One Pot Synthesis of Xanthan gum-g-N-vinyl-2-pyrrolidone and Study of Their Metal Ion Sorption Behavior and Water Swelling Property

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ABSTRACT: In this article, graft copolymerization of N-vinyl-2-pyrrolidone onto xanthan gum initiated by potassium peroxydiphosphate/Ag^+ system in an aqueous medium has been studied under oxygen free nitrogen atmosphere. Grafting ratio, grafting efficiency, and add on increase on increasing the concentration of potassium peroxydiphosphate (2.0×10^{-3} to 12×10^{-3} mol dm^{-3}), Ag^+ (0.4×10^{-3} to 2.8×10^{-3} mol dm^{-3}), and hydrogen ion concentration from 2×10^{-3} to 14.0×10^{-3} mol dm^{-3}. Maximum grafting has been obtained when xanthan gum and monomer concentration were 0.4 g dm^{-3} and $16 \times$ 10^{-2} mol dm^{-3}, respectively, at 35°C and 120 min. Water swelling capacity, swelling ratio, metal ion uptake, and metal retention capacity have also been studied, and it has been found that graft copolymer shows enhancement in these properties than pure xanthan gum. The graft copolymer has been characterized by FTIR and thermal analysis. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 2872–2880, 2009

Key words: xanthan gum; graft copolymer; thermal analysis; potassium peroxydiphosphate/Ag^+ system; N-vinyl-2-pyrrolidone; metal ion uptake

INTRODUCTION

Grafting provides a convenient method for tailoring material properties to specific end uses. Grafting of N-vinyl-2-pyrrolidone onto Xanthan gum has been studied with the objective of modifying the properties of xanthan gum, and an attempt has been made to develop new materials by combining the properties of both natural and synthetic polymer. Xanthan gum, the exopolysaccharide obtained from *Xanthomonas compestris*, has been evaluated in respect of its long-term thermal stability. Xanthan gum is produced commercially and widely used for food and nonfood applications. The properties like thickening, emulsion stabilization, water binding, and acid compatibility[1] give advantages of application in food and pharmaceuticals. It has been widely used in enhanced oil recovery[2] and drug delivery system for poor water-soluble drugs.[3]

However it is readily degraded by bacterial attack, which limit its uses. The properties and applications of grafted xanthan gum will depend upon the type of vinyl monomer grafted on to it. N-vinyl-2-pyrrolidone is an important hydrophilic vinyl monomer and its homo and copolymers are being used in many industries.[4–6] Poly N-vinyl-2-pyrrolidone is used in the preparation of odor masking compound, thus it acts as odor neutralizer in aerosol deodorants to remove unpleasant odor of human and animal hair.[7]

An attempt has been made to graft N-vinyl-2-pyrrolidone onto xanthan gum so as to produce a graft copolymer, which can be a better flocculating, drag reducing, and sizing agent than xanthan gum.

EXPERIMENTAL

Materials

N-vinyl-2-pyrrolidone (Aldrich, Milwaukee, WI) was distilled under reduce pressure at 11 mmHg and 60°C. Only middle fraction was used. Xanthan gum (XOH) was purchased from Sigma (USA). Potassium peroxydiphosphate was received as a gift sample from FMC, (USA). $AgNO_3$ (E. Merck, India) is used as such. For maintaining hydrogen ion concentration sulfuric acid (E. Merck, India) is used and all the solutions are prepared in triple distilled water.

Procedure for graft copolymerization

For each experiment, xanthan gum solution has been prepared by addition of weighed amount of xanthan gum into reactor containing triple distilled water. The calculated amount of $AgNO_3$, N-vinyl-2-

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pyrrolidone (NVP), and sulfuric acid solutions has been added to the reactor at constant temperature and a slow stream of oxygen free nitrogen is passed. After 30 min, a known amount of deoxygenated potassium peroxydiphosphate solution is added to initiate the reaction, and reaction has been carried under oxygen free nitrogen gas. After desired time period, the reaction was stopped by letting air into the reactor. Graft copolymer has been precipitated in water/methanol mixture. The grafted sample has been separated by filtration and then dried and weighed. Poly(N-vinyl-2-pyrrolidone) remained in the filtrate. To the filtrate, a pinch of hydroquinone has been added and then it is concentrated by distillation under reduced pressure. This concentrated solution is poured into the pure methanol to precipitate the poly(N-vinyl-2-pyrrolidone). The poly(N-vinyl-2-pyrrolidone) is separated, dried, and weighed.

RESULTS AND DISCUSSION

The graft copolymer has been characterized according to Fanta's definition[8]

$$\text{Grafting ratio } (\%G) = \frac{\text{Grafted polymer}}{\text{Weight of substrate}} \times 100$$

$$\text{Add on } (\%A) = \frac{\text{Synthetic polymer}}{\text{Graft copolymer}} \times 100$$

$$\text{Conversion } (\%C) = \frac{\text{Polymer formed}}{\text{Monomer charged}} \times 100$$

$$\text{Grafting efficiency } (\%E) = \frac{\text{Polymer in graft}}{\text{Polymer formed}} \times 100$$

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

The effect of variation of concentration of Ag^+ ion, potassium peroxydiphosphate, hydrogen ion, and N-vinyl-2-pyrrolidone xanthan gum along with the effect of time and temperature on grafting parameter has been studied. Beside these the swelling ratio percentage swelling and metal retention capacity of graft copolymer for different metal ions have also been studied by using the following definition[9,10].

