

Graft Copolymerization of Methacrylic Acid onto Xanthan Gum by $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ Redox Initiator

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ABSTRACT: The graft copolymer of xanthan gum with methacrylic acid was synthesized in inert atmosphere by using Fentos reagent as a redox initiator. The effect of reaction conditions on grafting parameters [$G(\%)$, $E(\%)$, $C(\%)$, $A(\%)$, $H(\%)$, and R_g] was investigated. Similar trend was observed on increasing the concentration of ferrous ion and hydrogen peroxide from 4.0 to $20.0 \times 10^{-3} \text{ mol dm}^{-3}$ and 2.5 to $10 \times 10^{-3} \text{ mol dm}^{-3}$ respectively, i.e., initially grafting parameters increased and after a certain range of concentration grafting parameters showed decreasing trend. Hydrogen ion shows influenced result i.e., small increment of concentration in hydrogen ion presents much increment in percent of grafting. It was observed that the [$G(\%)$, $E(\%)$,

$C(\%)$, $A(\%)$, and R_g] increased upto $6.67 \times 10^{-2} \text{ mol dm}^{-3}$ concentration of methacrylic acid after that it decreased. Maximum $G(\%)$ was obtained at minimum concentration of xanthan gum i.e., at $40 \times 10^{-2} \text{ g dm}^{-3}$. The optimum temperature and time duration of reaction for maximum percentage of grafting were found to be 45°C and 150 min respectively. Thermogravimetric analysis showed that the xanthan gum-g-methacrylic acid is thermally more stable than pure gum. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 1922–1929, 2007

Key words: polysaccharides; synthesis; graft copolymer; thermal properties; biodegradable

INTRODUCTION

Grafting provides a convenient method for tailoring material properties to specific end uses. Grafting of poly methacrylic acid onto xanthan gum has been studied with the objective of improving and modifying the properties of xanthan gum. An attempt made to develop new materials by combining the properties of both natural and synthetic polymer. Xanthan gum is an extracellular heteropolysaccharide of *Xanthomonas campestris*. Structural unit of xanthan gum consist of β -(1→4)-D-glucopyranose glucan (as cellulose) backbone with side chains of α -(3→1)-linked D-mannopyranose-(2→1)- β -D-glucuronic acid-(4→1)- β -D-mannopyranose on alternating residues. Because of its biocompatibility, high thickening efficiency,¹ hydrogen bonding properties,² good electrolytic compatibility and low cost, it has wide-range applications viz. in food,³ cosmetics,⁴ pharmaceuticals,⁵ additives.⁶ Thus it possesses various industrial applications but it suffers from major drawback like susceptibility on microbial attack. Therefore, to overcome this, it has been grafted with different vinyl monomers with employing different initiators.^{7,8} Kuniharan et al.⁹ used its graft copolymer for the absorption of heavy metal ions and Deshmukh and

Singh¹⁰ has pointed out that it has good drag reduction effectiveness

On the other hand methacrylic acid is a vinyl monomer and hydrophilic in nature that possesses same characteristics in chemical reactions as acrylic acid. Therefore, polymers derived from it may find many commercial applications. One of the earliest fields of application of polymethacrylic acid was in thickening. Crosslinked polymers of methacrylic acid may also be used to provide high water retention capacity and high viscosity in plasters¹¹ and other applications include adult incontinent products,¹² feminine hygiene products,¹³ absorbents in transmission cables,¹⁴ and agricultural mulches.¹⁵

Surface grafting of methacrylic acid onto poly (ethylene terephthalate) film resulted in improvement of wet ability and adhesion force, immobilization of proteins, coordinate bonding with Cu and Ag for antibacterial activity.^{16,17} Recent study reveals that the grafting of methacrylic acid onto guar gum¹⁸ and chitosan derivatives¹⁹ has found applications in drug delivery. In other reports^{20,21} authors have studied the grafting parameters of methacrylic acid with soyabean protein and starch in aqueous medium and study of deviation in copolymerization. Thus, it was thought worth while to graft methacrylic acid onto xanthan gum so as to produce a graft copolymer, which would be better flocculating, drag-reducing polymer than pure xanthan gum by using $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ redox pair. This graft copolymer will find various new applications such as ion exchange resin, desiccants antibacterial activity etc.

