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Synthesis, Characterization and Study of Metal Ion Sorption Capacity and Water Swelling Behavior of Xanthan Gum-g-N,N′-Dimethylacrylamide

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In the present paper Xanthan gum-g-N,N′-dimethyl acryl amide was synthesized by free radical polymerization using a bromate/thiourea redox pair in an inert atmosphere. Studies are done to observe the effect of reactants on grafting parameters by varying the reactant concentration and to study some physical-chemical properties. Grafting ratio, add on and conversion show a decrement on increasing the concentration of Xanthan gum. The grafting parameters increase on increasing the concentration of N,N′-dimethyl acrylamide from 8.3×10^{-2} to 20×10^{-2} mol dm^{-3}, BrO_3^- from 1×10^{-3} to 5×10^{-3} mol dm^{-3} and thiourea from 1.2×10^{-3} to 3.6×10^{-3} mol dm^{-3}. Optimum temperature and time for grafting of N,N′-dimethyl acrylamide on Xanthan gum are found to be 35°C and 120 min, respectively. Water swelling behavior, swelling ratio, and metal ion uptake, metal retention capacity are also studied. It was found that the graft copolymer shows a greater enhancement in these properties than the substrate. The graft copolymer is characterized by FTIR and thermal analysis.

Keywords: xanthan gum; graft copolymer; thermal analysis; bromate/thiourea redox pair; N,N′-dimethyl acrylamide; metal ion uptake; water swelling behavior

1 Introduction

At the present time, natural polymers and their biomedical application is the most fascinating and vastly investigated field. For this purpose, biodegradable natural polymers such as polysaccharides and protein have been widely used (1, 2). One is Xanthan gum; it is an extra cellular hetropolysaccharide of xanthamonas campestris. Its structure consists of a β-(1 → 4)-linked D-glucopyranosyl backbone chain. The properties, such as thickening, emulation stabilization, water binding and acid compatibilities (3) give the advantages of application in food and pharmaceutical. It is also widely used in enhanced oil recovery, (4) and as a drug delivery system for poor water-soluble drugs (5). In addition to these useful applications, it has some drawbacks that it is susceptible to microbial attack, which limits its uses. Modification of Xanthan gum by a graft copolymerization technique allows us to chemically change the polysaccharide chain by introducing a polymer chain that configures different structural characteristics to the initial materials. Several monomers like acrylamide, (6) acrylic acid (7) etc., have been grafted on Xanthan gum to utilize its properties in many ways.

N,N′-Dimethylacrylamide (DMA) is a weakly hydrogen-bonded amide and a hydrophilic monomer (8) and, due to this property, it is used to obtain polymeric biomaterials compatible to blood and tissue. Poly(N,N′-dimethylacrylamide) (DMA) and its copolymers were used in various fields, such as oil-recovery (9) slow release medical materials (10), and in the making of ocular contact lenses (11). Taking into consideration all of these interesting applications of N,N′dimethylacrylamide (DMA) and Xanthan gum, an attempt has been made to graft previously unreported dimethyl acrylamide onto Xanthan gum. The resulting graft copolymer showed better properties such as metal ion uptake, water-swelling capacity etc. than the substrate.

2 Experimental

2.1 Materials

N,N′-dimethyl acrylamide (Aldrich) was distilled at 14 mm Hg and 50°C and only the middle fraction was used. Xanthan gum (XOH) was purchased from Sigma (USA), potassium bromate (E. Merck) and thiourea (Merck Ltd.) were used as such, while for maintaining hydrogen ion

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concentration, sulphuric acid (E. Merck) was used. All the solutions were prepared in triple distilled water.

2.2 Procedure for Graft Copolymerization

For each experiment, Xanthan gum solution was prepared by the addition of a weighed amount of Xanthan gum into a reactor containing triple distilled water. A calculated amount of thiourea, N,N′-dimethyl acrylamide and sulphuric acid solution were added to the reactor at constant temperature and a slow stream of oxygen-free nitrogen was passed. After 30 min, a known amount of deoxygenated potassium bromate solution was added to initiate the reaction, and the reaction was carried out under inert atmosphere. After the desired time period, the reaction was stopped by allowing air into the reactor. The graft copolymer was precipitated by pouring the reaction mixture into the water methanol mixture. The grafted sample was separated by filtration and the homopolymer will pass into the filtrate. Now the grafted sample has been washed with a methanol-water mixture twice so that any homopolymer, which sticks to the graft copolymer, would pass into the filtrate, then the grafted sample was dried and weighed. The poly(N,N′dimethylacrylamide) (DMA) remains in the filtrate. In this filtrate, a pinch of hydroquinone was added and was concentrated by distillation under reduced pressure. This concentrated solution has been poured into the pure methanol to precipitate the poly(N,N′-dimethylacrylamide). The poly(N,N′-dimethylacrylamide) was separated, dried, and weighed.

3 Results and Discussion

The graft copolymer has been characterized according to Fanta's definition (12):

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

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

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

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

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

The effect of variation of concentration of BrO_3^-, thiourea, hydrogen ion, N,N′-dimethylacrylamide (DMA), and Xanthan gum, along with the effect of time and temperature on grafting parameter has been studied. In addition to these, the swelling ratio, percentage swelling and metal retention capacity of graft copolymer for different toxic metal ion was also studied by using the following expression (13, 14).