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

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

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

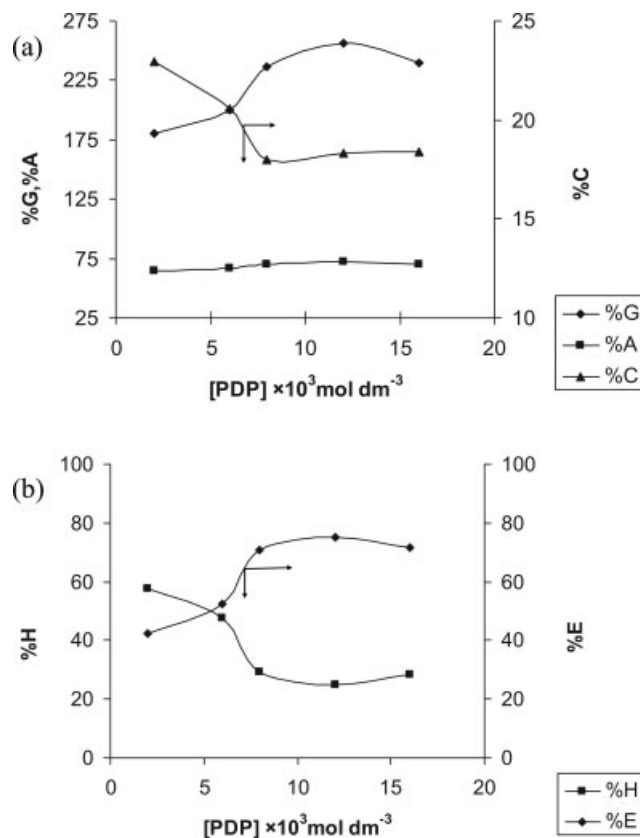**Figure 1** (a,b) Effect of PDP concentration. [NVP] = 16 × 10^{-2} mol dm^{-3}, [XOH] = 1.0 g dm^{-3}, [Ag$^+$] = 20 × 10^{-4} mol dm^{-3}, [H$^+$] = 10 × 10^{-3} mol dm^{-3}, Temp. = 35°C, Time = 120 min.

$$\text{Partition coefficient } (K_d) = \frac{\text{Amount of metal ion in the polymer}}{\text{Amount of metal ion left in the solution}} \times \frac{\text{Volume of solution (ml)}}{\text{Weight of dry polymer}}$$

$$\text{Retention capacity } (Q_r) = \frac{\text{Amount of metal ion in the Polymer (m Equiv.)}}{\text{Weight of dry Polymer (g)}}$$

Effect of potassium peroxydiphosphate concentration

The effect of potassium peroxydiphosphate concentration on grafting parameters has been studied by varying the concentration of peroxydiphosphate from 2 × 10^{-3} to 16 × 10^{-3} mol dm^{-3} and the results are shown in Figure 1(a,b). It has been observed that grafting ratio, efficiency, and add on increase on increasing the peroxydiphosphate

TABLE I
Effect of Ag^+ Ion Concentration

$[Ag^+] \times 10^4$ mol dm^{-3}	%G	%E	%A	%C	%H
4	158.8	35.5	61.4	24.1	64.5
12	194.2	48.3	66.0	21.7	51.7
20	236.8	70.7	70.3	18.0	29.3
28	300	78.9	75.0	20.5	21.0
36	268	74.9	72.8	19.3	25.1

$[NVP] = 16 \times 10^{-2}$ mol dm^{-3}, $[PDP] = 8 \times 10^{-3}$ mol dm^{-3}, $[XOH] = 1.0$ g dm^{-3}, $[H+] = 10 \times 10^{-3}$ mol dm^{-3}, Temp. $= 35°C$, Time $= 120$ min.

concentration from 2×10^{-3} to 12×10^{-3} mol dm^{-3} but at higher concentration i.e., 16×10^{-3} mol dm^{-3}, grafting ratio, efficiency, and add on decreases while homopolymer increases. The increase in grafting parameters can be explained due to the fact that more $H_2AgP_2O_8^-$ is formed which attacks[11] the xanthan gum molecule giving more radical ions. These radicals attack on the xanthan gum molecule to produce xanthan gum macro radicals by abstraction of hydrogen atom from xanthan gum molecules. But at higher concentration, these parameters are decreased due to the formation of more poly(N-vinyl-2-pyrrolidone).

Effect of Ag^+ ion concentration

By varying the concentration of Ag^+ ion from 0.4×10^{-3} to 3.6×10^{-3} mol dm^{-3}, it has been observed that grafting ratio, efficiency, add on increase up to 2.8×10^{-3} mol dm^{-3} but thereafter these parameters decrease and homopolymer increases. The increment in grafting parameters is due to higher concentration of complex ($H_2AgP_2O_8^-$). The result is given in Table I. This complex $H_2AgP_2O_8^-$ reacts with xanthan gum to give macro free radicals as shown in eq. (2). But at higher concentration of Ag^+ ion, i.e. 3.6×10^{-3} mol dm^{-3}, these parameters decrease. This may be attributed to the presence of large number of free radicals, which are terminated by oxidation of growing grafted chains causing decreasing trend.

