Carbohydrate Polymers 81 (2010) 626–632

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Graft copolymerization of 2-Acrylamidoglycolic acid on to xanthan gum and study of its physicochemical properties

Arpit Sand, Mithilesh Yadav, Kunj Behari*

Polymer Science Research Laboratory, Department of Chemistry, University of Allahabad, Allahabad 211002, India

ARTICLE INFO

Article history:
Received 9 February 2010
Accepted 9 March 2010
Available online 16 March 2010

Keywords:
Graft copolymer
Potassium bromate
Thiourea
IR spectroscopy
Thermal analysis

ABSTRACT

Graft copolymer of xanthan gum and 2-Acrylamidoglycolic acid has been synthesized by free radical polymerization using bromate/thiourea redox pair in an inert atmosphere. The grafting parameters, i.e. grafting ratio, add on and efficiency decrease with increase in concentration of xanthan gum from $1.0\,\mathrm{g\,dm^{-3}}$ and hydrogen ion from $5 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$, but these grafting parameters increase with increase in concentration of 2-Acrylamidoglycolic acid from 2.6×10^{-2} to $8.0 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$, and bromate 6×10^{-3} to $14 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$. Water swelling capacity, metal ion sorption, flocculation studies and resistance to biodegradation of synthesized graft copolymer has been performed with respect to the parent polymer. The graft copolymer has been characterized by infrared (IR) spectroscopy and thermogravimetric analysis.

1. Introduction

Grafting provides a convenient method for tailoring material properties to specific end uses. Now-a-days more emphasis is given to biodegradable polymers such as polysaccharides and proteins, which have been extensively used and investigated for industrial applications. Xanthan gum is extensively used in the petroleum industry for enhanced oil recovery because it is drag reducing agent with good shear stability. But it faces a tough competition from synthetic polymers such as polyacrylamide which are better drag reducing agents although they lack good shear stability. Studies have shown that graft copolymers formed between acrylamide and other polysaccharides, e.g. guar gum, carboxymethyl cellulose give the good drag reducing effectiveness of polyacrylamide and shear stability of polysaccharides (Deshmukh, Sudhakar, & Singh, 1991; Kanan, 1998; Prasad, Mark, & Fai, 1995; Singh et al., 1991). Therefore, in this paper, studies were carried out to graft 2-Acrylamidoglycolic acid onto xanthan gum. The change of thermal stability before and after grafting 2-Acrylamidoglycolic acid onto xanthan gum was also investigated. The synthesized graft copolymer (xanthan gum-g-2-Acrylamidoglycolic acid) may be used as superabsorbent, coating materials and flocculant to remove impurities from coal mine wastewater. 2-Acrylamidoglycolic acid (AGA) is a cationic hydrophilic monomer with the availability of improved process for the synthesis and purification of 2-Acrylamidoglycolic acid. 2-Acrylamidoglycolic acid (AGA) refers to a class of acrylamides containing –OH, –COOH and –CONH– functional groups (Rao, Chung & Ha, 2008).

2. Materials and methods

2.1. Materials

2-Acrylamidoglycolic acid (Aldrich), potassium bromate (E. Merck), Xanthan gum (Sigma, USA) and thiourea (E. Merck) were used as such. For maintaining the hydrogen ion concentration sulphuric acid (E. Merck) was used. The other chemical reagents were of analytical grade. All the solutions were prepared in triple distilled water. For flocculation studies, coking and non-coking coals were used received from Bokaro Steel Plant, India.

2.2. Procedure for copolymerization

For each experiment xanthan gum solution has been prepared by addition of weighed amount of xanthan gum into reactor containing triple distilled water with rapid stirring. A calculated amount of xanthan gum, 2-Acrylamidoglycolic acid, sulphuric acid and thiourea were added into the reactor and a slow stream of oxygen free nitrogen gas was passed for 30 min at constant temperature. A known amount of deoxygenated bromate solution was added to initiate the reaction. The reaction was performed under a continuous flow of oxygen free nitrogen gas. After desired time period, the reaction was stopped by letting air into reactor. The reaction mixture was poured in a water methanol mixture. Thus grafted material was precipitated, separated, dried and weighed. The poly 2-Acrylamidoglycolic acid remained in the filtrate. To the filtrate a pinch of hydroquinone was added and concentrated by

---

* Corresponding author. Tel.: +91 9005807357.
E-mail address: sand.arpit@gmail.com (K. Behari).

0144-8617/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2010.03.022

Table 1
Effect of $BrO^-{}_3$ ion concentration.

