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Characterization of graft copolymer based on polyacrylamide and dextran

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Abstract

Graft copolymers of dextran and polyacrylamide have been synthesized by grafting polyacrylamide chains onto dextran backbone using a ceric-ion-induced solution polymerization technique. By varying the amount of CAN (ceric ammonium nitrate) initiator, four different grades of graft copolymers (Dx-g-PAM) are synthesized. These graft copolymers are characterized by elemental analysis, infrared spectroscopy, intrinsic viscosity measurement, molecular weight determination, rheological technique, scanning electron microscopy, thermal analysis (DTG) and X-ray diffractometry. They exhibit efficient flocculation characteristics in various suspensions and viscosifying characteristics as well.

Keywords: Flocculation; Graft copolymer; Polysaccharides; Rheology; Water soluble polymers

1. Introduction

Dextran (Dx), $(C_6H_{10}O_5)_n$ is a polysaccharide consisting of glucose (Santos, Jose, & Rodrigues, 1999) monomers, which are linked mainly (95%) by α-D-(1–6) linked units and (5%) α-D-(1–3) linked branch units. It is produced from sugar beet sucrose, which is fermented by bacterium leuconostoc mesenteroids-B512F. Dextran is a water soluble, biodegradable and versatile polysaccharide used extensively in the waste-water treatment (flocculation), pharmaceutical industry, photographic, cosmetic and agricultural industries. The structure (Lapasin & Pricle, 1999) of dextran is shown in Fig. 1.

Flocculation is a process of bringing together small particles to form large particles (flocs), often highly porous in nature. Whereas coagulation of colloidal dispersions by addition of electrolyte such as alum, calcium and iron salts, etc., generally yields coagulants of small sediment volume that filter poorly. Sediments of flocculated suspensions display larger volumes and exhibit greatly enhanced filtration rates. Among polymeric flocculants, the synthetic polymers can be tailor made by controlling molecular weight, molecular weight distribution, the structure of polymers and the nature and percentage of ionic groups. Thus the synthetic polymers are very efficient flocculants (Krishnamoorthi & Singh, 2006).

Many attempts have been made to combine the best properties of both natural and synthetic polymers by grafting synthetic polymers onto the backbone of natural polymers (Swanson, Shogren, Fanta, & Imam, 1993). It has been observed that grafting of shear degradable polymers onto the rigid polysaccharides backbone provides fairly shear stable systems. This can be observed from rheological studies.

In the authors' laboratory, many graft copolymers have been synthesized by grafting polyacrylamide chains onto amylopectin, carboxy methyl cellulose, glycogen, guar gum, sodium alginate, starch and xanthan gum (Singh, Nayak, Biswal, Tripathy, & Banik, 2003; Singh et al., 2000a; Singh et al., 2000b). It has been observed that the graft copolymers having longer chains are more efficient as drag reducing agent as well as flocculating agent. This is due to the

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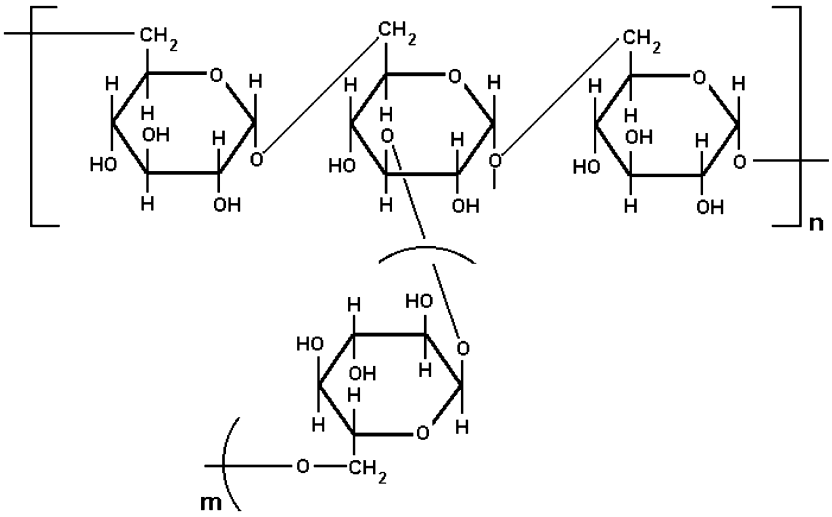

Fig. 1. Structure of dextran.

highly branched structure of graft copolymer, which leads to better approachability of the dangling grafted chains to the contaminants as per Singh's model (Singh, 1995).