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

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

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

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

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

3.1 Determination of Optimum Reaction Condition

3.1.1 Effect of Bromate Ion Concentration

The bromate-thiourea system is a novel initiator for the aqueous polymerization of vinyl monomers. It has been tested that neither potassium bromate nor thiourea when used alone can initiate polymerization. On the other hand, thiourea coupled with bromate ion can initiate polymerization. Therefore, the effect of bromate ion concentration of grafting reaction was studied and the results are summarized in Table 1. It was observed that the grafting ratio, efficiency and add on, increases on increasing the bromate ion concentration from 1.0×10^{-3} to 5×10^{-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 ion concentration was due to the progressive reduction of potassium bromate with thiourea producing bromide ion and isothiocarbamide free radicals which attack the Xanthan gum molecule creating a free radicals site onto which monomer addition takes place. The grafting ratio, efficiency and add on, decreases on increasing the bromate ion concentration due to one of following reasons:

1. At higher bromate ion concentration, it might react with the gum macroradical or with the growing radical, thus reducing the extent of grafting.
2. Oxidation of the active groups on the backbone, thereby preventing the formation of free radicals.
3. Due to the liberation of appreciable amount of oxygen, the radical may die, causing a decrease in concentration of radicals.

Table 1. Effect of BrO_3. [Thiourea] = 2.8×10^{-3} mol dm^{-3}, [DMA] = 16.6×10^{-2} mol dm^{-3}, [XOH] = 1.0 g dm^{-3}, [H^+]= 10.0×10^{-3} mol dm^{-3}, Time = 120 min., Temp. = 40°C

[BrO_3] × 10^3 mol dm^{-3}	%G	%E	%A	%C	%H
1	90.0	55.8	47.4	9.7	44.2
3	94.0	60.8	48.4	9.3	39.2
5	105.0	70.0	51.2	9.1	30.0
8	96.0	63.0	48.9	9.2	37.0
12	92.2	58.3	47.9	9.4	41.7

3.1.2 *Effect of Thiourea Concentration*

Increment in the concentration of thiourea from 1.2×10^{-3} to 3.6×10^{-3} mol dm^{-3} (Table 2) shows the increment in grafting parameters but beyond the 3.6×10^{-3} mol dm^{-3}, the grafting ratio, efficiency and add on decrease. The increment in grafting parameters within the cited range of thiourea concentration was due to the availability of more primary free radicals that were produced from the reaction of protonated species of thiourea with bromate ion. At a higher concentration, grafting parameters show a decrease, which might be due to the facilitation of the homopolymer over grafting.

3.1.3 *Effect of N,N′-Dimethyl Acrylamide (DMA) Concentrations*

The effect of the N,N′-dimethyl acrylamide concentration on grafting parameters has been studied by varying the concentration of N,N′-dimethylacrylamide (DMA) and the results are shown in Figures 1(a) and(b). It was clear from Figure 1(a) and (b) that the grafting ratio, efficiency and add on, increases on increasing the concentration of N,N′-dimethylacrylamide (DMA) up to 20×10^{-2} mol dm^{-3}. Thereafter, the values of these grafting parameters decrease. This behavior could be explained by the fact that the increase of N,N′-dimethylacrylamide (DMA) concentration leads to an accumulation of monomer molecules, which was at the immediate vicinity of reaction sites, and becomes the acceptor of Xanthan gum macroradicals resulting in chain initiation. Thereafter, they become a free radical donor to neighboring molecules causing the lowering of termination. The decrease in grafting ratio, efficiency, add on could be interpreted in terms of an increase in viscosity of the medium due to the formation of (poly)N-N′-dimethylacrylamide (DMA), which is soluble in water.

Table 2. Effect of Thiourea. [BrO_3] = 5×10^{-3} mol dm^{-3}, [DMA] = 16.6×10^{-2} mol dm^{-3},[XOH] = 1.0 g dm^{-3}, [H^+] = 10.0×10^{-3} mol dm^{-3}, Time = 120 min., Temp. = 40°C

[Thiourea] × 10^3mol dm^{-3}	%G	%E	%A	%C	%H
1.2	71	49.7	41.5	8.6	50.3
2.0	100.9	67.3	50.2	9.1	32.7
2.8	105	70	51.2	9.1	30
3.6	110	74.8	52.4	8.9	25.2
4.4	72	51.2	41.9	8.5	48.8

