 1729 X-ray generator (Phillips, Almelo, Holland) were used for the study; Cu K $\alpha$  radiation was used. The results are shown later in Figure 7.

#### Flocculation study: settling test

The test employed a 25-mL stoppered, graduated cylinder and a stop watch. The slurry sample was placed in the cylinder, the polymer solution was added, and the cylinder was inverted 10 times. After mixing, the cylinder was set upright, and the height of the interface between the supernatant liquid and setting solid bed was measured over time. The settling test was carried out with an iron-ore suspension. A comparison of the settling efficiency of Hyd2 Dx-g-PAM3 was performed with that of the unhydrolyzed graft copolymer Dx-g-PAM3.

## RESULTS AND DISCUSSION

### Synthesis of the graft copolymers

Table I shows the synthetic details of the graft copolymers based on Dx and PAM and produced by a radical polymerization technique in an aqueous medium with a ceric ion/HNO<sub>3</sub> initiation system. The mechanism of ceric-ion-induced initiation involves the formation of a chelate complex that decomposes to generate free-radical sites on the polysaccharide backbone. These active free radicals in the presence of acrylic monomers generate graft copolymers. The amount of CAN was varied to observe the effect with various numbers and lengths of grafted PAM chains. Four grades of graft copolymers (Dx-g-PAM1 to Dx-g-PAM4) were synthesized through the grafting of PAM onto the Dx backbone. In this series, the quantities of Dx and acrylamide were kept constant; only the CAN concentration was changed. The ratio of acrylamide to CAN (parameter X) decreased from Dx-g-PAM1 to Dx-g-PAM4. As the concentration of acrylamide was the same, with an increase in the CAN concentration, the parameter Y relatively increased because of the increase in the conversion efficiency. The average number of grafting sites per backbone molecule depends on the concentration of ceric ion with respect to the polysaccharide, Dx. A low concentration of the catalyst should initiate very few grafting sites, resulting in longer PAM chains. A high concentration of the catalyst should initiate a larger number of grafting sites, thus making the average PAM chains shorter for the same acrylamide concentration. The optimal concentration of the catalyst should initiate a few grafting sites, resulting in longer PAM chains being pro-

duced. This is reflected in the high intrinsic viscosity values and high performance of the flocculants (Dx-g-PAM3).

### Synthesis of the hydrolyzed graft copolymer

In hydrolyzing the graft copolymer (Dx-g-PAM3) of Dx and PAM, the aim was to straighten and expand flexible PAM chains. Three grades of the hydrolyzed product (Hyd1 Dx-g-PAM3 to Hyd3 Dx-g-PAM3) were synthesized through the variation of the amount of the alkali (NaOH). With a low amount of the NaOH solution, a saponification reaction occurred. With the optimum amount of the NaOH solution (Hyd2 Dx-g-PAM3), the maximum number of amide groups was converted to carboxyl groups. A further increase of the NaOH solution led to deetherification of the polysaccharide and depolymerization reactions of the polyacrylate component of the graft copolymers.<sup>13</sup> The details of the alkaline hydrolysis of the graft copolymers are shown in Table II.

### Elemental analysis

The results of the elemental analysis of hydrolyzed graft copolymers are given in Table III. Dx did not show any significant presence of nitrogen. In the case of the graft copolymer (Dx-g-PAM3), there was a considerable percentage of nitrogen, proving the grafting of PAM chains onto the polysaccharide backbone. This can be explained on the basis of fewer and longer branches of PAM on the polysaccharide backbone. In the case of the hydrolyzed graft copolymers, the percentage of nitrogen decreased in comparison with the graft copolymers because of the conversion of  $\text{CONH}_2$  groups to  $\text{COO}^-$  groups.

### IR spectroscopy

A comparison of the IR spectra (Fig. 1) of the graft copolymer (Dx-g-PAM3) and hydrolyzed graft copolymer (Hyd2 Dx-g-PAM3) was undertaken. The presence of strong absorption bands of  $>\text{C}=\text{O}$  ( $1650\text{ cm}^{-1}$ ),  $-\text{NH}$  ( $3331$  and  $3192\text{ cm}^{-1}$ ), and  $\text{C}-\text{N}$  ( $1420\text{ cm}^{-1}$ ) groups for the graft copolymers was proof of the grafting of PAM branches onto the polysaccharide backbone. In the case of the hydrolyzed product, the  $-\text{COO}^-$  (carboxylate ion) group showed clear, strong bands at  $1630$  and  $1500\text{ cm}^{-1}$  due to asymmetric and symmetric stretching of the  $\text{COO}^-$  group. These factors proved the hydrolysis of the grafted product.