Effect of N-vinyl-2-pyrrolidone concentration

The effect of N-vinyl-2-pyrrolidone on graft copolymerization has been studied by varying the concentration of N-vinyl-2-pyrrolidone from 8×10^{-2} to 24×10^{-2} dm^{-3}. It has been observed that grafting ratio, add on, efficiency increase on increasing the concentration of N-vinyl-2-pyrrolidone from 8×10^{-2} to 16×10^{-2} mol dm^{-3}. The results are presented in Figure 2(a,b). The increment in grafting parameters might be due to the greater availability of monomer molecules at the close proximity of polymer backbone. The monomer molecules, which are
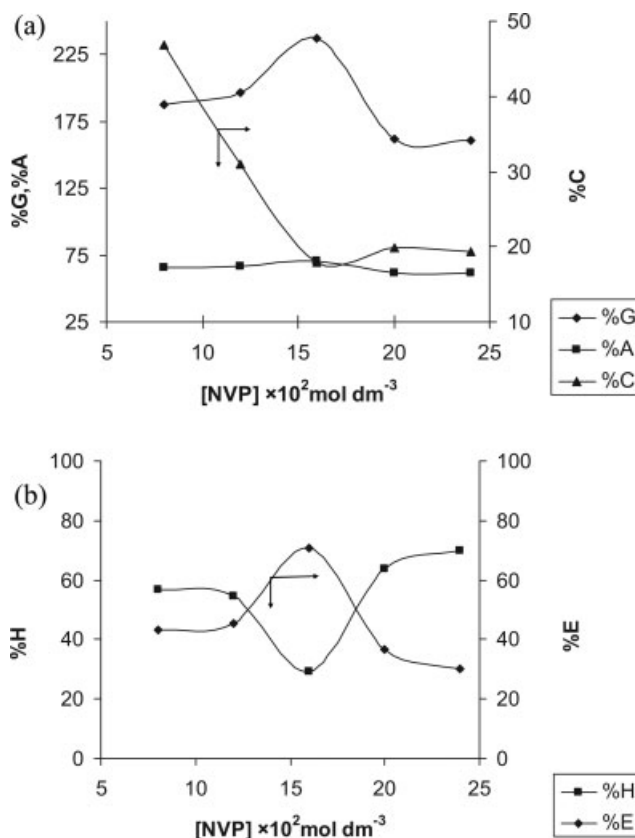
Figure 2 (a,b) Effect of monomer concentration. $[XOH] = 1.0$ g dm^{-3}, $[PDP] = 8 \times 10^{-3}$ mol dm^{-3}, $[Ag^+] = 20 \times 10^{-4}$ mol dm^{-3}, $[H^+] = 10 \times 10^{-3}$ mol dm^{-3}, Temp. $= 35°C$, Time $= 120$ min.

at the immediate vicinity of the reaction sites, become acceptors of xanthan gum radicals ($XO^•$) resulting in chain initiation and thereafter themselves becomes free radical donors to the neighboring molecule (monomer) leading to lowering of termination. But beyond cited range i.e., 8×10^{-2} to 16×10^{-2} mol dm^{-3}, these grafting parameters decrease. The decrement in grafting parameters is due greater solubility of poly N-vinyl-2-pyrrolidone in water, which causes higher viscosity of reaction medium, in which movement of free radicals is hindered.

Effect of xanthan gum concentration

The effect of xanthan gum concentration on grafting parameters has been studied by varying the concentration of xanthan gum from 0.4 to 1.8 g dm^{-3} and results are given in Table II. The grafting parameters i.e., grafting ratio, add on, and conversion have been decreased with increase in concentration of xanthan gum. This may be due to high viscosity of reaction medium by which accessibility of monomer molecules to growing polymeric chain is restricted.

TABLE II
Effect of Xanthan Gum Concentration

[XOH] g dm^{-3}	%G	%E	%A	%C	%H
0.4	421.5	73.8	80.8	12.3	26.3
0.6	367.7	73.4	78.6	16.3	26.6
1.0	236.8	70.7	70.3	18.0	29.3
1.4	148.2	53.3	59.7	21.0	46.7
1.8	103.55	45.9	50.9	21.9	54.1

[NVP] = 16 × 10^{-2} mol dm^{-3}, [PDP] = 8 × 10^{-3} mol dm^{-3}, [Ag$^+$] = 20 × 10^{-4} mol dm^{-3}, [H$^+$] = 10 × 10^{-3} mol dm^{-3}, Temp. = 35°C, Time = 120 min.