$[BrO^-{}_3] \times 10^3$ mol dm^{-3}	%G	%E	%A	%C	%H
6	204.2	64.8	67.1	36.1	35.1
8	236.6	67.9	70.2	40.2	30.6
10	243.3	74.3	71.1	38.4	25.8
12	259.6	78.5	72.1	38.2	21.5
14	182.5	64.2	65.1	33.5	35.8

[AGA] = 5.3×10^{-2} mol dm^{-3}, [H$^+$] = 4×10^{-3} mol dm^{-3}, Time = 120 min, [XOH] = 1.0 g dm^{-3}, [TU] = 2.8×10^{-3} mol dm^{-3}, Temp. = 40 °C.

distillation under reduced pressure. The poly 2-Acrylamidoglycolic acid was precipitated by pouring it into pure methanol, separated, dried and weighed.

3. Methods of characterization of xanthan gum/xanthan gum-g-2-Acrylamidoglycolic acid

3.1. FTIR analysis

The grafting reaction is confirmed by Perkin-Elmer FTIR model and infrared spectra of xanthan gum and grafted samples have been recorded in the range of 500–4000 cm^{-1}.

3.2. TGA/DTA analysis

The thermograms have been recorded with NETZSCH—Geratebau GmbH thermal analyser in an inert atmosphere.

4. Study of physicochemical properties

4.1. Swelling test

For the swelling studies, 0.02 g of each grafted sample synthesized by varying the concentration of 2-Acrylamidoglycolic acid, has been taken and immersed in 20 ml of triple distilled water and kept undisturbed for 24 h. The surface water on the swollen graft copolymer has been removed by softly pressing it between the folds of filter paper. An increase in weight of graft copolymer has been recorded. Calculation of the percent swelling (P_S) and swelling ratio (S_R) has been made by the following expression (Hegazy El-Sayed, EL-Rehim Abd, & Ali, 2000):

$$\text{swelling ratio } (S_R) = \frac{\text{weight of swollen sample} - \text{weight of dry sample}}{\text{weight of dry sample}}$$

$$\text{Percent swelling } (\mathrm{P_S}) = \mathrm{S_R} \times 100$$

4.2. Metal ion sorption test

The metal ion sorption study has been carried out by using samples of graft copolymers synthesized by varying the concentration of 2-Acrylamidoglycolic acid from 2.6×10^{-2} to 8.0×10^{-2} mol dm^{-3}. For this study, 0.02 g of graft copolymer has been taken in 10 ml of metal ion solution of known concentration, and kept for 24 h. The strength of sorbed metal ion has been determined by titrating the remaining metal ions. The results of sorption behaviour of xanthan gum and its grafted polymer with 2-Acrylamidoglycolic acid have been determined in terms of different parameters (Rivas, Maturana, Molina, Gomez-Anton, & Pierola, 1998), i.e. percent ion-uptake (P_u), partition coefficient (K_d), retention capacity (Q_r):

$$\text{percent uptake } (P_u) = \frac{\text{amount of metal ion in the polymer}}{\text{amount of metal ion in feed}} \times 100$$

$$\text{partition coefficient } (K_d) = \frac{\text{amount of metal ion in the polymer}}{\text{amount of metal ion left in the solution}} \times \frac{\text{volume of solution (ml)}}{\text{weight of dry polymer}}$$

$$\text{retention capacity } (Q_r) = \frac{\text{amount of metal ion in the polymer (m Eq.)}}{\text{weight of dry polymer (g)}}$$

4.3. Flocculation test

In 1.0 l beaker, 200 ml of 1 wt.% coal suspension was taken. The stirrer blade of the flocculator was dipped in the suspension. Under low stirring condition, required quantity of polymer solution was added to beaker to make predetermined dose with respect of suspension volume. After the addition of polymer solution, the suspension was stirred at a constant speed for 15 min. The flocs were allowed to settle down for half an hour. Clean supernatant liquid was withdrawn from a depth of 1.0 cm and its turbidity was measured using a digital nephelometer (supplied by ISO-TECH System, Varanasi, India) to express the turbidity in nephelometric unit (NTU).

4.4. Resistance to biodegradability

Resistance to biodegradability of xanthan gum and xanthan gum-g-2-Acrylamidoglycolic acid has been measured in terms of viscosity and hence viscosity is calculated with the help of Ubbelohde capillary viscometer at constant temperature, i.e. at 30 °C.

5. Results and discussion

5.1. Estimation of grafting parameters

Grafting parameters were calculated according to Fanta (1973) definition:

$$\text{grafting ratio } (\%G) = \frac{\text{grafted polymer}}{\text{weight of substrate}} \times 100$$

$$\text{add on } (\%A) = \frac{\text{synthetic polymer}}{\text{graft copolymer}} \times 100$$

$$\text{conversion } (\%C) = \frac{\text{polymer formed}}{\text{monomer charged}} \times 100$$

$$\text{grafting efficiency } (\%E) = \frac{\text{grafted polymer}}{\text{polymer formed}} \times 100$$

$$\text{homopolymer } (\%H) = 100 - \%E$$

5.2. Determination of optimum reaction conditions

The effect of variation of bromate, thiourea, 2-Acrylamidoglycolic acid, xanthan gum (XOH), sulphuric acid, along with time and temperature on grafting parameters has been studied.