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EXPERIMENTAL

Materials

Methacrylic acid (Sigma, USA) was freshly distilled over copper turnings under vacuum and the middle fraction was used. Xanthan gum (Sigma, USA), Ferrous sulfate (E. Merck, India), hydrogen peroxide (E. Merck, India) were used as such. The sulfuric acid (E. Merck, India) was used for maintaining hydrogen ion concentration; other reagents were also used from E. Merck, India.

Procedure of graft copolymerization

Xanthan gum solution was prepared by slow addition of weighed amount of gum to calculated amount of triple distilled water in a reactor, so that final volume is 50 mL, calculated amount of ferrous sulfate, sulfuric acid, and methacrylic acid were added into the reactor and purified nitrogen gas was allowed to pass through the mixture as well as hydrogen peroxide solution. After half an hour calculated amount of hydrogen peroxide solution was added to the reactor to initiate the reaction and the reaction was allowed running for desired interval of time at constant temperature. After the desired interval of time, letting air into the reactor stopped the reaction. The reaction mixture was poured in water-methanol mixture. The grafted sample separates out which was filtered dried and weighed.

Separation of homopolymer

The poly methacrylic acid remains in the filtrate. To the filtrate a pinch of hydroquinone was added and then it was concentrated by distillation under reduced pressure at 30°C. The concentrated filtrate was precipitated into the pure acetone. The poly methacrylic acid was separated, dried, and weighed.

RESULTS AND DISCUSSION

Several redox pairs were applied to graft methacrylic acid on to xanthan gum but these redox pairs did not give any successful results, either they failed to

graft or gave very low grafting values because of steric hindrance on substrate molecule, steric hindrance is due to lots of $-\text{COOH}$, pyruvate group etc. into xanthan gum. Because of this steric hindrance the free radicals, which are generated by AIBN, Ce^{4+} , $\text{S}_2\text{O}_8^{2-}$ are not capable (because of larger size of free radicals) to generate the free radical sites on xanthan gum. They only produces homopolymer (polymethacrylic acid) when were trying to graft onto xanthan gum, while with $\text{H}_2\text{O}_2/\text{Fe}^{2+}$, the $\dot{\text{O}}\text{H}$ free radical is generated which is smaller in size and capable to generate easily free radical sites onto xanthan gum and thus grafting takes place more easily, and sufficient amount of graft copolymer was obtained. This $\dot{\text{O}}\text{H}$ free radical are also reacting to methacrylic acid and giving $\text{OH}-\text{CH}_2-\dot{\text{C}}(\text{CH}_3)-\text{COOH}$ radical, which is stabilized by hyperconjugation and finally giving homopolymer with good result, because stability of intermediate affects the product ratio.

The graft copolymer has been characterized by following grafting parameters.²²⁻²⁴

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

$$\begin{aligned} \text{Grafting efficiency (\%E)} \\ = \frac{\text{weight of grafted polymer}}{\text{weight of polymer formed}} \times 100 \end{aligned}$$

$$\text{Add on (\%A)} = \frac{\text{weight of grafted polymer}}{\text{weight of graft copolymer}} \times 100$$

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

$$\text{Homopolymer (\%H)} = 100 - \text{Grafting efficiency (\%)}$$

$$\begin{aligned} \text{Rate of grafting (R}_g\text{)} \\ = \frac{1000 \times \text{weight of grafted polymer}}{\text{volume} \times \text{time} \times \text{mol.wt.of MAA}} \text{mol L}^{-1}\text{s}^{-1} \end{aligned}$$

The effect of variation in concentration of Fe^{2+} , hydrogen ion, xanthan gum, methacrylic acid, and

TABLE I
Effect of Ferrous Ion Concentration $[\text{H}^2\text{O}^2] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$;
 $[\text{MAA}] = 10.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{XOH}] = 100.0 \times 10^{-2} \text{ g dm}^{-3}$; Time = 120 min.;
Temperature = 40°C; $[\text{H}^+] = 0.5 \times 10^{-3} \text{ mol dm}^{-3}$

$[\text{Fe}^{2+}] \times 10^3 \text{ mol dm}^{-3}$	G (%)	E (%)	C (%)	A (%)	H (%)	$R_g \times 10^7 \text{ mol L}^{-1} \text{ S}^{-1}$
4.0	48.0	60.75	09.18	32.43	39.25	7.74
5.0	114.00	61.95	21.27	53.27	38.05	18.38
6.7	152.00	66.66	26.48	60.32	33.34	24.47
10.0	104.00	69.77	17.42	50.98	30.67	16.74
20.0	44.00	61.11	8.36	30.55	38.89	7.08