Effect of hydrogen ion concentration

The preliminary experimental results show that grafting does not take place in the absence of hydrogen ions. But as soon as little amount of acid is added into the reaction mixture, grafting starts which indicate that protonated species of peroxydiphosphate is an active species. Therefore it was thought properly to study the effect of acid concentration. The results are given in Table III, which reveals that as the H$_2$SO$_4$ concentration is increased from 2 × 10^{-3} mol dm^{-3} to 14 × 10^{-3} mol dm^{-3}, grafting ratio, efficiency, and add on increase. This may be due to the increase in concentration of active species,[12,13] i.e. H$_2$P$_2$O$_8^{2-}$. But when the concentration of sulfuric acid is increased beyond 14 × 10^{-3} mol dm^{-3}, the parameters decrease, which could be explained due to the formation of inactive species[14] such as H$_4$P$_2$O$_8$ and H$_5$P$_2$O$_8^+$ which decrease the concentration of active species H$_2$P$_2$O$_8^{2-}$. Hence decreasing trend is observed.

Effect of time period

The effect of time duration on grafting parameters has been studied by varying time period from 60 to 180 min [Fig. 3(a,b)]. Grafting parameters increase with increasing the time period from 60 to 120 min but beyond this time period grafting ratio, efficiency, and add on decrease. On increasing the time period,

TABLE III
Effect of H$^+$ Concentration

[H]$^+$ × 10^3 mol dm^{-3}	%G	%E	%A	%C	%H
2	160.4	40.1	61.6	21.6	59.9
6	179.2	44.0	64.2	21.5	56.0
10	236.8	70.7	70.3	18.0	29.3
14	238.8	72.6	70.5	17.8	27.4
18	218.0	53.8	68.6	21.9	46.2

[NVP] = 16 × 10^{-2} mol dm^{-3}, [PDP] = 8 × 10^{-3} mol dm^{-3}, [Ag$^+$] = 20 × 10^{-4} mol dm^{-3}, [XOH] = 1.0 g dm^{-3}, Temp. = 35°C, Time = 120 min.
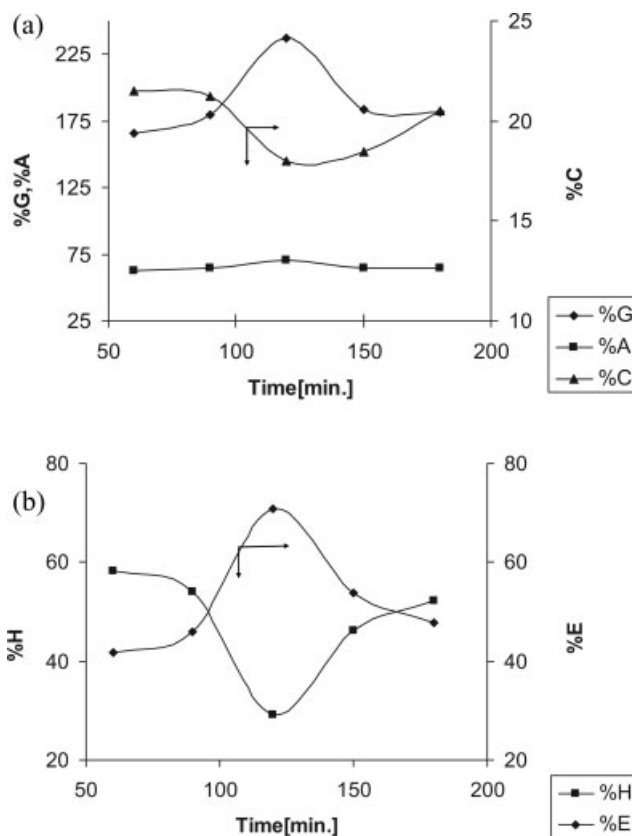
Figure 3 (a,b) Effect of time. [NVP] = 16 × 10^{-2} mol dm^{-3}, [PDP] = 8 × 10^{-3} mol dm^{-3}, [Ag$^+$] = 20 × 10^{-4} mol dm^{-3}, [XOH] = 1.0 g dm^{-3}, [H$^+$] = 10 × 10^{-3} mol dm^{-3}, Temp. = 35°C.

propagation of grafted chain takes place due to availability of more active species, which may lead to increase in grafting parameters. But with further increase in time period, these parameters decrease; this may be due to termination of growing grafted chain.

Effect of temperature

The effect of temperature on grafting parameters has been studied by varying the temperature from 25 to 45°C and results are summarized in Table IV. Grafting parameters show increment order on increasing the temperature up to 35°C, but on further increase in temperature, these parameters show a decreasing trend. The increase in grafting ratio, efficiency, add on up to certain range of temperature could be explained due to the increase in rate of production of primary free radicals and also diffusion of *N*-viny-2-pyrrolidone molecules into the domain of xanthan gum macro free radicals. However, further increase in temperature may result in decomposition of peroxydiphosphate, which may occur at higher

TABLE IV
Effect of Temperature

Temp. (°C)	%G	%E	%A	%C	%H
25	179.2	40.8	64.2	23.7	59.2
30	194.6	51.4	66.1	20.4	48.6
35	236.8	70.7	70.3	18.0	29.3
40	219.0	54.9	68.7	21.6	45.1
45	180.0	40.7	64.3	23.9	59.3

$[NVP] = 16 \times 10^{-2}$ mol dm^{-3}, $[PDP] = 8 \times 10^{-3}$ mol dm^{-3}, $[Ag^+] = 20 \times 10^{-4}$ mol dm^{-3}, $[XOH] = 1.0$ g dm^{-3}, $[H^+] = 10 \times 10^{-3}$ mol dm^{-3}, Time = 120 min.

temperature causing decrement in the concentration of peroxydiphosphate thereby decreasing the grafting parameters.