Table 2
Effect of concentration of hydrogen ion.

$[H^+] \times 10^3$ mol dm^{-3}	%G	%E	%A	%C	%H
2	244.1	57.1	70.9	39.6	42.8
3	274.3	61.3	73.2	41.5	38.7
4	243.3	74.3	71.1	38.4	25.8
5	227.1	72.9	73.9	36.1	27.1
6	200.3	60.3	72.1	40.1	39.6

$[AGA] = 5.3 \times 10^{-2}$ mol dm^{-3}, $[BrO^-{}_3] = 10 \times 10^{-3}$, Time = 120 min, [XOH] = 1.0 g dm^{-3}, $[TU] = 2.8 \times 10^{-3}$ mol dm^{-3}, Temp. = 40 °C.

5.3. Effect of bromate concentration

The bromate–thiourea system was a novel initiator for the aqueous polymerization of vinyl monomers (Srivastava et al., 2007). It has been found that neither potassium bromate nor thiourea, when used alone, can initiate the polymerization. The effect of bromate ion concentration on grafting reaction was studied and the results were summarised in Table 1. It was observed that grafting ratio, efficiency and add on increase on increasing the bromate concentration from 6.0×10^{-3} to 10×10^{-3} mol dm^{-3} but beyond this concentration range grafting ratio, efficiency and add on decrease. The enhancement of grafting parameters within the cited range of bromate concentration is due to the progressive reduction of potassium bromate with thiourea producing bromide anion and isothiocarbamide free radicals which attack on the xanthan gum molecule creating more free radicals site onto which monomer addition takes place. The grafting ratio, efficiency and add on decrease on increasing the bromate ion concentration due to one of following reason:

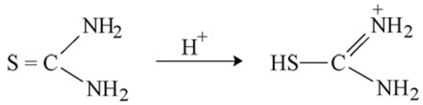
1. At higher bromate ion concentration, it might react with the gum macro radical or with the growing radical, thus inhibiting the extent of grafting.
2. Oxidation of the active groups on the backbone takes place, thereby preventing the formation of free radicals.
3. Inhibition due to the liberation of appreciable amount of oxygen takes place, which acts as a scavenger.

5.4. Effect of thiourea concentration

The effect of thiourea on grafting parameters has been studied by varying the concentration from 1.2×10^{-3} to 4.4×10^{-3} mol dm^{-3}. It has been observed that grafting ratio, add on, and efficiency increase on increasing the concentration of thiourea up to 2.8×10^{-2} mol dm^{-3} but thereafter grafting parameters decrease. The increase in grafting parameters might be attributed to the increase in number of primary free radicals with increase in thiourea concentration up to a certain value. The decrease in these grafting parameters might be due to the premature termination of growing grafted chains.

5.5. Effect of hydrogen ion concentration

The effect of hydrogen ion concentration on grafting parameters has been presented in Table 2 and it reveals that grafting ratio, efficiency, add on increase up to 4.0×10^{-3} mol dm^{-3} this can be explained that on increasing $[H^+]$, the formation of protonated thiourea species also increases which reacts with bromate ion giving rise to primary free radicals and these radicals react with xanthan gum and 2-Acrylamidoglycolic acid, giving rise to free radicals which were responsible for increasing grafting parameters:



But on further increasing the concentration of hydrogen ion, i.e. beyond 4×10^{-3} mol dm^{-3} the grafting ratio, efficiency and add on was found to decrease, might be due to the fact that hydrogen ion react with bromate to form $HBrO_3$. This species further decompose to give oxygen which act as scavenger and grafting parameters show decreasing trend:

$$2KBrO_3 + H_2SO_4 \rightarrow 2HBrO_3 + K_2SO_4$$

$$2HBrO_3 + Br_2 \rightarrow H_2O + O_2$$

5.6. Effect of 2-Acrylamidoglycolic acid

The effect of concentration of 2-Acrylamidoglycolic acid on grafting parameters has been investigated by varying the concentration of 2-Acrylamidoglycolic acid from 2.6×10^{-2} to 8.0×10^{-2} mol dm^{-3}. It has been observed that grafting ratio, add on and efficiency increase on increasing the concentration up to 5.3×10^{-2} mol dm^{-3} and thereafter, grafting parameters decrease. However the formation of homopolymer shows a reverse trend with respect to grafting efficiency. This behaviour is attributed to accumulation of monomer molecules at close proximity of polymeric backbone. The monomer molecules, which are at the immediate vicinity of reaction sites, become acceptors of xanthan gum macro radicals resulting in chain initiation and thereafter themselves become free radical donor to the neighbouring molecules causing the lowering of termination. The decrease in grafting ratio and add on could be interpreted in terms of increase in viscosity of the medium.