### Intrinsic viscosity measurements

The intrinsic viscosities of the graft copolymers and the hydrolyzed graft copolymers are shown in

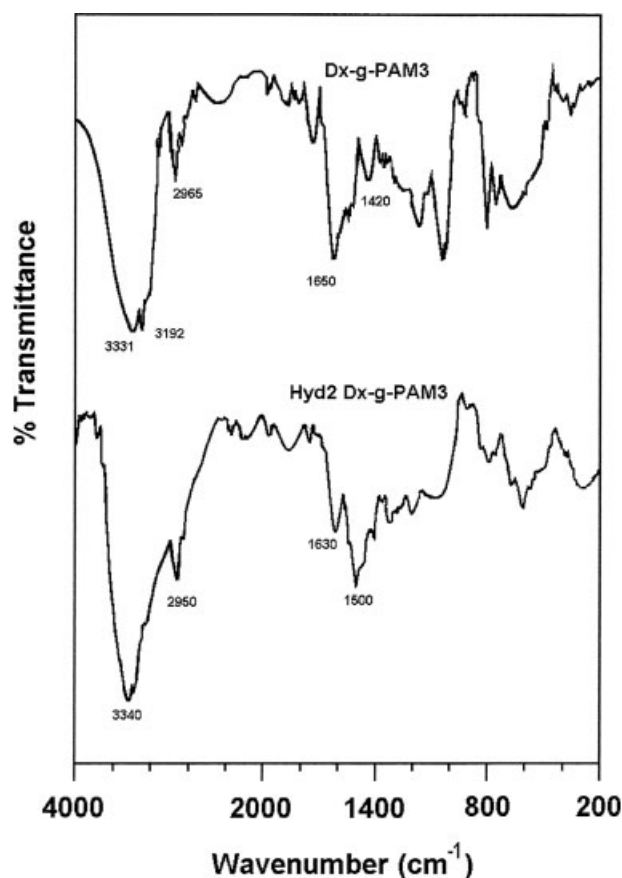


Figure 1 IR spectra of Dx-g-PAM3 and Hyd2 Dx-g-PAM3.

Tables I and II, respectively. With the grafting of PAM chains onto the polysaccharide backbone, two extreme situations are possible. One can have either a large number of short PAM chains or a small number of long PAM chains. In the former case, the original compact shape of the polysaccharide would not be changed to a great extent because of the presence of a large number of short PAM chains. This would result in a lower hydrodynamic volume. In contrast, the presence of a small number of longer PAM chains would change the shape of the polysaccharide to a greater extent, which would thus retain its larger hydrodynamic volume. This would be reflected in its high intrinsic viscosity value.

Furthermore, in a series of graft copolymers, fewer and longer PAM branches lead to a higher intrinsic viscosity. This has been observed in practice. Thus, in the case of Dx-g-PAM3, an increase in the intrinsic viscosity was expected because of the increase in the CAN concentration at a constant acrylamide concentration. It was observed that the hydrolyzed graft copolymers had higher intrinsic viscosities than the graft copolymers. On alkaline hydrolysis,  $\text{CONH}_2$  groups were converted to  $\text{COO}^-$  groups. The electrostatic repulsion among the carboxylic groups led to chain extension, thereby increasing the intrinsic