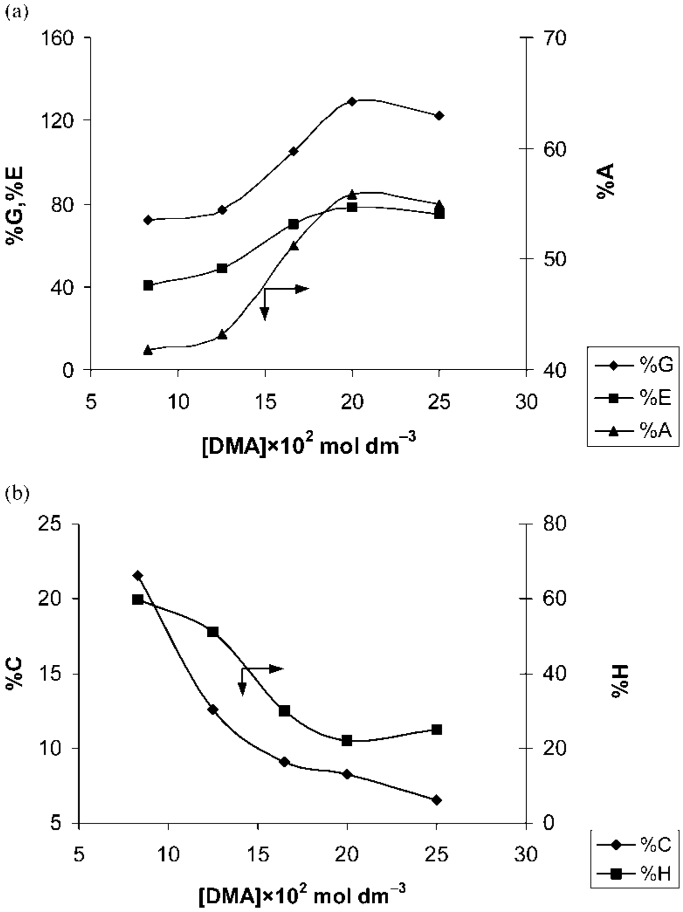


Fig. 1. (a). Effect of Monomer. [XOH] = 1.0 g dm^{-3}, [Thiourea] = 2.8×10^{-3} mol dm^{-3}, [BrO_3]$^-$ = 5×10^{-3} mol dm^{-3}, [H^+] = 10×10^{-3} mol dm^{-3}, Temp. = 40°C, Time = 120 min. (b) Effect of Monomer. [XOH] = 1.0 g dm^{-3}, [Thiourea] = 2.8×10^{-3} mol dm^{-3}, [BrO_3]$^-$ = 5×10^{-3} mol dm^{-3}, [H^+] = 10×10^{-3} mol dm^{-3}, Temp. = 40°C, Time = 120 min.

3.1.4 *Effect of Xanthan Gum*

The effect of the Xanthan gum concentration on grafting parameter was studied by varying the concentration of Xanthan gum from 0.6 to 1.4 gm dm^{-3} (Table 3). The grafting parameters decrease with increase in concentration of Xanthan gum. This may be due to the increase in viscosity which may restrict the accessibility of monomer to the growing polymeric chain leading to the decrease in grafting ratio, efficiency, add on, efficiency and conversion.

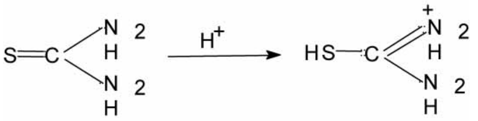
3.1.5 *Effect of Hydrogen Ion Concentration*

The effects of hydrogen ion concentration on grafting parameters were shown in Figure 2(a and b) and reveal that

Table 3. Effect of XOH. $[BrO_3] = 5 \times 10^{-3}$ mol dm^{-3}, [DMA] $= 16.6 \times 10^{-2}$ mol dm^{-3}, $[H^+] = 10.0 \times 10^{-3}$ mol dm^{-3}, [Thiourea] $= 2.8 \times 10^{-3}$ mol dm^{-3}, Time = 120 min., Temp. = 40°C

[XOH] g dm^{-3}	%G	%E	%A	%C	%H
0.6	145	90.0	60	10.1	9.9
0.8	120.4	82.7	54.5	9.8	17.3
1.0	105	70	51.2	9.1	30
1.2	100	67.8	50	8.9	32.2
1.4	82.1	51.3	45.1	9.6	48.7

grafting ratio, efficiency, add on increase up to 10×10^{-3} mol dm^{-3} which can be explained that on increasing the concentration of H^+ ion, the concentration of protonated thiourea species also increases which reacts with bromate ion giving rise to primary free radicals. These primary free radicals react with Xanthan gum molecules giving rise to Xanthan gum free radicals, which are responsible for increasing grafting parameters



But on further increase in the concentration of H^+ ion i.e., beyond 10×10^{-3} and dm^{-3} the grafting ratio, efficiency and add on, decreases, which was may be due to excess hydrogen ion reacting with bromate to form $HBrO_3$. This species further decomposes to give oxygen in excess quantity, which acts as a scavenger and grafting parameters show decreasing trends.

$$2KBrO_3 + H_2SO_4 \rightarrow 2HBrO_3 + KSO_4$$

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

3.1.6 Effect of Time Period

The effect of time duration of the grafting reaction was studied by varying time periods from 60 to 180 min.

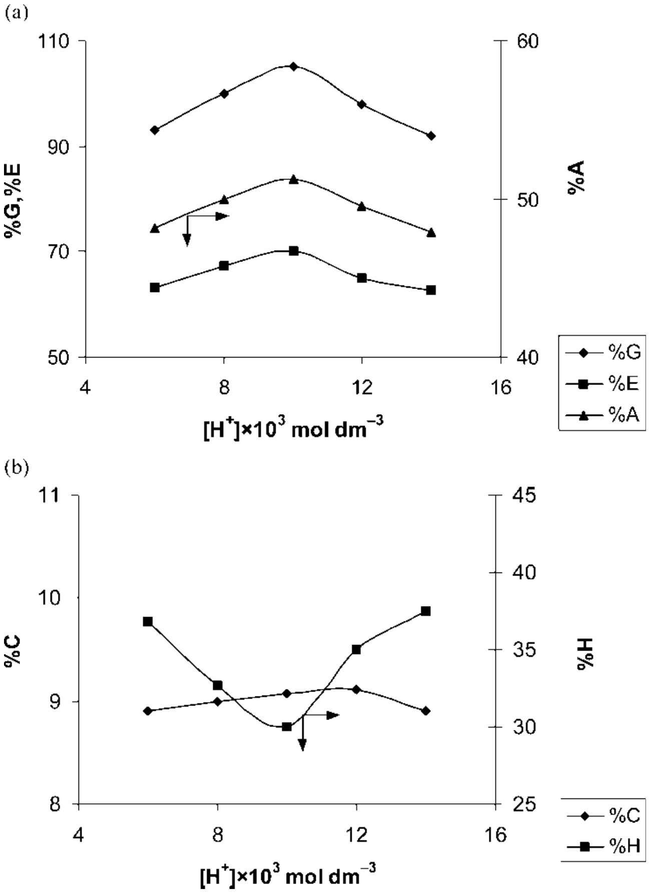


Fig. 2. (a) Effect of H^+. [DMA] $= 16.6 \times 10^{-2}$ mol dm^{-3}, [Thiourea] $= 2.8 \times 10^{-3}$ mol dm^{-3}, [XOH] = 1.0 g dm^{-3}, $[BrO_3^-] = 5 \times 10^{-3}$ mol dm^{-3}, Temp. = 40°C, Time = 120 min. (b). Effect of H^+. [DMA] $= 16.6 \times 10^{-2}$ mol dm^{-3}, [Thiourea] $= 2.8 \times 10^{-3}$ mol dm^{-3}, [XOH] = 1.0 g dm^{-3}, $[BrO_3^-] = 5 \times 10^{-3}$ mol dm^{-3}, Temp. = 40°C, Time = 120 min.