The graft copolymers (Dx-g-PAM1 to Dx-g-PAM4) of dextran (Dx) and polyacrylamide (PAM) are synthesized by using ceric ammonium nitrate/nitric acid induced solution polymerization. In this article, we report the characterization of graft copolymers of dextran and polyacrylamide by elemental analysis, IR spectroscopy, intrinsic viscosity measurement, rheological technique, scanning electron microscopy, thermal analysis and X-ray diffractometry.

2. Experimental

2.1. Materials

Dextran was procured from Sigma chemicals USA. Acrylamide was procured from E. Merck, Germany. CAN was obtained from Loba chemie, Mumbai, India. Acetone and hydroquinone was supplied by S.D Fine chemicals, Bombay. Nitric acid was obtained from E. Merck, Mumbai, India.

2.2. Synthesis of graft copolymers

Grafting reaction was carried out by Ce (IV)/HNO_3 induced solution polymerization technique to synthesize graftcopolymers (Dx-g-PAM1 to Dx-g-PAM4). The details of synthetic procedure are given elsewhere (Singh et al., 2004). The graft copolymers were treated with a mixture of formamide and acetic acid (1:1 by volume) to remove the homopolymers (Fanta, 1973). The details of synthetic parameters of the graft copolymers are summarized in Table 1.

2.3. Characterization

2.3.1. Elemental analysis

The elemental analysis of dextran and all the graft copolymers was performed using Series II CHNS/O Analyzer 2400, USA. The estimated analysis of three elements like carbon, hydrogen and nitrogen was undertaken. The results are shown in Table 2.

Table 1
Synthetic details of graft copolymer

Polymer	Parameter ('X')	Parameter ('Y')	Intrinsic viscosity (dl/g)	$M_w \times 10^6$
Dx-g-PAM1	0.0306	7.645	6.55	1.136
Dx-g-PAM2	0.0204	7.899	6.92	1.235
Dx-g-PAM3	**0.0153**	**8.808**	**7.21**	**1.314**
Dx-g-PAM4	0.0122	7.792	7.03	1.265

Parameter ('X') = acrylamide (mole)/CAN (mole $\times 10^{-5}$).
Parameter ('Y') = acrylamide (mole) × conversion efficiency.
Conversion efficiency = (wt of graft copolymer − wt of polysaccharide)/wt of acrylamide.
The bold values represent the polymer showing best flocculation performance.

Table 2
Elemental analysis of graft copolymers

Polymer	Carbon%	Hydrogen%	Nitrogen%
Dx	39.67	6.81	0.08
Dx-g-PAM1	44.19	7.18	8.16
Dx-g-PAM2	46.72	7.14	14.64
Dx-g-PAM3	**44.28**	**7.01**	**14.71**
Dx-g-PAM4	43.97	7.36	14.16

The bold values represent the polymer showing best flocculation performance.

2.3.2. IR spectroscopy

A Perkin-Elmer 630 IR spectrophotometer was used to record the IR spectra within the range of 4000–400 cm^{-1}. The IR spectra of dextran and graft copolymer (Dx-g-PAM3) were recorded in solid state using a KBr pellet method.

2.3.3. Intrinsic viscosity measurements

Viscosity measurements of the aqueous solution of dextran and the graft copolymers (Dx-g-PAM1 to Dx-g-PAM4) were carried out with the help of Ubbelohde viscometer (P/2741) at 25 ± 0.1 °C.

2.3.4. Rheological measurements

The rheological (viscosity vs shear rate) measurements of aqueous solutions of dextran and graft copolymer (Dx-g-PAM3) were carried out using controlled stress AR-1000 Advanced Rheometer. A 2° cone of diameter 4 cm and with truncation of 46 μm was used for the measurements.

2.3.5. Scanning electron microcopy

For this study, dextran was used in the powder form, whereas the graft copolymer (Dx-g-PAM3) was in the form of small granules. A CAM SCAN SERIES-2 (Cambridge Scanning Company, UK) was used for the above study.

2.3.6. Thermal analysis

The differential thermo gravimetric (DTG) analysis of dextran and the graft copolymer (Dx-g-PAM3) were carried out with a PYRIS Diamond TG/DTA Perkin-Elmer SII Instrument (USA). DTG analysis of the samples was performed upto a temperature of 500 °C, starting from 50 °C in an atmosphere of nitrogen. The heating rate was uniform in all cases at 10°/min.