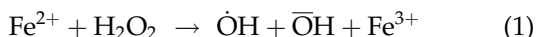
TABLE II
 Effect of H_2O_2 Concentration $[\text{Fe}^{2+}] = 10.0 \times 10^{-3} \text{ mol dm}^{-3}$;
 $[\text{MAA}] = 10.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{XOH}] = 100.0 \times 10^{-2} \text{ g dm}^{-3}$; Time = 120 min.;
 Temperature = 40°C ; $[\text{H}^+] = 0.5 \times 10^{-3} \text{ mol dm}^{-3}$

$[\text{H}_2\text{O}_2] \times 10^3 \text{ mol dm}^{-3}$	G (%)	E (%)	C (%)	A (%)	H (%)	$R^g \times 10^7 \text{ mol L}^{-1} \text{ S}^{-1}$
2.5	58.00	60.10	11.20	36.70	39.90	9.33
3.3	65.00	60.74	12.43	39.39	39.26	10.30
4.0	70.00	62.05	13.10	41.17	37.95	11.27
5.0	104.00	69.77	17.42	50.98	30.67	16.74
6.7	85.00	63.35	15.58	45.95	36.64	13.52
10.0	59.00	57.95	11.82	37.10	42.05	9.33

hydrogen peroxide along with the effect of time period and temperature on grafting parameter was studied.

Effect of ferrous ion concentration

The effect of Fe^{2+} concentration was studied by varying the concentration of ferrous ion from 4.0×10^{-3} to $20.0 \times 10^{-3} \text{ mol dm}^{-3}$. Table I shows that the grafting ratio, add on, conversion, and rate of grafting increased on increasing the concentration from 4.0×10^{-3} to $6.7 \times 10^{-3} \text{ mol dm}^{-3}$; however, efficiency increases upto 10.0×10^{-3} , beyond this concentration, the values of these parameters decreased. The increase in the values of grafting parameters upto the cited range of concentration might be due to the increased production of free radicals ($\cdot\text{OH}$) as given in eq. (1) by $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ redox pair resulting in the production of xanthan gum and methacrylic acid macro-radicals at the faster rate which are responsible for chain propagation of graft copolymer.



The decrease in grafting ratio beyond $6.7 \times 10^{-3} \text{ mol dm}^{-3}$ might be attributed to a detrimental factor arising from excess of $\text{Fe}(\text{III})$ ions production by

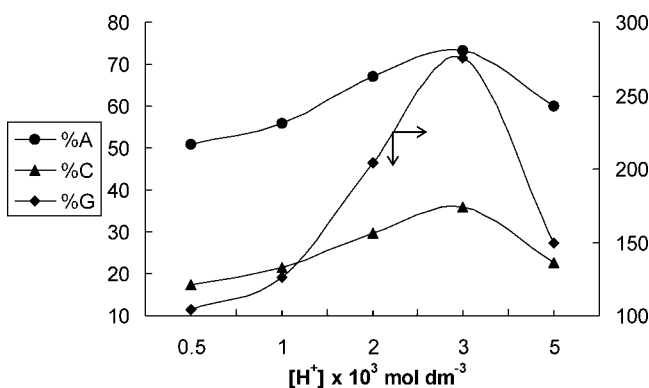
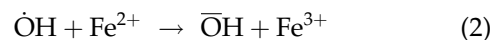


Figure 1 Effect of hydrogen ion concentration $[\text{Fe}^{2+}] = 10.0 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{MAA}] = 10.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{XOH}] = 1.0 \text{ g dm}^{-3}$ $[\text{H}_2\text{O}_2] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$; Time = 120 min; Temperature = 40°C ; A (%) = Add on; C (%) = Conversion; G (%) = Grafting ratio.

oxidation of $\text{Fe}(\text{II})$ eq. (2) and also the premature termination of growing grafted chains was observed by Morin and Rogovin²⁵ and Misra et al.²⁶ in graft copolymerization initiated with $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ system beyond certain concentration of Fe^{2+} .