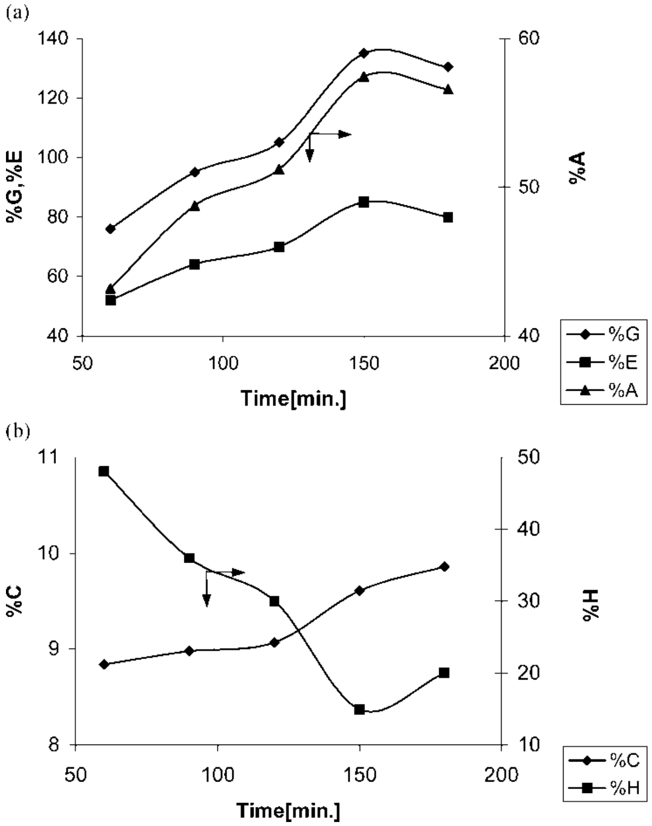


Fig. 3. (a) Effect of Time. [DMA] $= 16.6 \times 10^{-2}$ mol dm^{-3}, [Thiourea] $= 2.8 \times 10^{-3}$ mol dm^{-3}, [XOH] = 1.0 g dm^{-3}, $[H^+] = 10 \times 10^{-3}$ mol dm^{-3}, $[BrO_3^-] = 5 \times 10^{-3}$ mol dm^{-3}, Temp. = 40°C. (b) Effect of Time. [DMA] $= 16.6 \times 10^{-2}$ mol dm^{-3}, [Thiourea] $= 2.8 \times 10^{-3}$ mol dm^{-3}, [XOH] = 1.0 g dm^{-3}, $[H^+] = 10 \times 10^{-3}$ mol dm^{-3}, $[BrO_3^-] = 5 \times 10^{-3}$ mol dm^{-3}, Temp. = 40°C.

(Figure 3(a and b)). Grafting parameters increase with increasing the time period from 60 to 150 min. but beyond this time period, grafting ratio, efficiency and add on decreases. On increasing the time period, propagation of grafted chain takes place due to a longer time period, which results in an increase in grafting parameters. But on a further increase in time period, these parameters decrease; this may be due to termination of the growing grafted chain.

3.1.7 *Effect of Temperature*

The effect of temperature on grafting parameters was studied by varying the temperature from 30°C to 50°C and results were depicted in Figure 4(a and b). Grafting parameters show increment on increasing the temperature up to 45°C, but on further increase in temperature, these parameters show a decreasing trend. The increase in the grafting ratio, efficiency, add on and conversion up to the cited range may be attributed to the fact that with an increase in temperature, rate of production of primary free radicals increases causing an increase in these parameters and also diffusion of N,N′-dimethylacrylamide (DMA) molecule into the domain of Xanthan gum free radicals. However, there is a further parameter decrease, which might be due to destruction primary free radicals due to a higher temperature.