2.3.7. X-ray diffractometry

Dextran and the graft copolymer (Dx-g-PAM3) were subjected to XRD analysis. A PW 1840 diffractometer and PW 1729 X-ray generator (Phillips, Holland) were used. For this study CuK_{α} radiation was used.

2.4. Flocculation study

2.4.1. Settling test

The test employs a 25 ml stoppered graduated cylinder and stop watch. The slurry sample is placed in the cylinder, the polymer solution is added, and the cylinder is inverted 10 times. After mixing, the cylinder is set upright and the height of interface between the supernatant liquid and setting solid bed is measured over time. The settling test was carried out using iron ore suspension. Comparison of settling efficiency of Dx-g-PAM3 was done with polyacrylamide and commercially available flocculants.

3. Results and discussion

3.1. Synthesis of graft copolymer

Table 1 shows the synthetic details of the graft copolymers based on dextran and polyacrylamide by a radical polymerization technique in aqueous medium using a ceric-ion/HNO_3 initiation system. The mechanism of ceric-ion-induced initiation involves the formation of 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 in order to observe the effect with varying number and length of grafted PAM chains. Four grades of graft copolymers (Dx-g-PAM1 to Dx-g-PAM4) were synthesized by grafting polyacrylamide onto the dextran 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') decreases from Dx-g-PAM1 to Dx-g-PAM4. As the concentration of acrylamide was the same, by increasing the CAN concentration the parameter 'Y' relatively increases, because of the increase in conversion efficiency. The average number of grafting sites per backbone molecule depends on the concentration of ceric-ion to polysaccharide, Dx. At low concentration of catalyst should initiate a very few grafting sites resulting in longer polyacrylamide chains. The high concentration of catalyst will initiate a larger number of grafting sites thus making the average polyacrylamide chains shorter for the same acrylamide concentration. The optimal concentration of catalyst should initiate a few grafting sites resulting in longer polyacrylamide chains. This is reflected into high intrinsic viscosity value and high performance as flocculants of (Dx-g-PAM3).

3.2. Elemental analysis

The results of elemental analysis of Dx and its graft copolymers are given in Table 2. Dx does not show any significant presence of nitrogen. In case of graft copolymers, it is found that there is considerable percentage of nitrogen proving the grafting of PAM chains on the polysaccharides backbone. In the series of graft copolymers with Dx, highest percentage of nitrogen is observed in case of Dx-g-PAM3. This can be explained on the basis of fewer and longer branches of polyacrylamide on the polysaccharide backbone.

3.3. IR spectroscopy

The comparison of IR spectra (Fig. 2) of dextran (Dx) and graft copolymer (Dx-g-PAM3) have been undertaken. In the IR spectrum of Dx, the peak present at 3400 cm^{-1} is due to the stretching frequency of O–H groups. The bands at 1020 and 2950 cm^{-1} are assigned to C–O and C–H stretching, respectively. One peak at 1250 is due to –OH bending vibrations. It is apparent that the presence of strong absorption bands of >C═O (1650 cm^{-1}), –NH (3331 and 3192 cm^{-1}) and C–N (1420 cm^{-1}) groups in the graft copolymer is a proof of grafting of PAM branches onto the polysaccharide backbone. (Since homopolymers were removed by solvent extraction.)

3.4. Intrinsic viscosity measurements

The intrinsic viscosities of dextran (Fig. 3a) and the graft copolymer are shown in Table 1. With grafting of PAM chains onto the polysaccharides 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 polysaccharide would not be changed to a greater extent because of