Effect of H_2O_2 concentration

The graft copolymerization reaction was conducted by varying the concentration of H_2O_2 from 2.5×10^{-3} to $10.0 \times 10^{-3} \text{ mol dm}^{-3}$ (Table II). It was observed that the grafting ratio, add on, conversion, efficiency, and rate of grafting increased with increasing H_2O_2 concentration from 2.5×10^{-3} to $5.0 \times 10^{-3} \text{ mol dm}^{-3}$. The increment in grafting parameters might be due to progressive reduction of H_2O_2 with ferrous ion that produces increased number of free radicals. The decrease in grafting parameters beyond $5.0 \times 10^{-3} \text{ mol dm}^{-3}$ is explained in view of the radical termination. This is also explained by Medalia and Kolthoff,²⁷ when H_2O_2 is in large excess then it is decomposed to oxygen and water, since, O_2 acts as scavenger of free radicals so all the grafting parameters decreased.

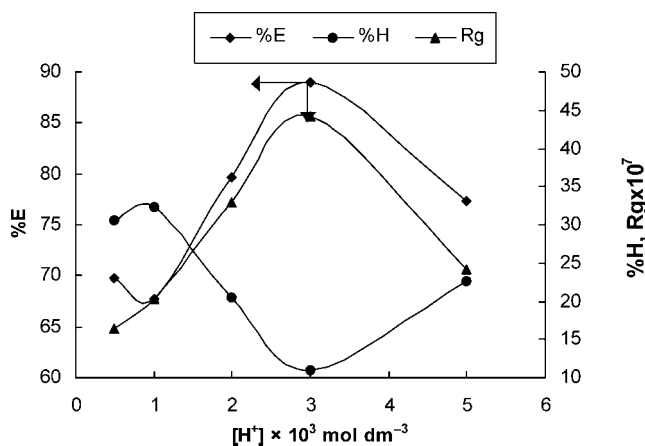


Figure 2 Effect of hydrogen ion Concentration $[\text{Fe}^{2+}] = 10.0 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{MAA}] = 10.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{XOH}] = 1.0 \text{ g dm}^{-3}$ $[\text{H}_2\text{O}_2] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$; Time = 120 min; Temperature = 40°C ; E (%) = Efficiency; H (%) = Homopolymer, R_g = Rate of grafting.

TABLE III
Effect of Methacrylic Acid Concentration $[\text{Fe}^{2+}] = 10.0 \times 10^{-3} \text{ mol dm}^{-3}$;
 $[\text{H}^2\text{O}^2] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{XOH}] = 100.0 \times 10^{-2} \text{ g dm}^{-3}$; **Time = 120 min.**;
Temperature = 40°C; $[\text{H}^+] = 0.5 \times 10^{-3} \text{ mol dm}^{-3}$

$[\text{MAA}] \times 10^2 \text{ mol dm}^{-3}$	G (%)	E (%)	C (%)	A (%)	H (%)	$R_g \times 10^7 \text{ mol L}^{-1} \text{ S}^{-1}$
4.0	90.00	43.69	35.89	43.37	56.31	14.49
5.0	102.00	63.05	37.73	50.59	36.95	16.42
6.67	122.00	85.92	41.23	54.95	14.08	19.64
10.0	104.00	69.77	17.42	50.98	30.67	16.74
20.0	102.80	64.32	8.97	50.69	35.68	16.42

Effect of hydrogen ion concentration

The effect of hydrogen ion concentration was studied by varying the concentration of hydrogen ion from 0.5×10^{-3} to $5.0 \times 10^{-3} \text{ mol dm}^{-3}$ (Figs. 1 and 2). As the hydrogen ion concentration is increased from 0.5×10^{-3} to $3.0 \times 10^{-3} \text{ mol dm}^{-3}$, grafting ratio, add on, conversion, and rate of grafting increase, but decrease thereafter. This could be explained in terms of an accelerated oxidation/reduction reaction at higher hydrogen ion concentration. At the same time the fast disintegration and oxidation processes of xanthan gum had to the destruction of the $\bullet\text{OH}$ free radicals by ferrous ions.