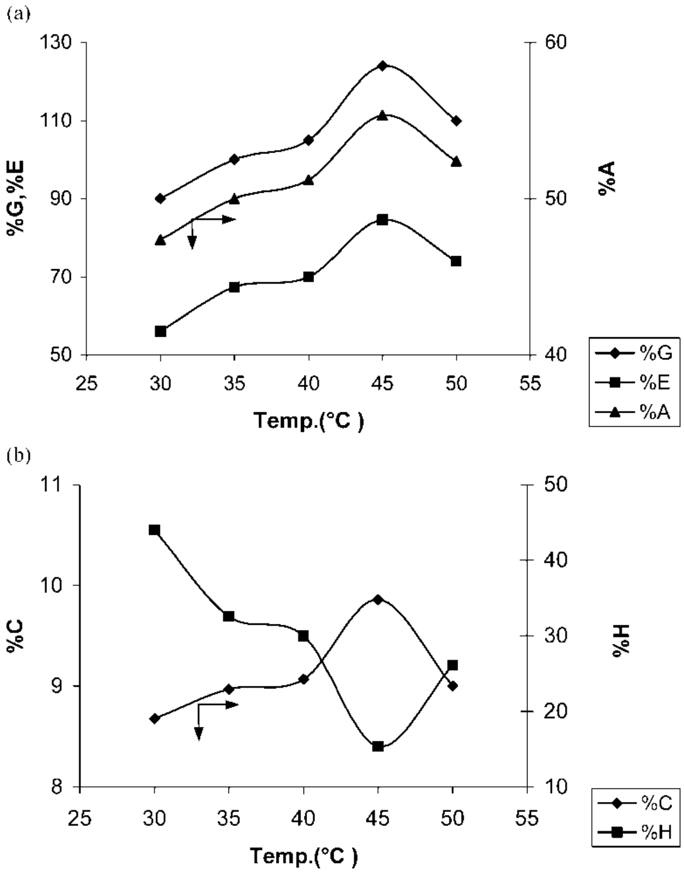
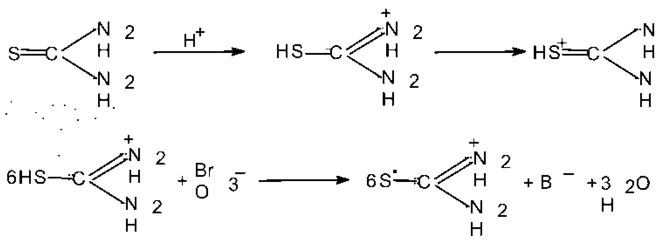


Fig. 4. (a) Effect of Temperature. [DMA] = 16.6×10^{-2} mol dm^{-3}, [Thiourea] = 2.8×10^{-3} mol dm^{-3}, [XOH] = 1.0 g dm^{-3}, [H$^+$] = 10×10^{-3} mol dm^{-3}, [BrO$_3^-$] = 5×10^{-3} mol dm^{-3}, Time = 120 min. (b) Effect of Temperature. [DMA] = 16.6×10^{-2} mol dm^{-3}, [Thiourea] = 2.8×10^{-3} mol dm^{-3}, [XOH] = 1.0 g dm^{-3}, [H$^+$] = 10×10^{-3} mol dm^{-3}, [BrO$_3^-$] = 5×10^{-3} mol dm^{-3}, Time = 120 min.

3.2 *Mechanism*

The following tentative mechanism is proposed. It has been found that bromate ion and thiourea alone cannot initiate the reaction. It was assumed that in the presence of hydrogen ion, thiourea was protonated and this species reacts with bromate ion to give isothiocarbamido radicals. These radicals abstract hydrogen atom from the Xanthan gum molecules producing Xanthan gum free radicals. The monomer molecules which were near the vicinity of the reaction site become an acceptor of Xanthan gum radicals resulting in chain initiation and thereafter they become a free radical donor to neighboring molecules, thus the grafted chain grows. Termination of chain by coupling yields graft copolymer.



Initiation:

$$XOH + R^{\bullet} \longrightarrow XO^{\bullet} + RH$$
$$M + R^{\bullet} \longrightarrow RM^{\bullet}$$

Propagation:

$$XO^{\bullet} + M \longrightarrow XOM_1^{\bullet}$$
$$XOM_1^{\bullet} + M \longrightarrow XOM_2^{\bullet}$$
$$XOM_2^{\bullet} + M \longrightarrow XOM_3^{\bullet}$$

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$$XOM_{n-1}^{\bullet} + M \longrightarrow XOM_n^{\bullet}$$
$$RM^{\bullet} + M \longrightarrow RM_1^{\bullet}$$
$$RM_1^{\bullet} + M \longrightarrow RM_2^{\bullet}$$

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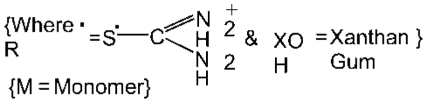
$$RM_{n-1}^{\bullet} + M \longrightarrow RM_n^{\bullet}$$

Termination:

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



3.3 Evidence of Grafting

3.3.1 I.R. Spectra

IR spectra of pure and grafted Xanthan gum (%G = 105) has been record on Perkin-Elmer FTIR. On comparing the IR spectra of Xanthan gum and Xanthan gum-g-N,N′-dimethylacrylamide (DMA), additional peaks appeared in the spectra of Xanthan gum-g-N,N′-dimethylacrylamide (DMA). Tertiary amide band appeared at 1632.3 cm^{-3} due to C═O stretching vibration. A band at 1500 cm^{-1} appeared due to C—N stretching vibration. The disappearance of some OH bending vibration from the Xanthan gum-g-N,N′ dimethylacrylamide (DMA) spectra indicates that grafting might have taken place on the OH site (Figures 5 and 6).

3.3.2 Thermo Gravimetric Analysis

Grafting of N,N′-dimethyl acrylamide on Xanthan gum seemed to be a successful attempt as it increases the thermal stability of Xanthan gum. Thermal analysis of Xanthan gum and Xanthan gum-g-N,N′-dimethyl acrylamide (%G = 105) was carried in inert atmosphere at a heating rate of 15°C/min on Netzsch-Geratebau GmbH Thermal Analysis.

3.4 Xanthan Gum

The degradation of Xanthan gum (XOH) started at about 200°C and occurs in a single step, the weight loss about 10% at 100°C was due to the loss of absorbed water and almost 50% weight loss was found at 300°C. The rate of wt loss increases with temperature and reached a maximum value at 700°C. Polymer decomposition temperature (PDT), the temperature at which maximum degradation occurs (T_{max}), and integral procedural decomposition temperature i.e., IPDT were obtained at 250°C, 278.5°C, and 274.6°C, respectively (Table 4). The final decomposition temperature (FDT) was found at 825°C and a char yield of 10.40% was obtained at 1498.5°C (Figure 7).