Mechanism

The following tentative mechanism was proposed. The interaction of $P_2O_8^{4-}$ with H^+ ion give rise to protonated species $H_2P_2O_8^{2-}$, which forms a complex with Ag^+, this complex interacts with xanthan gum molecule and forms free radicals.

Formation of free radicals

$$H_2P_2O_8^{2-} + Ag^+ \longrightarrow \underset{\text{Complex}}{H_2AgP_2O_8^-} \quad (1)$$

$$H_2AgP_2O_8^- + XOH \longrightarrow XO^\bullet + HPO_4^{-\bullet} + Ag^+ + H_2PO_4^- \quad (2)$$

$$XOH + HPO_4^{-\bullet} \longrightarrow XO^\bullet + H_2PO_4^- \quad (3)$$
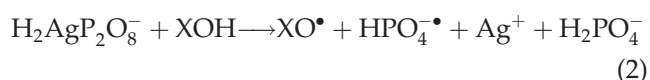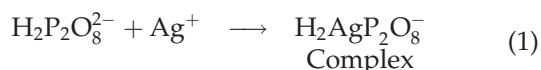
where $R^\bullet = HPO_4^{-\bullet}$, M = Monomer, and XOH = Xanthan gum.

Initiation:

$$XO^\bullet + M \longrightarrow XOM_1^\bullet$$

$$R^\bullet + M \longrightarrow RM_1^\bullet$$

Propagation:

$$XOM_1^\bullet + M \longrightarrow XOM_2^\bullet$$

$$XOM_2^\bullet + M \longrightarrow XOM_3^\bullet$$

$$.............$$
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$$XOM_{(n-1)}^\bullet + M \longrightarrow XOM_n^\bullet$$
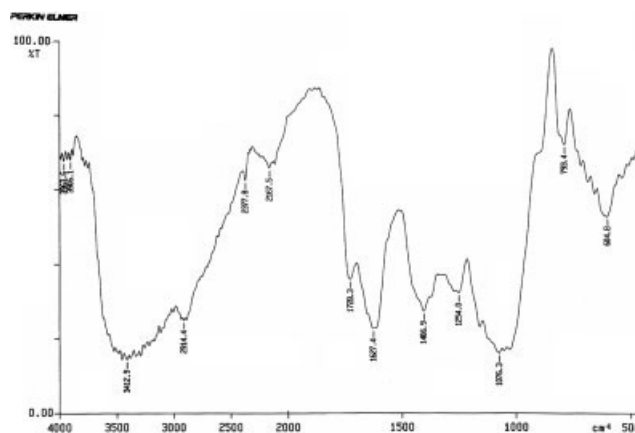
Figure 4 IR spectra of xanthan gum.

$$RM_1^\bullet + M \longrightarrow RM_2^\bullet$$

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

Termination:

$$XOM_n^\bullet + DOM_m^\bullet \longrightarrow \text{Graft copolymer}$$

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

$$RM_n^\bullet + RM_m^\bullet \longrightarrow \text{Homopolymer.}$$
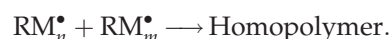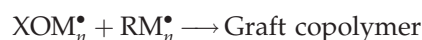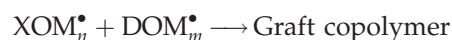
Evidence of grafting

IR spectroscopy

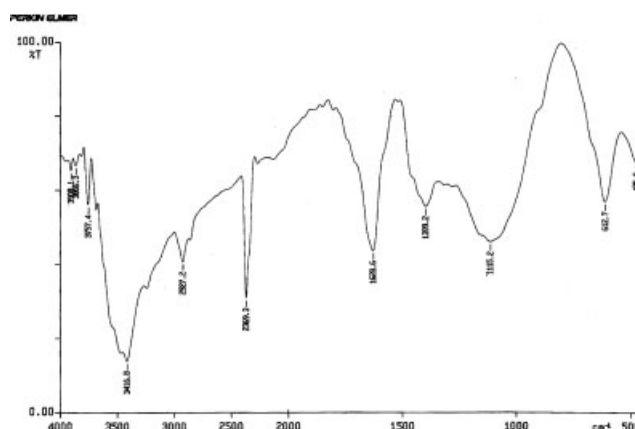IR Spectra of pure xanthan gum (Fig. 4) and grafted xanthan-g-N-vinyl-2-pyrrolidone (%G = 236) (Fig. 5)