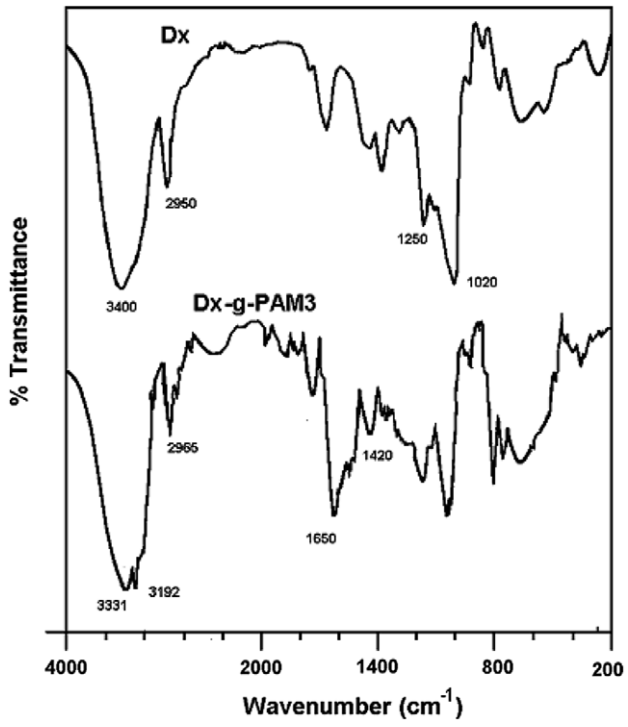

Fig. 2. IR spectrum of Dx and Dx-g-PAM3.

the presence of a large number of short PAM chains. This would result in lower hydrodynamic volume. By contrast, presence of small number of longer PAM chains would change the shape of polysaccharide to a greater extent, thus retaining its larger hydrodynamic volume. This is reflected in its high intrinsic viscosity value.

Further, along a series of graft copolymers, fewer and longer PAM branches leads to higher intrinsic viscosity (Fig. 3b). This has been observed in practice. Thus in case of Dx-g-PAM3, an increase in intrinsic viscosity is expected because of the optimum CAN concentration at the constant acrylamide concentration.

3.5. Calculation of approximate molecular weight

Molecular weight of the polymer samples can be estimated from the intrinsic viscosity [η] values. Mark Houwink equation, $[\eta]=KM^{\alpha}$ is generally employed for the estimation of molecular weight of linear polymers where K and α values are constant for a particular polymer/solvent/temperature system. For PAM the values of K and α are $[\eta]=6.31\times10^{-5}\ (M_w)^{0.80}$ where M_w is the weight-average molecular weight (Biswal & Singh, 2004). The percentage of polysaccharides is small in comparison with the polyacrylamide. Hence, in case of the grafted polysaccharides, several workers (Erciyes, Erim, Hazar, & Yagaci, 1992; Tripathy, Karmakar, & Singh, 2000) have used the Mark Houwink equation for PAM to estimate approximate M_w. It has been observed that due to the longer PAM chains, Dx-g-PAM3 has highest molecular weight than the other graft copolymers.The results of M_w of graft copolymers are shown in Table 1.