5.7. Effect of xanthan gum concentration

The effect of concentration of xanthan gum has been observed with an aim to study the effect of its concentration (from 0.6 to 1.6 g dm^{-3}) on grafting parameters. It is observed that the grafting parameters decrease continuously with increasing the concentration of xanthan gum (Fig. 1). This might be due to the increase in the viscosity of reaction medium, which hinders the movement of free radicals.

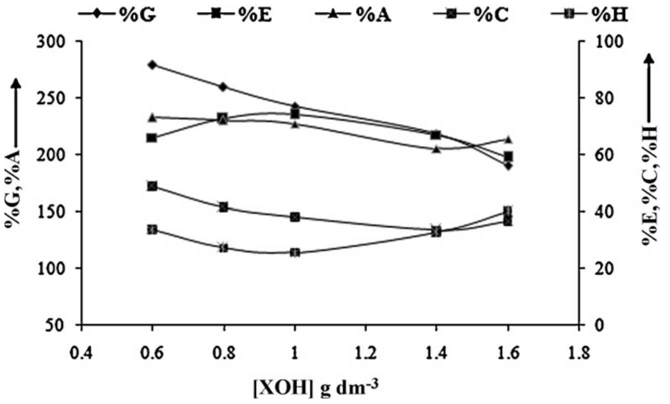


Fig. 1. Effect of concentration of xanthan gum. $[AGA] = 5.3 \times 10^{-2}$ mol dm^{-3}, $[BrO^-{}_3] = 10 \times 10^{-3}$ mol dm^{-3}, Time = 120 min, $[H^+] = 4 \times 10^{-3}$ mol dm^{-3}, $[TU] = 2.8 \times 10^{-3}$ mol dm^{-3}, Temp. = 40 °C.

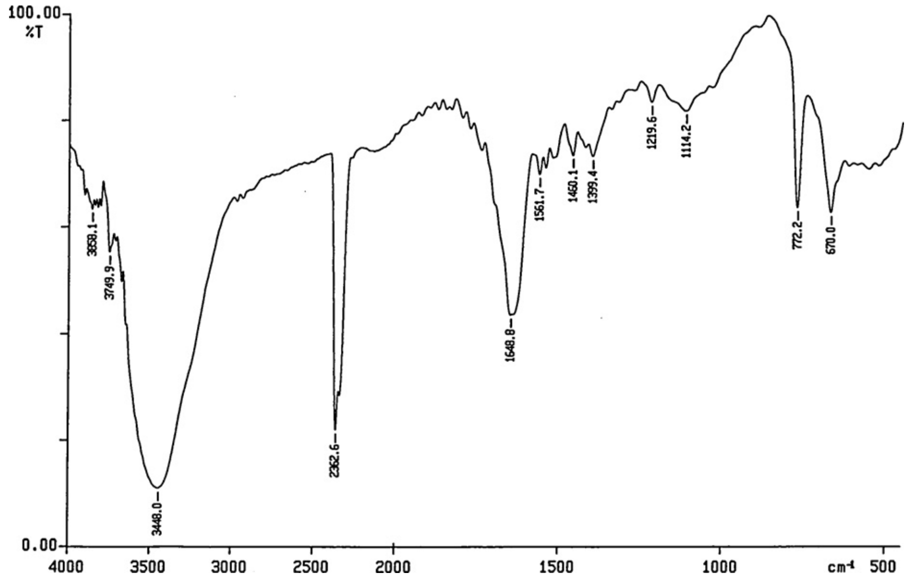


Fig. 2. IR spectrum of xanthan gum-g-2-Acrylamidoglycolic acid.

5.8. *Effect of time period*

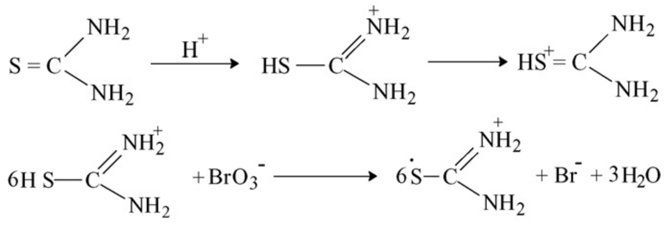
The effect of time duration on grafting reaction has been studied by varying the time period from 60 to 180 min. On increasing the time period from 60 to 120 min the availability of more active species results into the increase in grafting ratio (%G = increases from 170.8 to 243.3), efficiency and add on. But further increase in time period, the decrement in these parameters (up to %G = 100) is observed which might be due to termination of growing grafted chains.

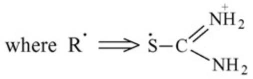
5.9. *Effect of temperature*

It has been observed that grafting ratio, add on and efficiency increases on increasing the temperature from 30 to 50 °C. The increment in grafting parameters is attributed to the increase in production of primary free radicals with consequent increase in number of grafting sites at polymer backbone and increase in rate of diffusion of poly (2-Acrylamidoglycolic acid) onto polymer backbone. These parameters decrease due to the premature termination of growing grafted chains at higher temperature.