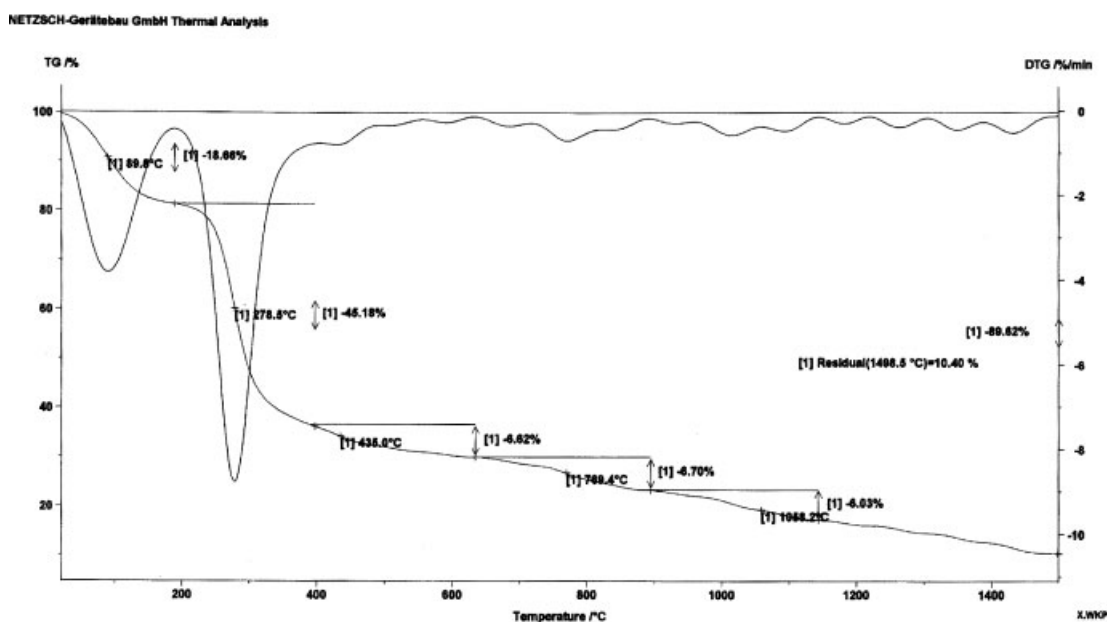**Figure 5** IR spectra of xanthan gum-g-N-vinyl-2-pyrrolidone.

Figure 6 Thermogravimetric trace of xanthan gum.

have been recorded with Perkin-Elmer FTIR model in the range from 500 to 4000 cm^{-1} to provide the proof of grafting. A broad band at 3412.9 cm^{-1} has been appeared in the spectrum of xanthan gum due to OH stretching vibration. On comparing the IR spectra of xanthan gum and xanthan gum-*g-N*-Vinyl-2-pyrrolidone, a sharp peak at 3416.8 cm^{-1} has been appeared due to OH stretching vibration in xanthan gum-*g-N*-vinyl-2-pyrrolidone. The shifting of this peak from 3412.9 to 3416.8 cm^{-1} indicates the participation of hydroxyl groups in chemical reaction. The grafting of *N*-vinyl-2-pyrrolidone is further confirmed by a variation in intensity of peak at 1628 cm^{-1} appeared due to >C=O stretching in xanthan gum-*g-N*-vinyl-2-pyrrolidone which has appeared in xanthan gum at 1627.4 cm^{-1}. A characteristic absorption band at 1399 cm^{-1} has been appeared due to CN stretching vibration of *N*-vinyl-2-pyrrolidone. The appearance of additional band due to CN stretching as well as shifting of OH stretching vibration appeared at 3412.9 cm^{-1} and >C=O stretching vibration appeared at 1627 cm^{-1} appeared in pure xanthan gum suggest that grafting has taken place on OH site of pure xanthan gum.
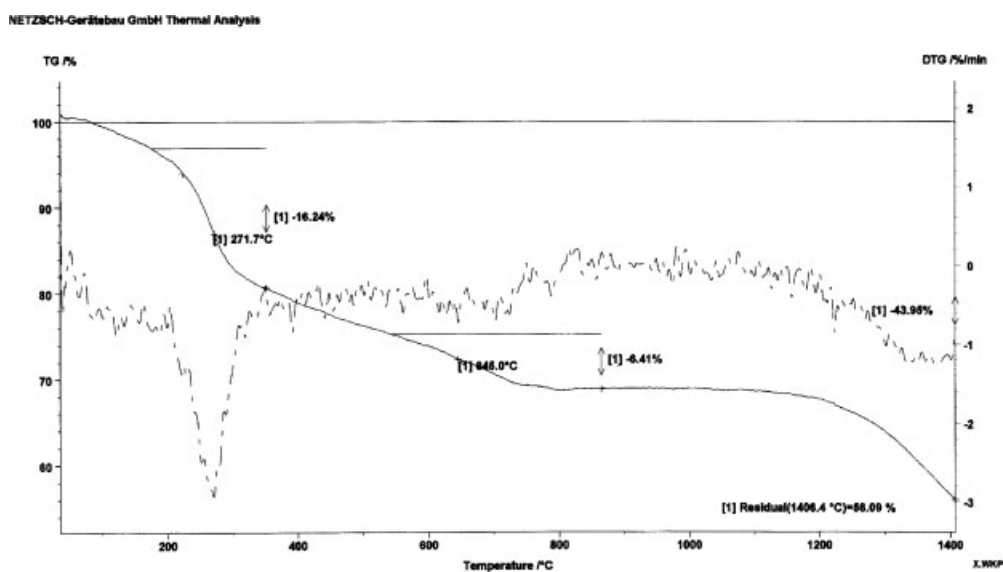

Figure 7 Thermogravimetric trace of xanthan gum-*g-N*-vinyl-2-pyrrolidone.