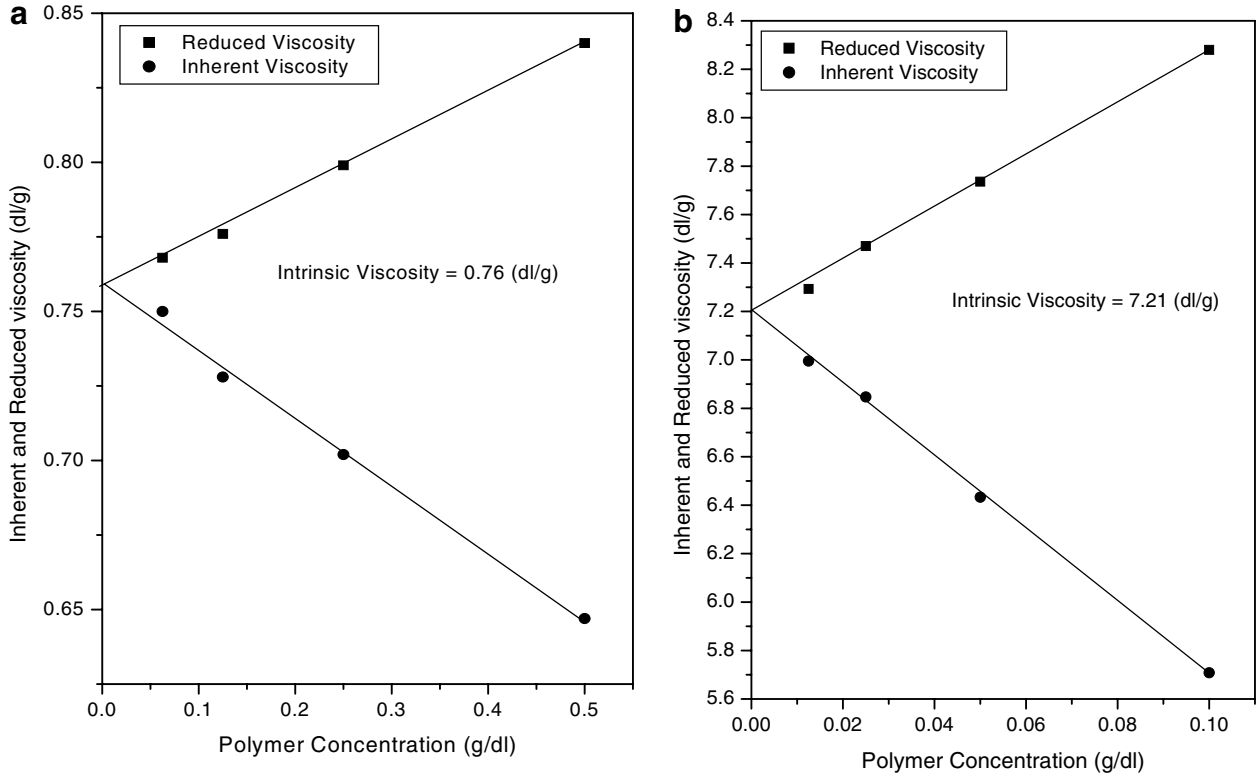

Fig. 3. (a) Intrinsic viscosity measurement of Dx. (b) Intrinsic viscosity measurement of Dx-g-PAM3.

3.6. Rheological studies

The rheological studies of aqueous solution of Dx and Dx-g-PAM3 were carried out at concentrations of 2 and 0.5 wt%, respectively. The shear viscosity and shear rate on two axes in logarithmic scales were plotted.

Fig. 4 illustrates the shear viscosity versus shear rate curves of dextran and PAM grafted dextran in aqueous solution. In both the cases, the shear viscosity decreases with increase in shear rate and the samples show shear thinning non-Newtonian behaviour (pseudoplastic). The viscosity of 0.5 wt% of graft copolymer solution is more than 2 wt% of dextran solution at all shear rates. This is due to the longer PAM chains grafted onto the dextran backbone, similar results also obtain from intrinsic viscosity values. From the above rheological study, it is observed that, by the grafting of PAM chains on to polysaccharide backbone, shear stable and viscosifying polymer materials are obtained.

3.7. Scanning electron microcopy

Fig. 5 shows the scanning electron micrographs Dx, Dx-g-PAM3. Surface morphology of Dx before grafting shows a spherical structure, which has been changed to fibrillar form after grafting. Some indication of chain straightening is clearly evident.

3.8. Thermal analysis

The DTG curves of Dx and Dx-g-PAM3 are shown in Fig. 6. DTG analysis of Dx shows a small peak at 110 °C due to the absorbed moisture in the sample. The second weight lose peak at 312 °C due to the total decomposition of dextran molecule. Whereas in the graft copolymer, peak at 300 °C corresponds to the loss of ammonia in the side

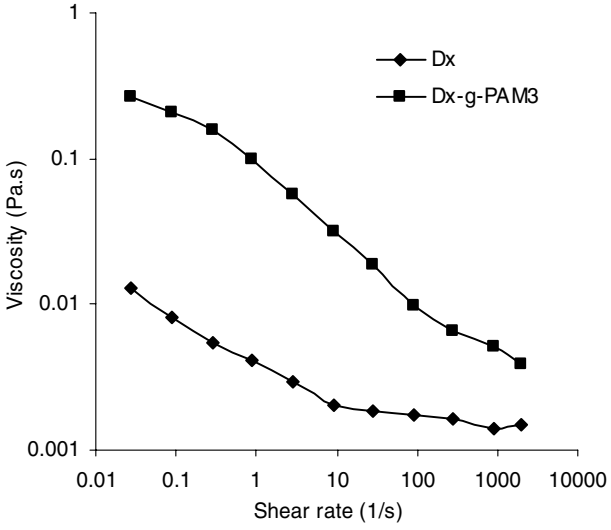

Fig. 4. Viscosity versus shear rate curves of the aqueous solutions Dx and Dx-g-PAM3.