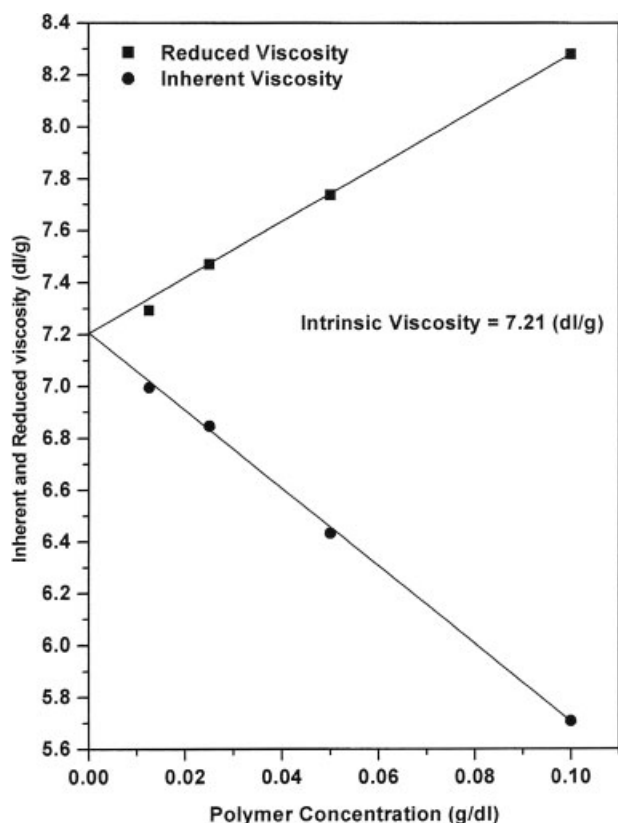


Figure 2 Intrinsic viscosity measurement of Dx-g-PAM3.

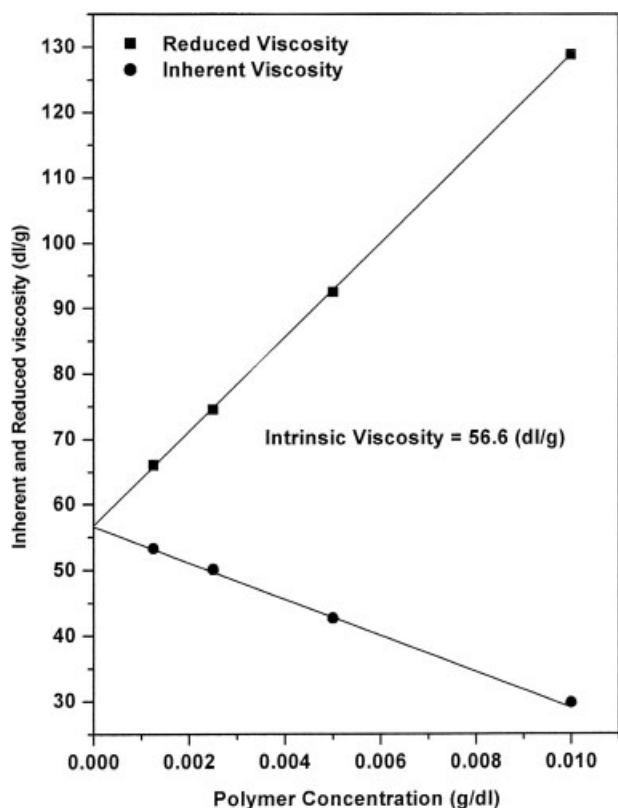


Figure 3 Intrinsic viscosity measurement of Hyd2 Dx-g-PAM3.

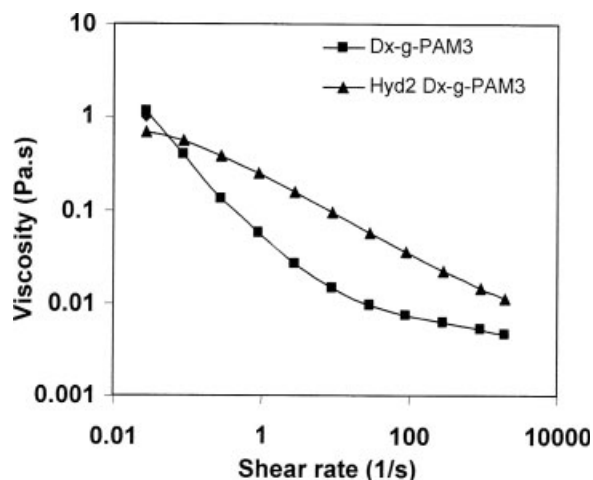


Figure 4 Viscosity versus shear rate curves of the aqueous solutions of Dx-g-PAM3 and Hyd2 Dx-g-PAM3.

viscosity. Curves showing the intrinsic viscosity values of Dx-g-PAM3 and Hyd2 Dx-g-PAM3 are shown in Figures 2 and 3, respectively.