TABLE V
Thermogravimetric Analysis

Sample	PDT (°C)	FDT (°C)	T_{max} (°C)	IPDT
Xanthan gum	250.00	825.00	278.5	274.5
Xanthan gum-g-N-vinyl-2-pyrrolidone	212	1212.5	271.7645 768	347.8

Thermogravimetric analysis

Grafting of N-vinyl-2-pyrrolidone on xanthan gum may be a fruitful attempt as it increases the thermal stability of xanthan gum. Thermal analysis of xanthan gum and xanthan gum-g-N-vinyl-2-pyrrolidone has been carried out in inert atmosphere at heating rate of 15°C/min on NETZSCH-Geratebau GmbH Thermal Analyser.

Xanthan gum

Thermogravimetric trace of xanthan gum has been presented in the form of graph in Figure 6. It has been observed that xanthan gum starts to degrade at 200°C. It occurs in single step. The 10% weight loss has been found at 100°C due to loss of absorbed water. The polymer decomposition temperature has been found at 250°C. The rate of weight loss increases continuously with increase in temperature and attains a maximum at 700°C. T_{max}, temperature at which maximum degradation has been occurred, is 278°C. The integral procedural decomposition temperature (IPDT) and final decomposition temperature (FDT) have been found at 247.7 and 825°C, respectively. A char yield of 10.4% is obtained at 1498.5°C.

Xanthan gum-g-N-vinyl-2-pyrrolidone

The thermogravimetric trace of xanthan gum-g-N-vinyl-2-pyrrolidone has been presented in the form of graph (Fig. 7). The 2.5% weight loss at 200°C has been found due to loss of absorbed water. The graft copolymer (xanthan gum-g-N-vinyl-2-pyrrolidone) starts to degrade at 256°C. The rate of weight loss increases with increase in temperature and attains a maximum value at 271°C. T_{max}, temperature at which maximum degradation has been found, is 271°C, which is due to elimination of CO_2. Second T_{max} has been found at about 645°C due to elimination of pyruvate group attached to the backbone. Further third T_{max} has been found at about 768°C, which is due to elimination of pyrrolidone ring. The polymer decomposition temperature has been found at 256°C. The integral procedural decomposition temperature (IPDT) and final decomposition temperature (FDT) have been found at 347.8 and 1212°C, respectively. The high value of integral procedural decomposition temperature, final decomposition temperature, and three step degradation supports that xanthan gum-g-N-vinyl-2-pyrrolidone is thermally more stable than pure xanthan gum. The result is given in Table V.
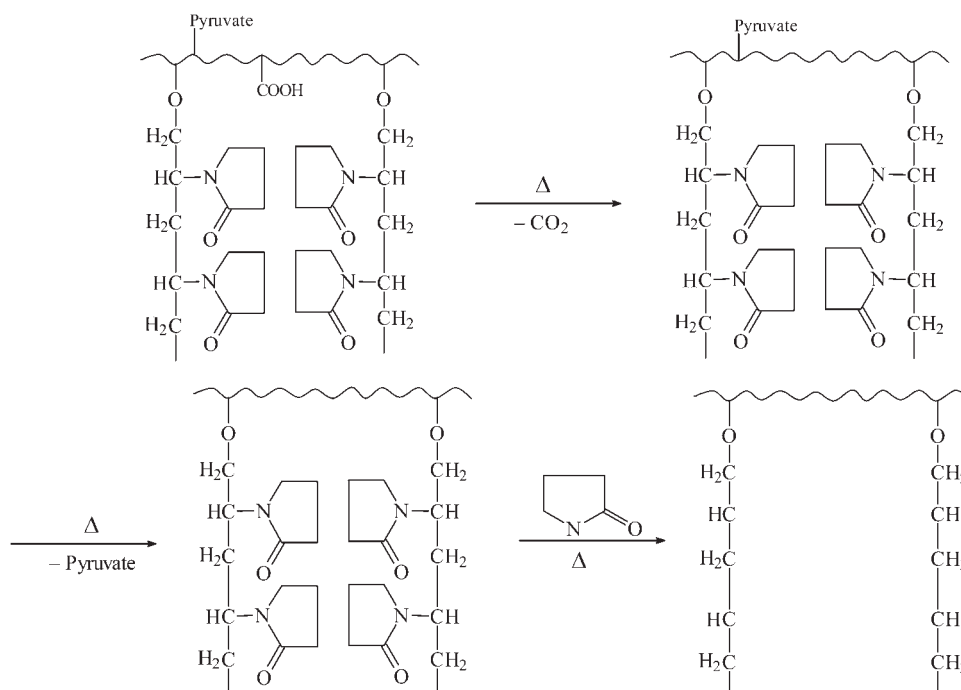
TABLE VI
Swelling Behavior

Sample	$[NVP] \times 10^2$ mol dm^{-3}	%G	Percent swelling (P_S)	Swelling ratio (S_R)
A	8	188	160	1.6
B	12	196	173	1.7
C	16	236	205	2.1
D	20	162	146	1.5
E	24	161	143	1.4

$[NVP] = 16 \times 10^{-2}$ mol dm^{-3}, $[PDP] = 8 \times 10^{-3}$ mol dm^{-3}, $[Ag^+] = 20 \times 10^{-4}$ mol dm^{-3}, $[XOH] = 1.0$ g dm^{-3}, $[H^+] = 10 \times 10^{-3}$ mol dm^{-3}, Time = 120 min, Temp. = 35°C.