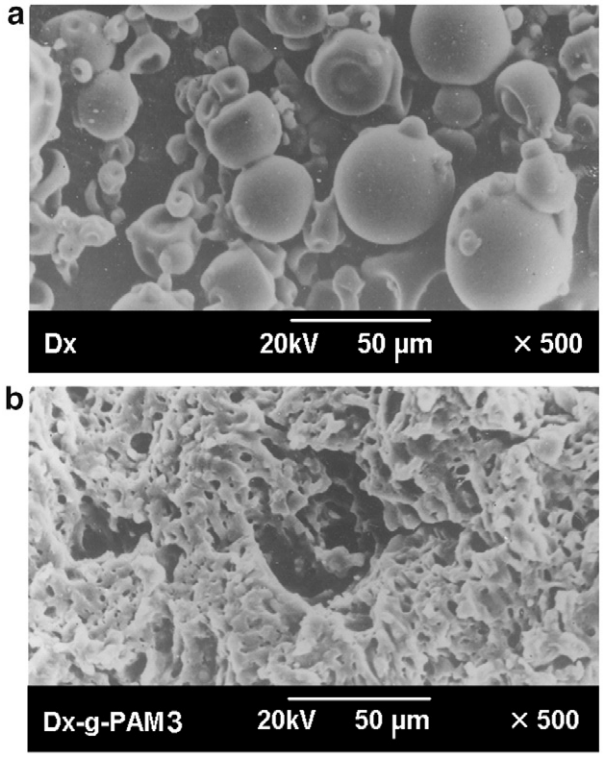

Fig. 5. (a) Scanning electron micrographs of Dx. (b) Scanning electron micrographs of Dx-g-PAM3.

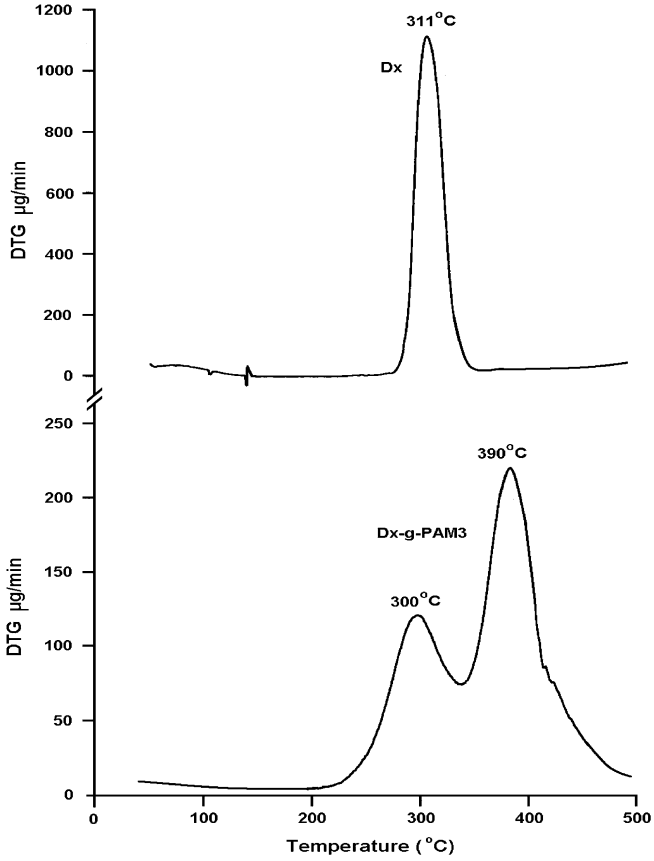

Fig. 6. DTG curves of Dx and Dx-g-PAM3.