3.4.1 Xanthan Gum-g-N,N′-Dimethyl Acrylamide

The grafted copolymer starts degrading about 180°C. The 8.18% weight loss at 100°C was due to a loss of absorbed water. The degradation takes place in three steps. The rate

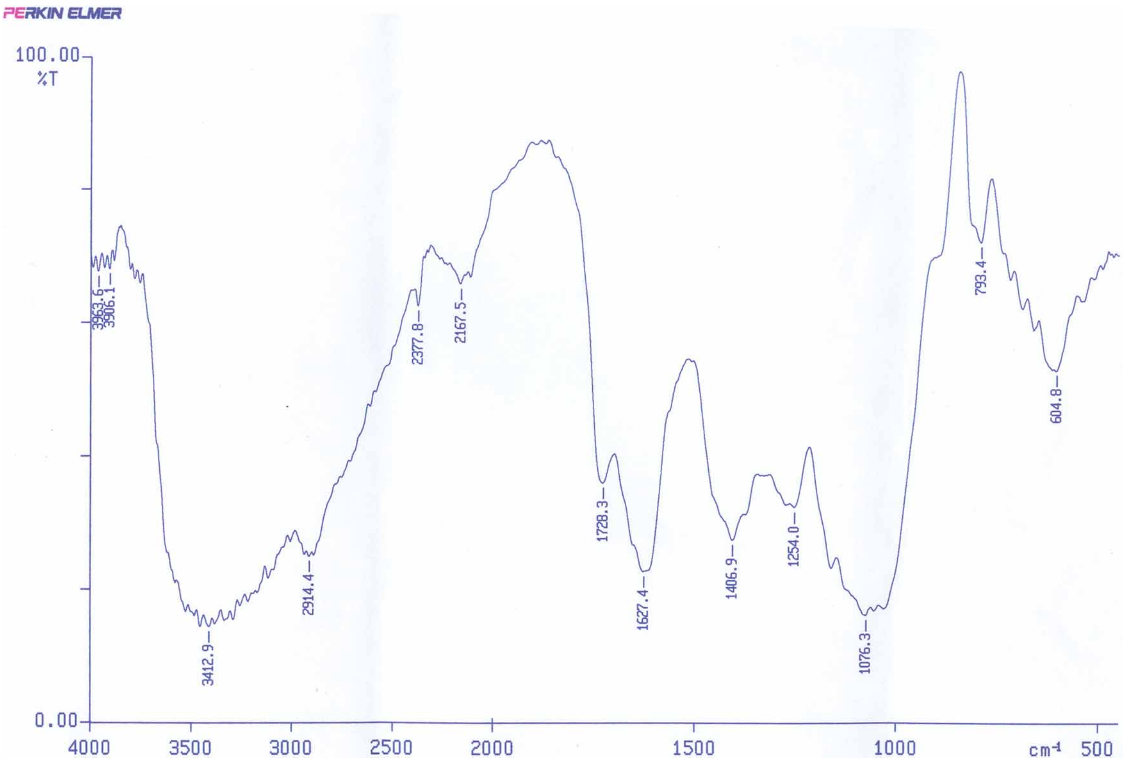


Fig. 5. IR spectra of Xanthan gum.

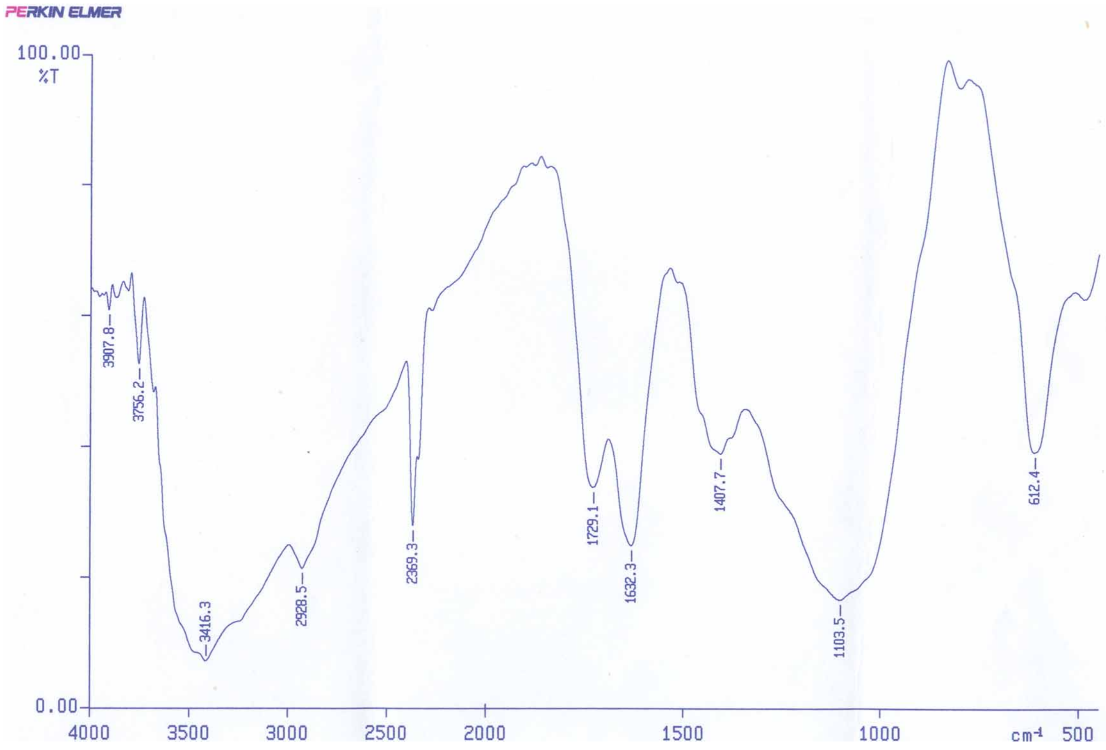
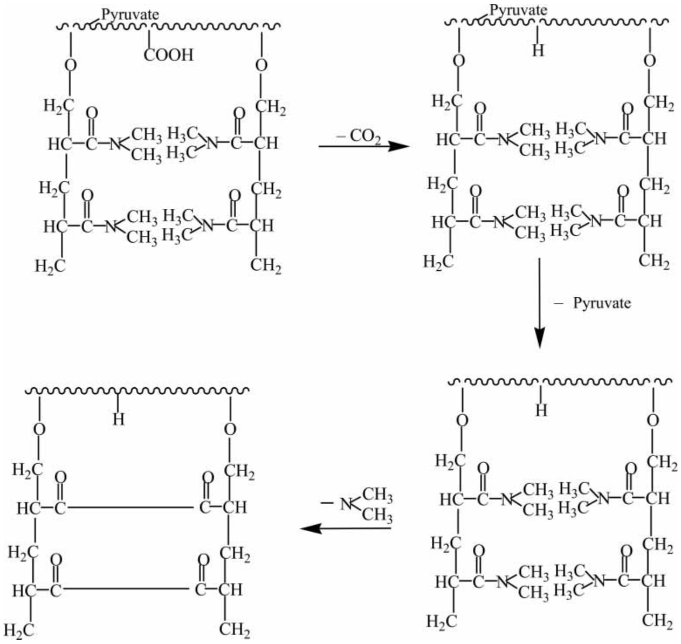