NE measurements

From the NE measurements of partially hydrolyzed Dx-g-PAM3 (Table II), it can be concluded that the carboxyl content of the hydrolyzed samples depended on the alkali concentration. The carboxyl content of the hydrolyzed products increased with

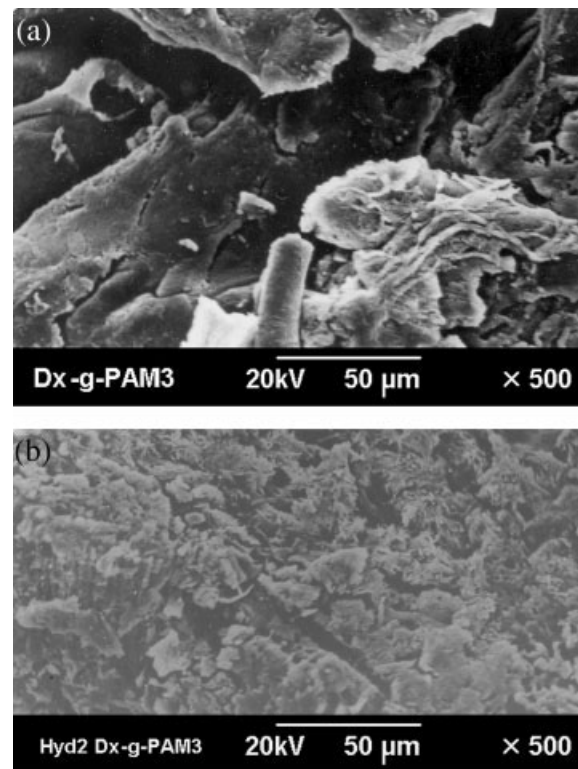


Figure 5 Scanning electron micrographs of (a) Dx-g-PAM3 and (b) Hyd2 Dx-g-PAM3.

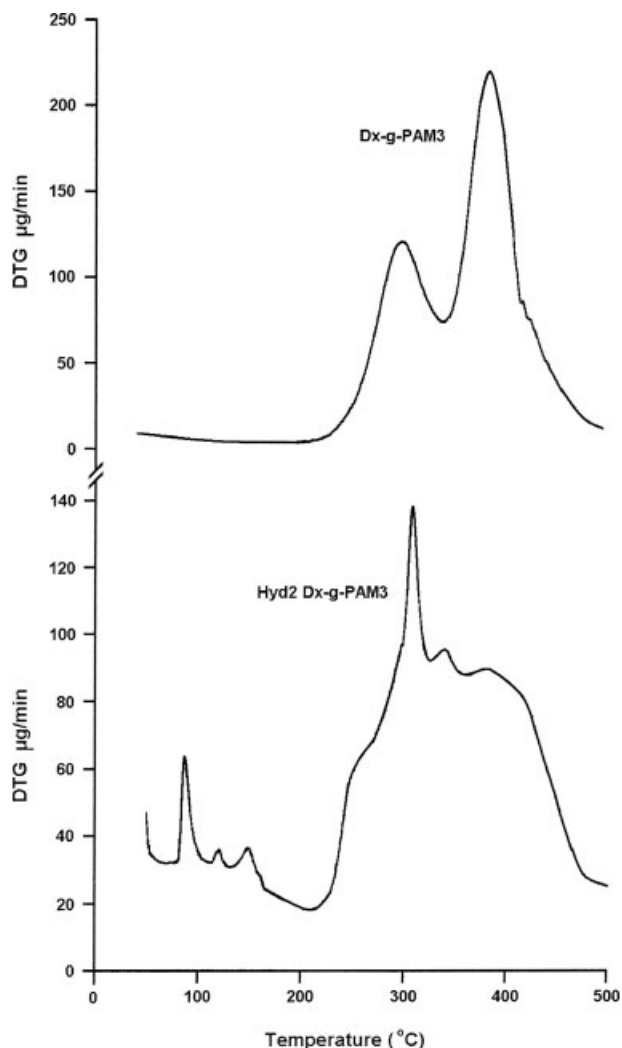


Figure 6 DTG curves of Dx-g-PAM3 and Hyd2 Dx-g-PAM3.

the alkali concentration increasing. NE is equal to the molecular weight of the acid/basicity. During the alkaline hydrolysis of the amide groups, the molecular weight of the polymer would remain the same (because one  $-\text{OH}$  group is incorporated after the expulsion of  $\text{NH}_3$ ). Hence, the greater the number of carboxyl groups is, the lower the NE value will be.