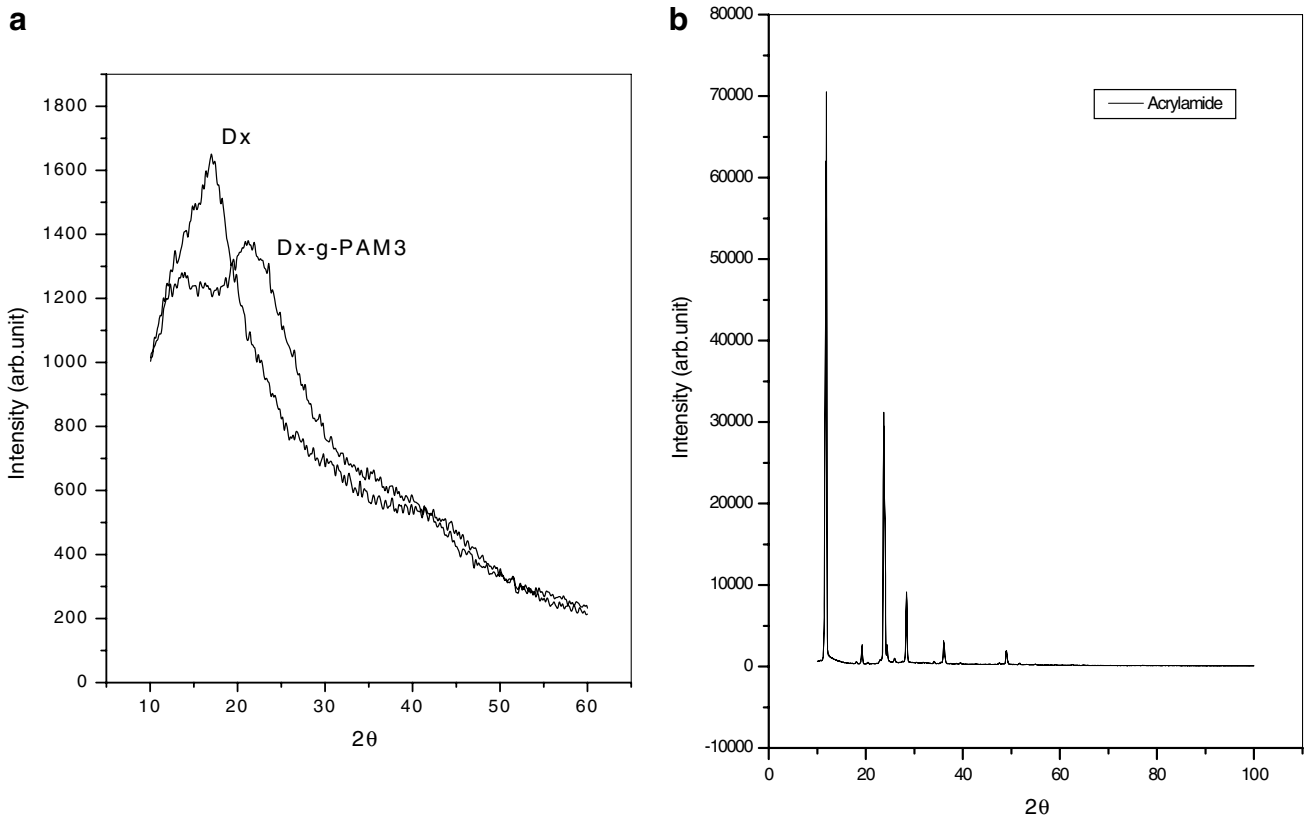

Fig. 7. (a) X-ray diffractograms of Dx and Dx-g-PAM3. (b) X-ray diffractograms of acrylamide.

chains of PAM. The second peaks at 390 °C which is corresponding to the decomposition of the polymer. From this study, it is observed that graft copolymer has more thermal stability than the polysaccharide. Absence of peak near 100 °C shows the absence of hydrophilic nature of graft copolymer.

3.9. X-ray diffractometry

XRD analysis of Dx and Dx-g-PAM3 (Fig. 7a) does not indicate crystallinity in contrast to acrylamide (Fig. 7b) which shows high crystallinity. This is indicative of absence of acrylamide.

4. Settling test

Fig. 8 is a comparison among the various graft copolymers (Dx-g-PAM1 to Dx-g-PAM4) in iron ore suspension. Among all the graft copolymers Dx-g-PAM3 which has fewer and longer polyacrylamide branches as evident from intrinsic viscosity values, performs, as the best flocculant.

In Fig. 9 the efficiency of Dx-g-PAM3 has been compared with polyacrylamide and three commercial flocculants, namely, Magnafloc LT22, Rishfloc 440 HV and Rishfloc 226 LV in iron ore suspension.