5.10. *Mechanism*

It has been assumed that in presence of hydrogen ion, thiourea is protonated, which react with bromate ion to give isothiocarbamido radicals. These radicals abstract hydrogen atom from the xanthan gum molecule producing xanthan gum free radicals. The monomer molecules, which were near vicinity of the reaction site become acceptor of xanthan gum radicals resulting in chain initiation and thereafter themselves become free radicals donor to neighbouring molecules thus grafted chain grows. Termination of chain by coupling yield graft copolymer:





$$\text{where } R^{\cdot} \Longrightarrow \dot{S}{-}C(=\overset{+}{N}H_2)NH_2$$

& XOH ⟹ xanthan gum

M=2-Acrylamidoglycolic acid

Initiation:

$$XOH + R^{\bullet} \rightarrow XO^{\bullet} + RH$$

$$M + R^{\bullet} \rightarrow RM^{\bullet},$$

Propagation:

$$XO^{\bullet} + M \rightarrow XOM_1^{\bullet}$$

$$XOM_1^{\bullet} + M \rightarrow XOM_2^{\bullet}$$

$$XOM_2^{\bullet} + M \rightarrow XOM_3^{\bullet}$$

$$XOM_{(n-1)}^{\bullet} + M \rightarrow XOM_n^{\bullet}$$

$$RM^{\bullet} + M \rightarrow RM_1^{\bullet}$$

$$RM_1^{\bullet} + M \rightarrow RM_2^{\bullet}$$

$$RM_{n-1}^{\bullet} + M \rightarrow RM_n^{\bullet}$$

Termination:

$$XOM_n^{\bullet} + XOM_n^{\bullet} \rightarrow \text{Graft copolymer}$$

$$XOM_n^{\bullet} + RM_n^{\bullet} \rightarrow \text{Graft copolymer}$$

$$RM_n^{\bullet} + RM_n^{\bullet} \rightarrow \text{Homopolymer.}$$

5.10.1. *Evidence of grafting*

5.10.1.1. IR spectroscopy of xanthan gum xanthan gum-g-2-Acrylamidoglycolic acid. The IR spectra of ungrafted and grafted samples have been recorded with JASCO FTIR-5300 model in the range 500–4000 cm^{-1} to provide the proof of the grafting. Infrared spectrum of Xanthan gum (Srivastava, Mishra, Tripathy,

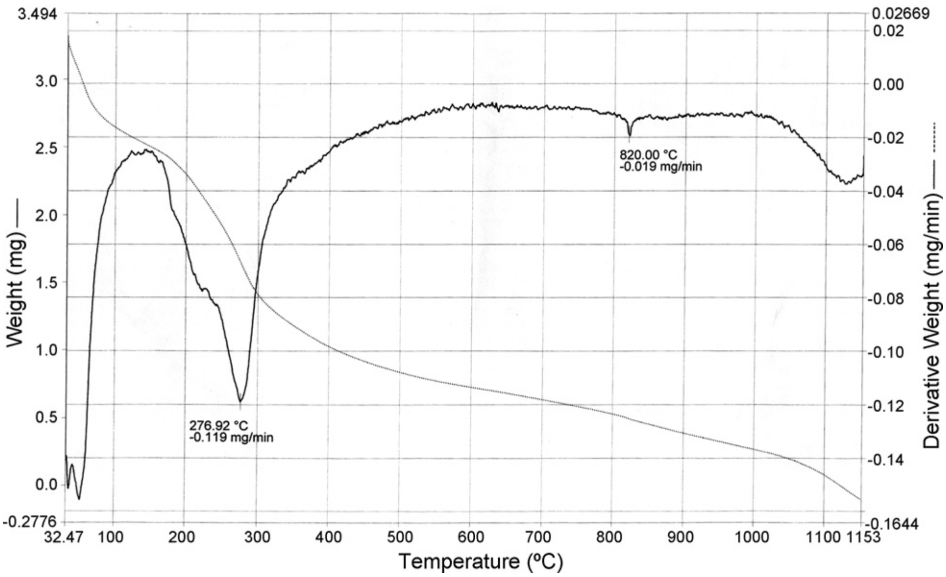


Fig. 3. Thermogravimetric trace of xanthan gum-g-2-Acrylamidoglycolic acid.