Fig. 6. IR spectra of Xanthan gum-g-N,N′-dimethyl acrylamide.

of weight loss increases with increase in temperature from 180°C and attains a maximum value at 266.7°C, after that it decreases. In the second step, the degradation starts from 631.1°C and attains a maximum value at 66.7°C, and in the third step degradation, the weight loss occurred in the 82.9°C to 1000°C temperature range. Thus, three T_{max} were observed in the degradation of Xanthan gum-g-N,N′-dimethyl acrylamide that were as follows 266.7°C, 664.7°C and 1006.9°C. These T_{max} were obtained due to the elimination of CO_2, pyruvate and dimethyl group. The gradual decrease in the endo peak of graft copolymer also indicates that the some physical and structural changes occur in the structure of graft copolymer. The polymer decomposition temperature has been found at 200°C; there is a 50% weight loss which occurs at 581.25°C. The final decomposition temperature (FDT) and integral procedural decomposition temperature (IPDT) have been found at 1137.5°C and 340.22°C, respectively (Figure 8).

Table 4. Thermo gravimetric analysis

Sample	PDT (°C)	FDT (°C)	T_{max} (°C)	IPDT
Xanthan gum	250.00	825.00	278.5	274.5
Xanthan gum–g–N,N′-Dimethyl acrylamide	218.75	1137.5	266.7 664.7 1006.9	340.22



3.5 Swelling Studies

Swelling studies were carried on graft copolymer, and samples were prepared by varying the monomer concentration. For the swelling studies, we took 0.020 gm of graft copolymer and kept it undisturbed for 24 h in triple distilled water. After this time period, the graft copolymer was removed and the surface water on the swollen graft copolymer was removed by gently pressing the graft copolymer in between the folds