Effect of methacrylic acid concentration

The effect of methacrylic acid was studied by varying the concentration of methacrylic acid from 4.0×10^{-2} to $20.0 \times 10^{-2} \text{ mol dm}^{-3}$ and the results are summarized in Table III. It was observed that grafting ratio, add on, conversion, efficiency, and rate of grafting increase with increase in concentration of methacrylic acid from 4.0×10^{-2} to $6.6 \times 10^{-2} \text{ mol}$

dm^{-3} but decrease thereafter. However, formation of homopolymer showed a reverse trend with respect to grafting efficiency. The increase in the grafting parameters might be attributed to the much ease accumulation of monomer at the close proximity of polymer backbone. The monomer molecules, which are at the immediate vicinity of the reaction site became acceptor of xanthan gum radicals resulting in chain initiation and thereafter themselves became free radicals donor to the neighboring molecules leading to lowering termination. The decrement in the grafting parameters might be due to the formation of more amount of homopolymer, which increases the viscosity of medium due to which the movement of free radicals restricted, therefore, grafting parameters showed decreasing order.

Effect of xanthan gum concentration

The concentration of xanthan gum was varied from 40.0×10^{-2} to $160.0 \times 10^{-2} \text{ g dm}^{-3}$ to study the effect of xanthan gum concentration on grafting parameters (Figs. 3 and 4). It was observed that the grafting ratio, add on, conversion and rate of graft-

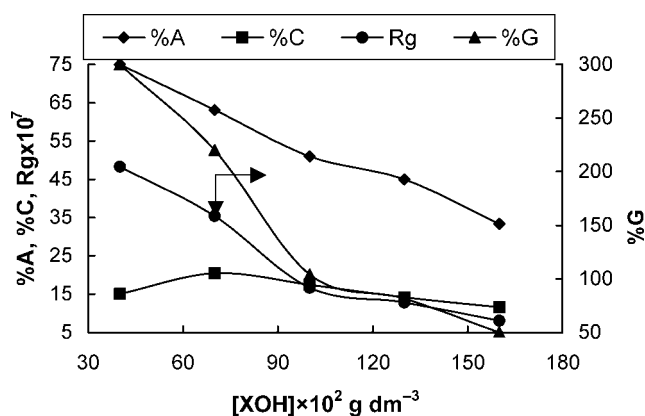


Figure 3 Effect of xanthan gum concentration $[\text{Fe}^{2+}] = 10.0 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{H}^+] = 0.5 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{MAA}] = 10.0 \times 10^{-2} \text{ mol dm}^{-3}$ $[\text{H}_2\text{O}_2] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$; **Time = 120 min**; **Temperature = 40°C**; A (%) = Add on; C (%) = Conversion; G (%) = Grafting ratio; R_g = Rate of grafting.

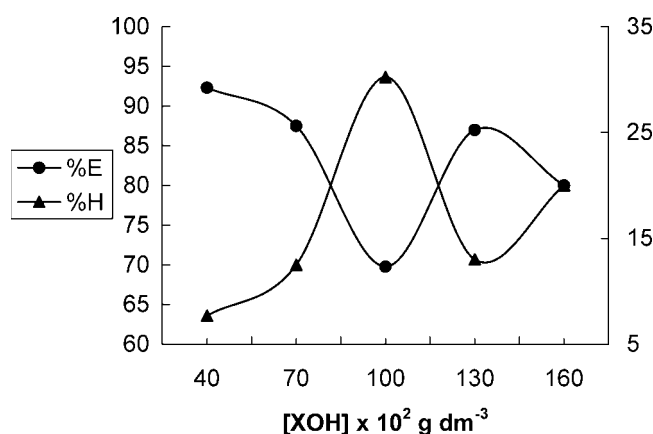


Figure 4 Effect of xanthan gum concentration $[\text{Fe}^{2+}] = 10.0 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{H}^+] = 0.5 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{MAA}] = 10.0 \times 10^{-2} \text{ mol dm}^{-3}$ $[\text{H}_2\text{O}_2] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$; **Time = 120 min**; **Temperature = 40°C**; E (%) = Efficiency; H (%) = Homopolymer.