& Behari, 2009) showed strong peaks at 3417.0 cm^{-1} due to OH stretching vibrations. On comparing the IR spectra of xanthan gum and xanthan gum-g-2-Acrylamidoglycolic acid (Fig. 2), a band at 3450.0 cm^{-1} is due to OH stretching vibration in the spectrum of xanthan gum. It is observed that there is variation in intensity of OH stretching vibration and shifting of this peak from 3417.0 to 3448.0 cm^{-1} appeared in xanthan gum-g-2-Acrylamidoglycolic acid, indicating the participation of hydroxyl groups in chemical reaction. The graft copolymerization is further confirmed by characteristic absorption band of amide I at 1649.0 cm^{-1} due to >C═O stretching vibration, and at 1424.0 cm^{-1} due to –CN stretching vibration of monomer molecule, respectively. The appearance of additional peaks in spectrum of graft copolymer and shifting of OH stretching vibration appeared in the spectrum of xanthan gum from the spectrum of xanthan gum-g-2-Acrylamidoglycolic acid showed that grafting might have taken place on OH sites of xanthan gum.

5.10.1.2. Thermal analysis of xanthan gum and xanthan gum-g-2-Acrylamidoglycolic acid. The degradation of xanthan gum starts (Banerjee, Srivastava, Srivastava, & Behari, 2006) at about 200 °C. It was a single step process the weight loss of 10% at 100 °C was due to loss of absorbed water. The weight loss increases with increase in temperature up to 300 °C but thereafter it decreases. Nearly 50% weight loss occurred between 200 and 300 °C, about 60% xanthan gum degraded at 337.5 °C. The polymer decomposition temperature (PDT) was found at 250 °C. The integral procedural decomposition temperature (IPDT), temperature at which maximum degradation occurs (T_{max}) and final decomposition temperature (FDT) of xanthan gum were 247.7, 278.5 and 825 °C, respectively. A char yield of about 25% was obtained at 900 °C. The integral procedural decomposition temperature which accounts the whole shape of the curve and it sum up all of its dips and meanderings in a single number by measuring the area under the curve. Thus thermal stability of pure xanthan gum and its graft copolymers has also been determined by calculating IPDT values using following equation (Doyle, 1961). The area under the curve divided by the total area is the total curve area, A^*, is normalized with respect to both residual mass and temperature. A^* is converted to a temperature, T_{A*}, by following equation:

$$T_{A*} = (T_{\text{end}} - T_{\text{initial}})A * + T_{\text{initial}} \tag{1}$$

T_{A*} represents a characteristic end of volatilization temperature rather than an IPDT having practical significance. The second curve area K^* can be derived by drawing rectangle bearing X-axis up to T_{A*} and the Y-axis mass fraction remaining at T_{end}. K^* is the ratio between the area under the curve (inside the rectangle) and total rectangle area. The IPDT determined by substituting A^*K^* for A^* in Eq. (1). The integral procedural decomposition temperature is found to be 261.07 °C. The degradation takes place in two steps (Fig. 3). The rate of weight loss increases with increase in temperature from 105 to 170.6 °C and attain a maximum value at 276.92 °C after that it decreases. In the second step the degradation attain a maximum value at 820.00 °C. Thus two T_{max} have been observed in the degradation of xanthan gum-g-2-Acrylamidoglycolic acid the values were 276.92 and 820.00 °C. First T_{max} at 276.92 °C might be due to elimination of group from the polymeric backbone, which is also confirmed exothermic peak present in DTA curve of graft copolymer at 290.56 °C. Second T_{max} at 820.00 °C might be due to

Table 3
Metal ion sorption.

Sample	[AGA] × 10^2 mol dm^{-3}	%*G*	Percent uptake (P_u)			Partition coefficient (K_d)			Retention capacity (Q_r)		
			Ni^{2+}	Pb^{2+}	Zn^{2+}	Ni^{2+}	Pb^{2+}	Zn^{2+}	Ni^{2+}	Pb^{2+}	Zn^{2+}
XOH			2.3	2.2	1.2	10.2	11.2	5.2	1.1	1.3	0.7
A	2.6	171.6	2.9	2.7	2.7	15.7	13.5	10.8	1.7	1.5	1.2
B	4.0	214.5	4.7	3.9	3.9	22.3	26.7	17.2	2.2	2.2	1.7
C	5.3	243.3	7.2	7.2	5.4	42.2	37.2	28.1	3.5	3.8	2.8
D	6.6	226.8	10.3	7.7	9.7	58.2	55.7	28.3	5.2	5.5	5.2
E	8.0	158.8	12.0	11.2	10.6	67.2	63.28	58.8	5.7	5.8	5.9

Where XOH = xanthan gum. A, B, C, D, E = graft copolymers.
[XOH] = 1.0 g dm^{-3}, [$BrO^{-}{}_3$] = 10 × 10^{-3} mol dm^{-3}, [TU] = 2.8 × 10^{-3} mol dm^{-3}, [H^+] = 4.0 × 10^{-3} mol dm^{-3}, Time = 120 min, Temp. = 40 °C.

elimination of group from the polymeric backbone, which is also confirmed exothermic peak present in DTA curve of graft copolymer at 840.56 °C. The gradual decrease in the end peak of graft copolymer also indicate the some physical and structural change were occurring in the structure of graft copolymer may be due to fusion. The polymer decomposition temperature (PDT) and final decomposition temperature (FDT) has been found at 150.9 and 1100 °C, respectively.