Dx-g-PAM3 has been chosen among the other graft copolymers because this is the best performing graft copolymer among other graft copolymers. Here, the graft

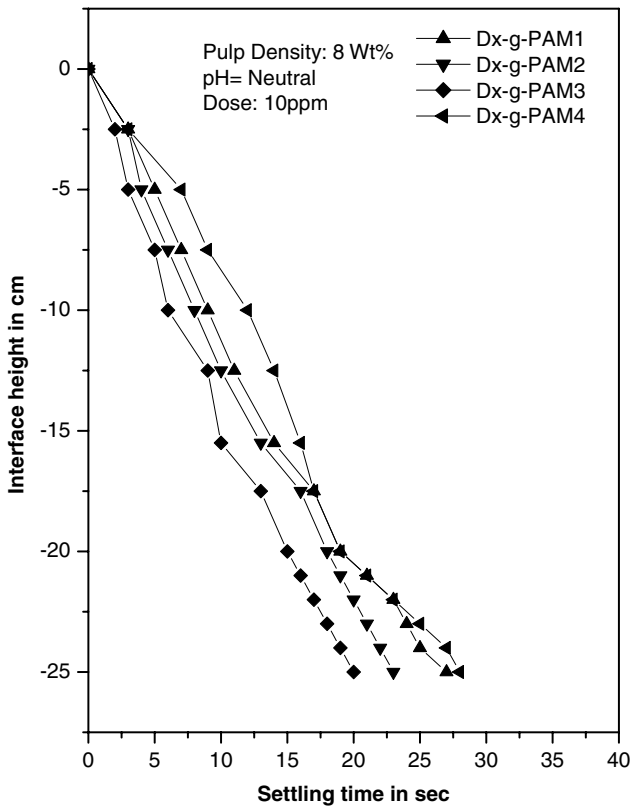

Fig. 8. Settling curves for iron ore suspension using various grades of graft copolymers of dextran and PAM.

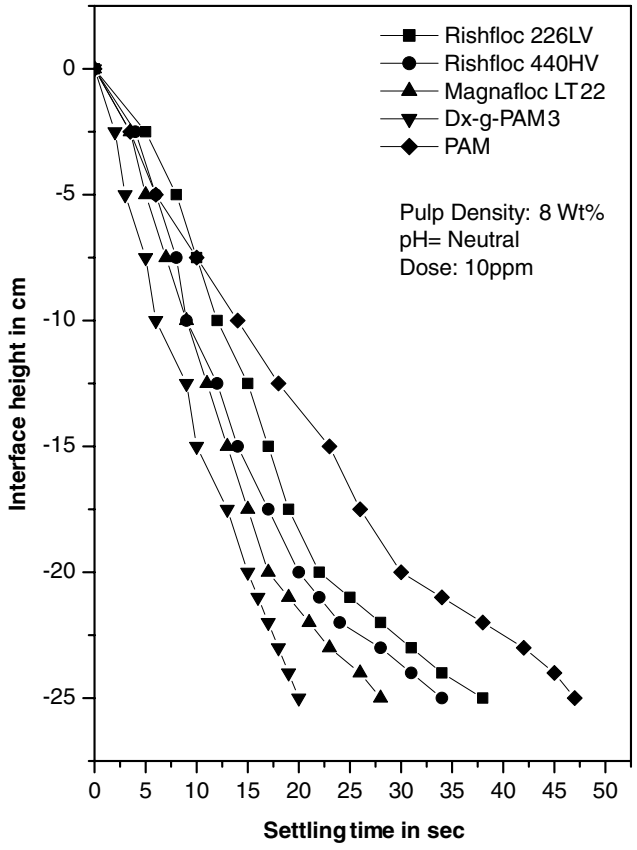

Fig. 9. Settling curves for iron ore suspension using Dx-g-PAM3, PAM and commercial flocculants.

copolymer dominates the commercial flocculants in terms of flocculation efficiency. In case of linear polymers, the polymer segments attach to the surface in trains, project into the solution as tails or to form a part of loops, which link tail together. By this way, they can form bridges between the colloidal particles to form flocs. In the case of graft copolymers, due to the better approachability of the grafted chains, they can easily bind the colloidal particles through bridging. This type of intense bridging is not possible in case of linear polymers.

5. Conclusions

The present results conclude the occurrence of grafting of PAM onto Dx. Variation in the synthetic parameters results in a series of graft copolymers with varying number and length of PAM chains results in different intrinsic viscosities as well as different molecular weights. Study of IR spectra provides a strong proof of grafting. DTG results shows thermal stability pattern for the base polysaccharide and the corresponding graft copolymer. Shear viscosity of the aqueous solution of the graft copolymer are larger than that of polysaccharide. Morphology variation of Dx and graft copolymers also supports the above conclusion. X-ray diffraction pattern shows the absence of acrylamide in the grafted product. The graft copolymer in every way is more stable than the base polysaccharide. It can thus used industrially as viscosifying agent as well as effective flocculant at various conditions.

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