### Rheological studies

The rheological studies of aqueous solutions of Dx-g-PAM3 and Hyd2 Dx-g-PAM3 were carried out at the concentrations of 0.5 and 0.25 wt %, respectively. We plotted the shear viscosity and shear rate on two axes in logarithmic scales.

Figure 4 illustrates a comparison of the viscosities of solutions of Dx-g-PAM3 and Hyd2 Dx-g-PAM3. All samples showed shear-thinning non-Newtonian behavior. The viscosity of a 0.25 wt % hydrolyzed graft copolymer solution was more than that of a 0.5 wt % unhydrolyzed graft copolymer solution. On

hydrolysis, the  $-\text{CONH}_2$  groups of the graft copolymer were converted to  $-\text{COO}^-$  groups. Two negatively charged groups on adjacent carbon atoms repelled each other, so the chain became straightened. Therefore, the viscosity of the hydrolyzed graft copolymers increased versus that of the corresponding graft copolymers.

### SEM

Figure 5(a,b) shows scanning electron micrographs of Dx-g-PAM3 and Hyd2 Dx-g-PAM3, respectively. The surface morphology of Dx-g-PAM3 changed to a porous form in the hydrolyzed product (Hyd2 Dx-g-PAM3). On alkaline hydrolysis of graft copolymer Dx-g-PAM3, polymer chains were straightened, and therefore the amorphous nature increased in Hyd2 Dx-g-PAM3.

### Thermal analysis

The DTG curves of Dx-g-PAM3 and Hyd2 Dx-g-PAM3 are shown in Figure 6. DTG analysis of the graft copolymer (Dx-g-PAM3) showed a peak at  $300^\circ\text{C}$  corresponding to the loss of ammonia in the side chains of PAM. The second peaks at  $390^\circ\text{C}$  corresponded to the decomposition of the polymer. In the hydrolyzed graft copolymer (Hyd2 Dx-g-PAM3),

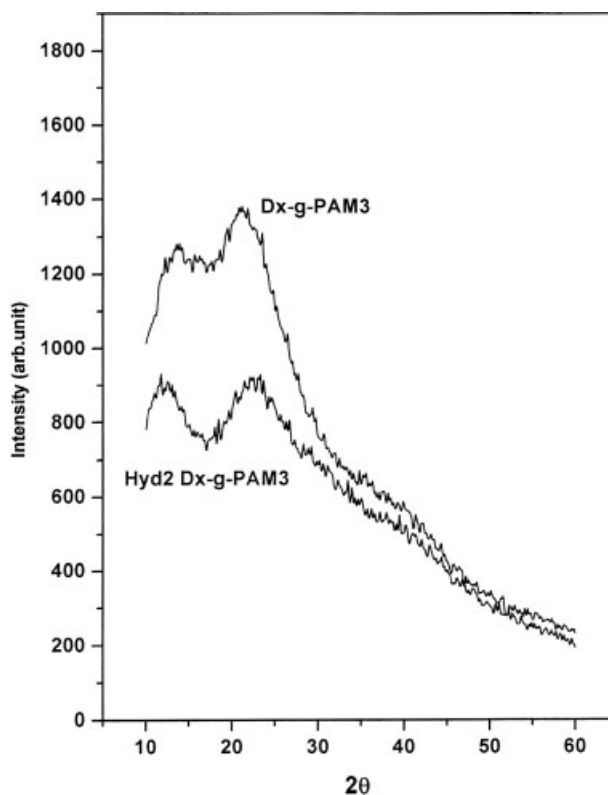
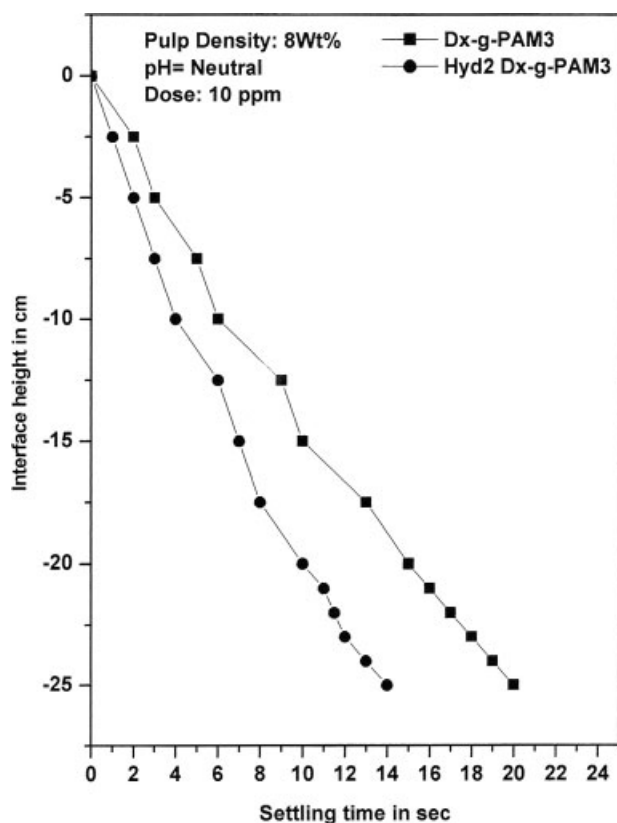