6. The physicochemical properties

6.1. Swelling studies

The percent swelling and swelling ratio increase with increase in grafting, which is dependent upon monomer concentration. It has been observed that a maximum percent swelling of 440% occurs when grafting ratio is 243%. Since 2-Acrylamidoglycolic acid is a hydrophilic monomer, it increases the water absorbing capacity and water retention character of graft copolymer. The long pendant chains of 2-Acrylamidoglycolic acid are responsible for maximum hydrophilic character (Nasef, Saidi, Nor, & Foo, 2000) in graft copolymer thereby increasing the value of swelling ratio.

6.2. Metal ion sorption behaviour of xanthan gum and its graft copolymer

The values of the ion-uptake percentage, partition coefficient, and retention capacity increased directly as the grafting percentage increased, and this was due to an increased number of pendent chains of 2-Acrylamidoglycolic acid on the xanthan gum backbone. The results also showed that Zn^{2+} was the ion least able to be uptake. The increment in all these parameters might be due to grafting of 2-Acrylamidoglycolic acid which accounts for the higher sorption of these divalent cations through a chelating reaction (Onsoyen & Skaugrud, 1990) as shown and the results are given in Table 3.

6.3. Flocculation performance

At the time of mixing, concentration of flocculants was very low so that to make a uniformly dispersed polymer solution and coal powder was uniformly suspended in the water by stirring. Turbidity values of supernatant liquids have been taken as the measurement of flocculation efficiency of backbone xanthan gum and graft copolymer of xanthan gum with 2-Acrylamidoglycolic acid. Plots of supernatant turbidity versus polymer dosage for coking and non-coking coals are given in Fig. 4. It has been found that grafted copolymer (xanthan gum-g-2-Acrylamidoglycolic acid) shows better performance than xanthan gum itself which could be explained due to the fact that in grafted copolymer, the dangling of poly (2-Acrylamidoglycolic acid) chains have better approachability (Deshmukh et al., 1985) to the contaminant coal particles. Here the bridging mechanism operates (Gregory, 1982), which involves binding or bridging individual particles to form flocs, hence increases its flocculation capability. By grafting of poly 2-Acrylamidoglycolic acid onto xanthan gum, efficient flocculant has been obtained.

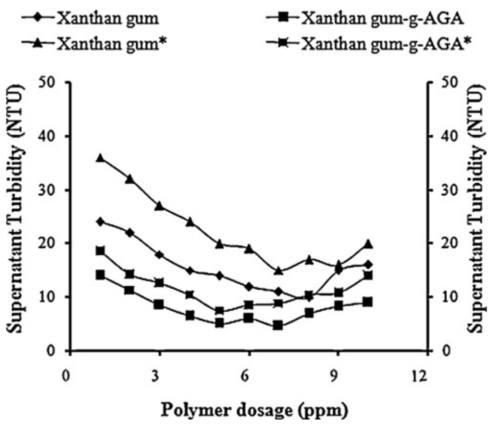


Fig. 4. Effect of polymer dosage on turbidity for coking coal and non-coking coal.

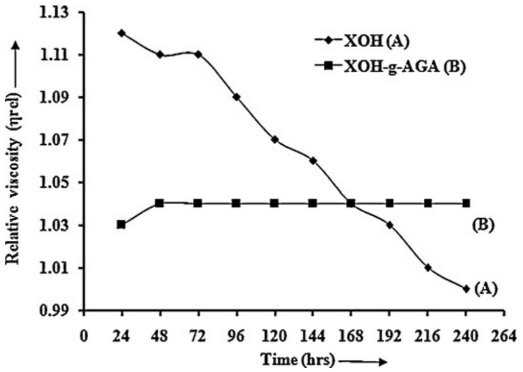


Fig. 5. Relative viscosity versus time period to study biodegradation of xanthan gum and graft copolymer.

6.4. Resistance to biodegradability

From efflux time of polymer solution (t) and that of solvent 1.0 M $NaNO_3$ (t_0), relative viscosity $\eta_{rel} = (\eta/\eta_0)$ was obtained. It has been observed that relative viscosity of xanthan gum-g-2-Acrylamidoglycolic acid is lower than xanthan gum (Fig. 5). This might be due to presence of grafted chains which make the molecule more flexible and reduce the viscosity drastically (Singh et al., 1989). Xanthan gum, like other polysaccharide solutions, is highly prone to biodegradation, and it was found that its solution after 72 h of its preparation starts degrading and during 10 days the solution showed considerable loss of viscosity (Fig. 5, Line A). The graft copolymer solution was subjected for same type of study for biodegradation, and it has been observed that graft copolymer solution showed no loss of viscosity up to 10 days (Fig. 5, Line B). These results show that the graft copolymer is less susceptible to biodegradation and results have also been reported by others (Ungeheur, Bewersdorff, & Singh 1989). This is in an agreement with the fact that by incorporating relatively poly (2-Acrylamidoglycolic acid) chains in graft copolymer it can be made less susceptible to bacterial attack (Seaman, 1980).