Swelling studies

Swelling studies have been carried with graft copolymer and samples were prepared by varying the monomer concentration. For the swelling studies, 0.02 g of graft copolymer was taken and kept undisturbed for 24 h in triple distilled water. The grafted sample was taken out and surface water on the swollen graft copolymer was removed by softly pressing the graft copolymer in between the folds of filter paper. An increase in weight was recorded. Percent swelling (P_S) and swelling ratio (S_R) were calculated.[9,10]

The results were summarized in Table VI and the data reveals that with increase in percent grafting, the percent swelling and swelling ratio increase up to a certain limits. This behavior could be explained due to the fact that *N*-vinyl-2-pyrrolidone is hydrophilic in nature and with increase in percent grafting the amount of *N*-vinyl-2-pyrrolidone was also increased.

Metal ion sorption studies

Different samples of graft copolymer of xanthan gum were synthesized by varying the monomer concentration. These samples were immersed for 24 h in 20 mL solutions of metal ions of known concentra-tion. Filtrates were analyzed for unabsorbed ions titrametrically.

Structural aspects of polymers and sorption behavior of metal ions

Hydrophilic–hydrophobic balance, nature of monomer, and extent of crosslinking of macromolecular supports are major factors which effect metal ion uptake.[15] This functionality can be tailored and incorporated by grafting to retain ions by polymer analogous reaction or by simple chelation. Out of these possibilities, all may contribute in metal ion sorption though extent of contribution of any factor may be different. However, functional group incorporated by grafting and its ability to interact with metal ion may play more important role in determination of selectivity and quantum of metal ion uptake.

Sorption behavior of xanthan gum and its graft copolymer

For the metal ion sorption studies, five metal ions have been chosen (Cu^{2+}, Zn^{2+}, Ni^{2+}, Pb^{2+}, and Hg^{2+}) and the amount of metal ion uptake is calculated by titrating the remaining metal ion. The results have been summarized in Table VII and the

TABLE VII
Metal Ion Sorption

Sample	$[NVP] \times 10^2$ mol dm^{-3}	%G	Percent uptake (P_u)					Partition coefficient (K_d)					Retention capacity (Q_r)				
			Cu^{2+}	Pb^{2+}	Ni^{2+}	Zn^{2+}	Hg^{2+}	Cu^{2+}	Pb^{2+}	Ni^{2+}	Zn^{2+}	Hg^{2+}	Cu^{2+}	Pb^{2+}	Ni^{2+}	Zn^{2+}	Hg^{2+}
XOH	–	–	4.5	1.4	3.7	2.5	0.7	39.1	6.9	19.4	13	3.5	2.2	0.6	1.9	1.5	0.4
A	8	188	18.5	5.5	15.7	11.2	1.7	113.4	29.4	93.8	62.7	8.6	9.0	2.5	7.9	6.9	0.8
B	12	196	18.9	5.7	16.9	11.6	1.9	116.3	30.2	101.7	65.8	9.5	9.2	2.6	8.5	6.7	0.9
C	16	236	19.7	6.3	18.4	13.2	2.1	122.7	33.8	112.4	75.9	10.8	9.7	2.9	9.2	7.6	1.1
D	20	162	18.3	5.2	14.8	10.7	1.7	112.3	27.5	86.8	60.0	8.4	8.9	2.4	7.4	6.1	0.8
E	24	161	16.7	5.2	14.6	10.7	1.6	100.3	27.2	85.3	59.8	8.3	8.2	2.4	7.3	6.1	0.8

$[NVP] = 16 \times 10^{-2}$ mol dm^{-3}, $[PDP] = 8 \times 10^{-3}$ mol dm^{-3}, $[Ag^+] = 20 \times 10^{-4}$ mol dm^{-3}, $[XOH] = 1.0$ g dm^{-3}, $[H^+] = 10 \times 10^{-3}$ mol dm^{-3}, Time = 120 min, Temp. = 35°C. Where XOH = xanthan gum; A, B, C, D, E = Graft copolymers.

data reveals that graft copolymer shows better metal ion uptake behavior than xanthan gum.

The effect of percent grafting on sorption behavior of graft copolymer has been studied in terms of percent ion uptake (P_u), partition coefficient (K_d), and retention capacity (Q_r). From Table VII it is evident that these parameters have direct relationship with percent grafting. It could be explained due to the fact that increase in percent grafting, i.e., the concentration of *N*-vinyl-2-pyrrolidone increases so the pendent groups of *N*-vinyl-2-pyrrolidone can hold more metal ions.

CONCLUSIONS

The spectroscopic data confirm that the grafting of *N*-vinyl-2-pyrrolidone has occurred at hydroxyl group and it also confirms the mechanism suggested for grafting. The thermal analysis data show that the grafted polymer is thermally more stable than pure gum. The data of metal ion uptake and swelling behavior show the enhancement of these properties due to grafting.

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