TABLE IV
Effect of Time Period $[\text{Fe}^{2+}] = 10.0 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{H}_2\text{O}_2] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$;
 $[\text{MAA}] = 10.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{XOH}] = 100.0 \times 10^{-2} \text{ g dm}^{-3}$;
Temperature = 40°C ; $[\text{H}^+] = 0.5 \times 10^{-3} \text{ mol dm}^{-3}$

Time (min)	G (%)	E (%)	C (%)	A (%)	H (%)	$R^g \times 10^7 \text{ mol L}^{-1} \text{ S}^{-1}$
60	60.40	71.73	9.78	37.66	28.26	19.35
90	79.00	75.35	12.17	44.13	24.65	16.77
120	104.00	69.77	17.42	50.98	30.67	16.74
150	168.00	93.33	20.90	62.68	6.67	21.68
180	134.00	85.89	18.12	57.26	14.10	14.41

ing decrease continuously on increasing the xanthan gum concentration. The decrease in grafting ratio may be attributed to the fact that with increase in xanthan gum concentration, its utilization ratio becomes smaller, is not enough for methacrylic acid to react with xanthan gum²⁸ and the increased viscosity may hinder the movement of free radicals, as is evident from the decrease in total conversion of methacrylic acid.

Effect of time period

The graft copolymerization was studied by increasing the time period of the reaction from 60 to 180 min. Table IV shows that the grafting ratio, add on, conversion, and rate of grafting increased on increasing the time period from 60 to 150 min, where as maximum grafting efficiency is found at 150 min. On further increasing the time period grafting parameters showed decreasing order. The increment in grafting parameters might be due to the more availability of active species which give more graft copolymer where as decrement in grafting parameters might be attributed as after long interval of time the concentration of all active species decrease, which cause decrement in the grafting parameters.

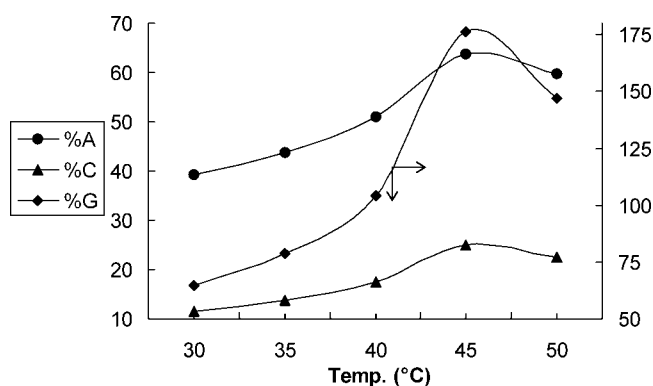


Figure 5 Effect of temperature $[\text{Fe}^{2+}] = 10.0 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{H}^+] = 0.5 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{MAA}] = 10.0 \times 10^{-2} \text{ mol dm}^{-3}$ $[\text{H}_2\text{O}_2] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{XOH}] = 1.0 \text{ g dm}^{-3}$; Time = 120 min; A (%) = Add on; C (%) = Conversion; G (%) = Grafting ratio.

Effect of temperature

Figures 5 and 6 show that grafting ratio, add on, conversion efficiency and rate of grafting increased as temperature increases from 30 to 45°C , but thereafter the values of these parameters were found to decrease. The increment in the values of grafting parameters might be ascribed to the increased rate of diffusion of monomer onto backbone and increased rate of production of primary free radicals. The decrement in grafting ratio, add on, conversion, and efficiency might be due to the premature termination of growing grafted chains by excess of free radicals at higher temperature.

Evidence of grafting

FTIR spectra of graft copolymer [XOH-g-MAA] and xanthan gum pure's were taken, compared and found that the xanthan gum $-\text{OH}$ broad band at 3350 cm^{-1} was not appeared in the XOH-g-MAA spectra (neither broad not sharp), suggesting that grafting taken place at xanthan gum $-\text{OH}$ sites. The band at 1768 cm^{-1} is occurred because of $-\text{COOH}$, which is common in both the spectra of. xanthan

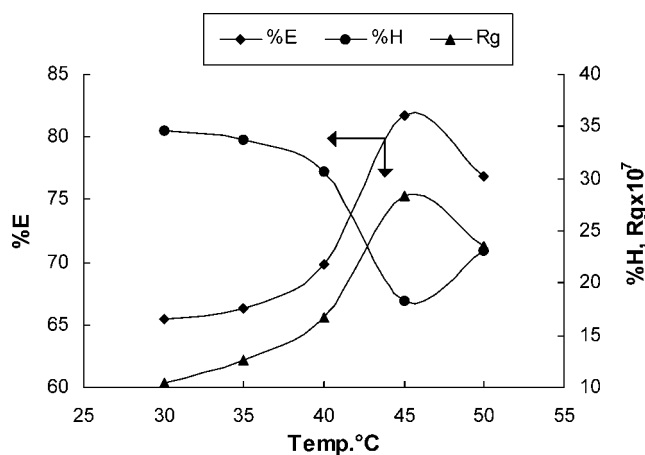


Figure 6 Effect of temperature $[\text{Fe}^{2+}] = 10.0 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{H}^+] = 0.5 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{MAA}] = 10.0 \times 10^{-2} \text{ mol dm}^{-3}$ $[\text{H}_2\text{O}_2] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{XOH}] = 1.0 \text{ g dm}^{-3}$; Time = 120 min; E (%) = Efficiency; H (%) = Homopolymer; R_g = Rate of grafting.