Thus, it can be concluded that, by incorporation of poly (2-Acrylamidoglycolic acid) graft onto xanthan gum through graft copolymerization biodegradation can be minimized.

7. Conclusion

The spectroscopic data confirm that the grafting of 2-Acrylamidoglycolic acid might have taken place at hydroxyl groups. The thermal analysis data show that the grafted polymer is more thermally stable than pure xanthan gum. Our synthesized graft copolymer, i.e. XOH-g-AGA shows better results for swelling, metal ion sorption, flocculation studies and resistance to biodegradation thus it could be interpreted that graft copolymer shows enhancement of the properties due to grafting, and thus could be exploited very well industrially.

Acknowledgement

Authors thankfully acknowledge to UGC, New Delhi for financial support. Vide Project No-37-393/2009(SR).

References

Banerjee, A., Srivastava, A., Srivastava, A., & Behari, K. (2006). Synthesis and characterization of xanthan gum-g-N-vinyl formamide with a potassium monopersulfate/Ag(I) system. *Journal of Applied Polymer Science*, *101*(3), 1637–1645.

Deshmukh, S. R., Sudhakar, K., & Singh, R. P. (1991). Drag reduction efficiency, shear stability and biodegradability resistance of carboxymethyl cellulose based and starch based graft copolymers. *Journal of Applied Polymer Science*, *43*, 1091–1101.

Doyle, C. D. (1961). Estimating thermal stability of experimental polymers by empirical thermogravimetric analysis. *Analytical Chemistry*, *33*, 77.

Fanta, G. F. (1973). Properties and applications of graft and block copolymers of starch. In R. J. Ceresa (Ed.), *Block and graft copolymerization* (pp. 29–45). New York, NY, London, England: Wiley-Interscience.

Gregory, J. (1982). In T. F. Tadros (Ed.), *Polymer flocculation in flowing dispersions*. London Academic Press;
Gregory, J. (1982). In T. F. Tadros (Ed.), *The Effect of polymers on dispersion properties* (pp. 301–321). London Academic Press.

Hegazy El-Sayed, A., EL-Rehim Abd, H. A., & Ali, A. M. (2000). Selective separation of some heavy metals by poly(vinyl alcohol)-grafted membranes. *Journal of Applied Polymer Science*, *76*, 125–132.

Seaman, J. K. (1980). In R. L. Davidson (Ed.), *Handbook of water soluble gums and resins* (pp. 6–9). New York: McGraw-Hill.

Kanan, K. (1998). Guar gum based graft copolymers flocculation and rheological behaviours. MTech thesis. IIT, Khragpur, India.

Nasef, M. M., Saidi, H., Nor, H. M., & Foo, O. M. (2000). Swelling behaviour cation exchange membranes by radiation-induced graft copolymerization of styrene onto PFA copolymer films. II. Characterization of sulfonated graft copolymer membranes. *Journal Applied Polymer Science*, *76*, 1–11.

Onsoyen, E., & Skaugrud, Q. (1990). *Journal of Chemical Technology & Biotechnology*, *49*, 395–404.

Prasad, P. N., Mark, J. E., & Fai, T. J. (1995). *Polymer and advanced materials: Emerging technologies and business opportunities*. New York: Plenum Press., pp. 227.

Rao, K. S. V., Chung, I., & Ha, C. S. (2008). Synthesis and characterization of poly (acrylamidoglycolic acid) grafted onto chitosan and its polyelectrolyte complexes with hydroxyapatite. *Reactive and Functional Polymer*, *68*, 943–953.

Rivas, B. L., Maturana, H. A., Molina, M. J., Gomez-Anton, M. R., & Pierola, I. F. (1998). Metal ion binding properties of poly (N-vinylimidazole) hydrogels. *Journal of Applied Polymer Science*, *67*, 1109–1118.

Srivastava, A., Mishra, D. K., Tripathy, J., & Behari, K. (2009). One pot synthesis of xanthan gum-g-N-vinyl-2-pyrrolidone and study of their metal ion sorption behavior and water swelling property. *Journal of Applied Polymer Science*, *111*(6), 2872–2880.

Ungeheur, S., Bewersdorff, H. W., & Singh, R. P. (1989). Turbulent drag effectiveness and shear stability of xanthan-gum-based graft copolymers. *Journal of Applied Polymer Science*, *37*, 2933–2948.