Figure 7 X-ray diffractograms of Dx-g-PAM3 and Hyd2 Dx-g-PAM3.



**Figure 8** Settling curves for the iron ore suspensions with Dx-g-PAM3 and Hyd2 Dx-g-PAM3.

a peak at 310°C corresponded to the degradation of the main chain. The presence of a peak near 100°C showed the hydrophilic nature of the hydrolyzed graft copolymer. From this study, we observed that the graft copolymer had more thermal stability than the corresponding hydrolyzed graft copolymer.

### XRD

The X-ray diffraction patterns of Dx-g-PAM3 and Hyd2 Dx-g-PAM3 at room temperature from  $2\theta = 10^\circ$  to  $2\theta = 60^\circ$  are shown in Figure 7, and the crystallinity was calculated to be 23.65 and 20.39%, respectively. X-ray diffraction studies showed that the crystallinity percentage of the graft copolymer decreased upon partial alkaline hydrolysis. As can be seen from the thermal analysis, alkaline hydrolysis reduced its thermal stability. This was due to the straightening of the partially hydrolyzed grafted PAM chains on Hyd2 Dx-g-PAM3.

### Settling test

Figure 8 shows a comparison of the flocculation performance of Dx-g-PAM3 and Hyd2 Dx-g-PAM3 in an iron-ore suspension. Hyd2 Dx-g-PAM3 showed better performance than the graft copolymer Dx-g-PAM3. In the case of the hydrolyzed graft copoly-

mer, negatively charged groups were created on the polymer backbone, the repulsion among which led to chain expansion and straightening; this led to better approachability toward the contaminants, and hence the flocculation efficiency increased.

### CONCLUSIONS

From this study, it can be concluded that during partial alkaline hydrolysis of Dx-g-PAM, it is possible to control the carboxyl content through the control of the amount of alkali. A decrease in nitrogen in the hydrolyzed graft copolymers proved that hydrolysis really took place. A study of IR spectra provided strong proof of hydrolysis. On hydrolysis, the intrinsic viscosity increased because of repulsion between anionic groups and chain straightening. From the NE values, it was evident that Hyd2 Dx-g-PAM3 had the maximum carboxylic content. According to the DTG curves, on alkaline hydrolysis, the thermal stability of the graft copolymer decreased. A study of the rheology showed that the shear viscosity of the aqueous solution of the hydrolyzed graft copolymer was larger than that of the graft copolymer. The difference in the porous natures of the grafted and hydrolyzed copolymers was clearly visible from the SEM studies.

X-ray diffraction patterns showed that the crystallinity percentage of the graft copolymer decreased upon partial alkaline hydrolysis. By the hydrolysis of PAM-grafted Dx, it is possible to enhance the flocculation capabilities of the virgin polymer. It can thus be used industrially as a viscosifying agent as well as an effective flocculant under various conditions.

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