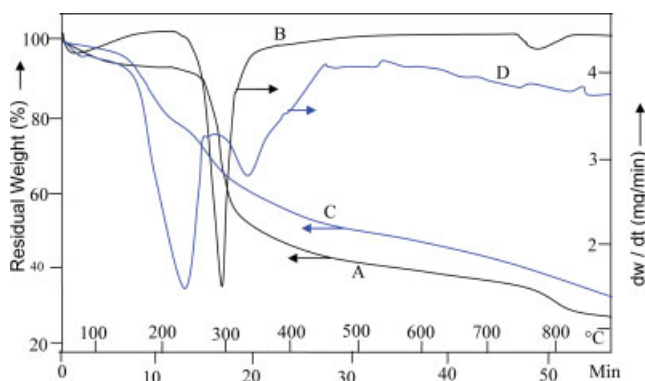


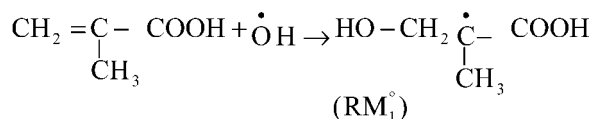
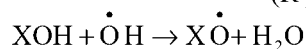
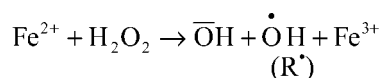
Figure 7 Thermogravimetric trace of xanthan gum and xanthan gum-g-methacrylic acid. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

gum and XOH-g-MAA, but disappearance of broad —OH band in graft copolymer supports the formation of graft copolymer.

Mechanism

Recently, Sheng et al.²⁹ and Kumar et al.³⁰ have grafted different vinyl monomers onto natural and synthetic polymer backbone using Fenton reagent as an initiator and observed that there exists a critical concentration of Fe^{2+} and H_2O_2 at which maximum percentage of grafting was obtained. The $\cdot\text{OH}$ free radical is generated by the interaction of Fe^{2+} with H_2O_2 . The $\cdot\text{OH}$ free radicals represented by $\text{R}\cdot$, extracts hydrogen atom from xanthan gum (XOH) molecule, producing xanthan gum ($\text{XO}\cdot$) macroradical. The methacrylic acid molecules, which are in close vicinity of the reaction site, became acceptor of xanthan gum radicals resulting in the chain initiation and thereafter it becomes free radical donor to the neighboring molecules. In this way grafted chains grow and after coupling to give graft copolymer.

The reaction mechanism can be represented by the following steps:



Initiation:

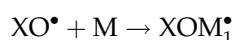


TABLE V
Decomposition Temperature (DT) in °C

	Weight Loss (%)						
	10	20	30	40	50	60	70
X_1	270.0	282.0	297.0	310.0	343.0	600.0	850.0
X_2	216.34	258.0	310.0	382.0	478.0	718.0	942.2

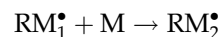
Where X_1 is xanthan gum and X_2 is xanthan gum-g-methacrylic acid.

Propagation:



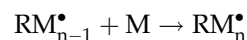
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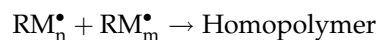
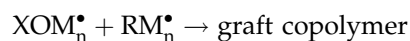
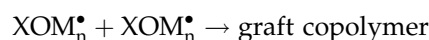


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Termination:



where = XOH – Xanthan gum

M – Methacrylic acid

$\text{R}\cdot$ – Hydroxyl free radical($\dot{\text{O}}\text{H}$)

$\text{M}\cdot$ – Methacrylic acid radical

$\text{XO}\cdot$ – Xanthan gum macroradical

Thermal analysis

Xanthan gum

Figure 7 (line A and B) shows that the degradation of xanthan gum started at about 232°C. The rate of

TABLE VI
Weight Loss (%) for Decomposition Temperature

	Temperature (°C)								
	100	200	300	400	500	600	700	800	900
X_1	3.3	6.0	33.0	55.0	57.0	60.0	65.0	73.0	–
X_2	4.0	8.0	29.0	42.0	52.00	54.00	58.0	63.00	66.0

Where X_1 is xanthan gum and X_2 is xanthan gum-g-methacrylic acid.

TABLE VII
Thermogravimetric Analyses of Graft Copolymer

Sample Code	PDT (°C)	FDT (°C)	T_{max} (°C)	IPDT (°C)	DTA peaks	
					Exopeaks (°C)	Endopeaks (°C)
X ₁	281.0	316.0	290.0	280.2	–	290.0
X ₂	216.36	452.0	243.9, 343.5	311.12	–	763.8

weight loss increases on increasing the temperature upto 296°C but thereafter it decreases therefore it is a single step degradation process. The char yield of 24% was obtained at 870°C. Nearly 45% weight loss occurred between 200 and 310°C. The 60% xanthan gum was degraded at 600°C (Tables V and VI). Therefore final decomposition temperature (FDT) is very low i.e., 316°C. Polymer decomposition temperature (PDT), temperature at which maximum degradation occurs (T_{max}) and integral procedural decomposition temperature (IPDT) of xanthan gum have been found to be 281, 290, and 280.12°C respectively, (Table VII).

Xanthan gum-g-methacrylic acid

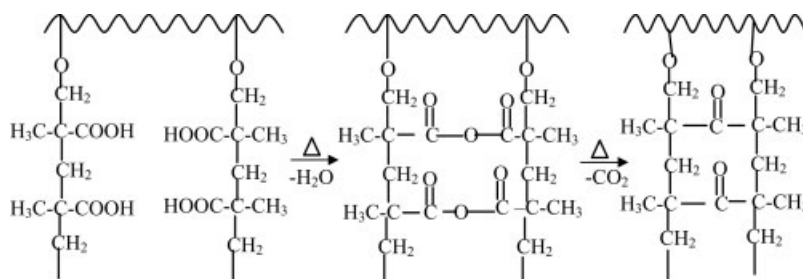
The graft copolymer began to degrade at about 100°C, 4.0% weight loss in the weight below this temperature is attributed due to the absorbed water (Scheme 1). The rate of weight loss increased with increase in the temperature upto 250°C and gradually decreases, thereafter, again the increase in the rate of weight loss is observed from 330 to 500 °C and thereafter it decreases. [Fig. 7 (line C and D)]. Therefore, two T_{max} are obtained at 243.9 and 343.5°C. The polymer decomposition temperature (PDT) is found to be 216.36°C but final decomposition temperature (FDT) is much higher than xanthan gum. The weight loss in the lower temperature range i.e., 150–250°C is due to the formation of anhydride with elimination of H₂O molecule from the two neighboring carboxylic group of the grafted chains.³¹ The second T_{max} is attributed to the decarboxylation of the anhydrides formed earlier. About 34% char yield was obtained at 900°C. The high

value of FDT, IPDT and char yield of graft copolymer in comparison to xanthan gum, indicates that the graft copolymer is thermally more stable than xanthan gum.

CONCLUSIONS

The graft copolymer of xanthan gum with methacrylic acid was synthesized by using H₂O₂/Fe²⁺. The effects of various factors on graft copolymerization were studied in detail

- The grafting ratio and rate of grafting increases as reaction temperature increases.
- High temperature does not favor homopolymerization
- High [H⁺] increases $G(\%)$, $E(\%)$, and R_g
- Grafting parameter increases on increasing the concentration of methacrylic acid.
- Increase in redox pair concentration, increases the grafting parameters
- High concentration of gum decreases the grafting parameters.
- Thermal degradation of xanthan gum-g-methacrylic acid shows that degradation completed in two stages therefore two T_{max} were found at 243.9 and 343.5°C because of loss of H₂O and CO₂ molecule respectively. About 50% xanthan gum degraded at 343°C, while 50% grafted xanthan gum degraded at 478°C indicating more thermal stability of graft copolymers and high value of FDT, IPDT, Char yield are also support the high thermal stability of graft copolymer in comparison to backbone.



Schematic representation of degradation of Xanthan gum-g-methacrylic acid

Scheme 1

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