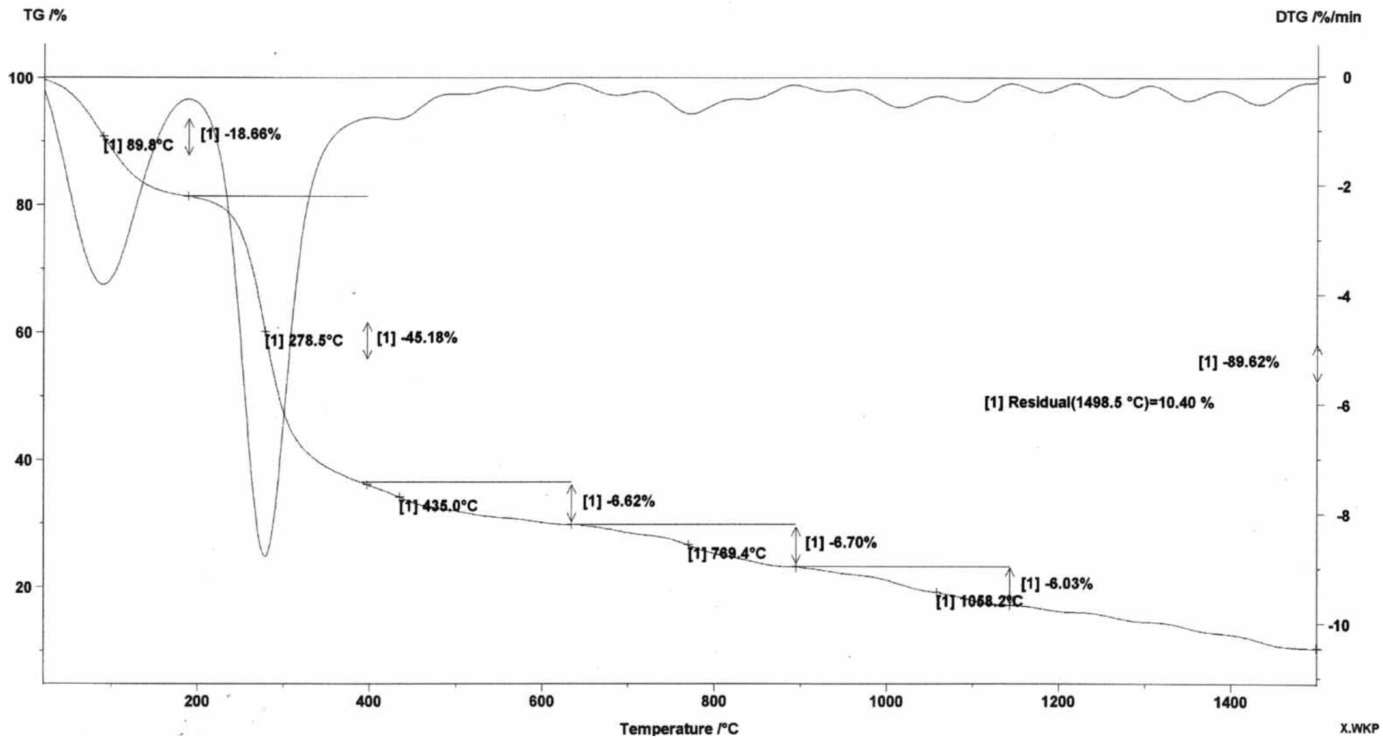


Fig. 7. Thermogravimetric trace of Xanthan gum.

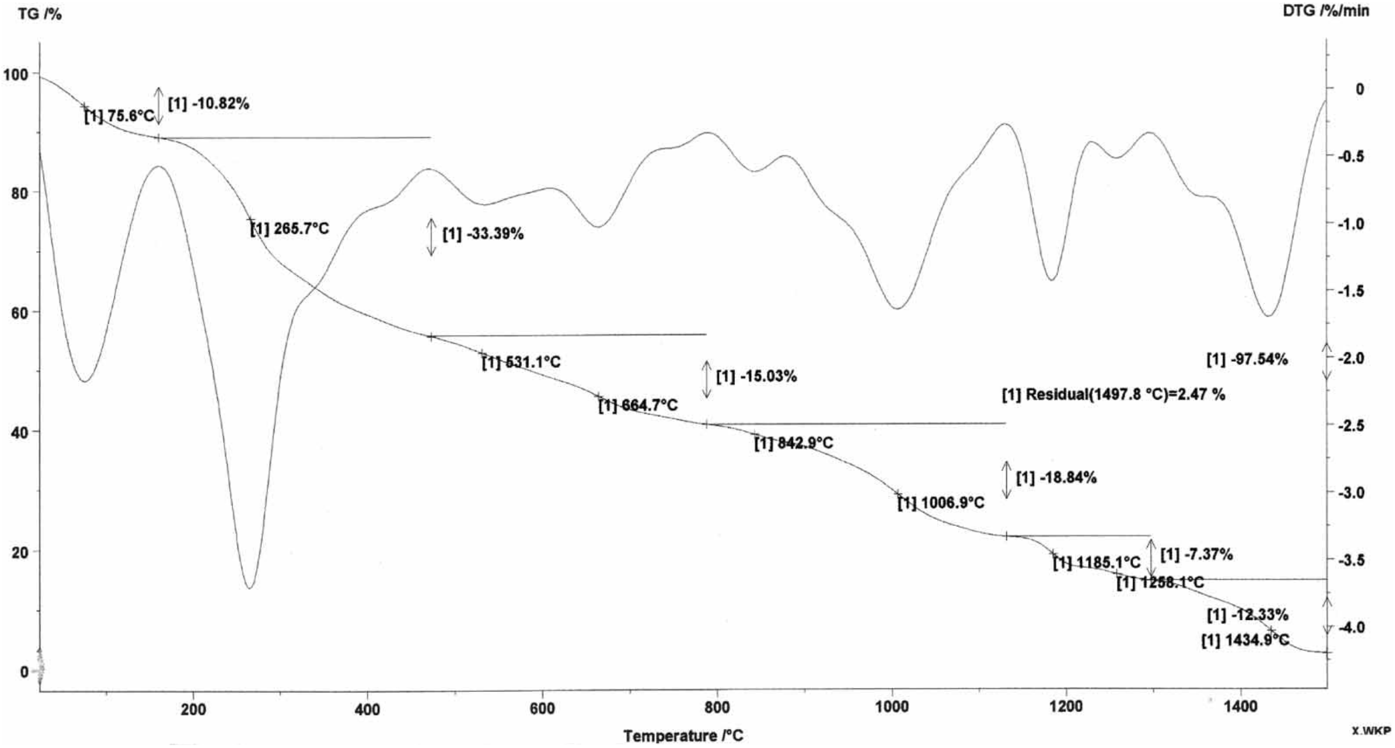


Fig. 8. Thermogravimetric trace of Xanthan gum-g-N,N′-dimethyl acrylamide.

Table 5. Swelling behavior

Sample	[DMA] × 10^2 mol dm^{-3}	% G	Percent swelling (Ps)	Swelling ratio (Sr)
A	8.3	72	435	4.4
B	12.5	77	518	5.2
C	16.6	105	765	7.7
D	20	129	840	8.4
E	25	122	816	8.2

of filter paper. An increase in weight was recorded. Percent swelling (Ps) and swelling ratio (Sr) were calculated (13,14).

The results of swelling studies were summarized in Table 5, and the data reveals that with an increase in percent grafting, the percent swelling and swelling ratio increases up to a certain limit. This character might be due to the fact that N,N′-dimethyl acrylamide is hydrophilic in nature, and with an increase in percent, the amount of N,N′-dimethyl acrylamide was also increased.

3.6 Metal Ion Sorption Studies:

3.6.1 Structural Aspects of Polymers and Sorption Behavior of Metal Ions

Hydrophilic–hydrophobic balance, nature of monomer and the extent of crosslinking of macromolecular supports are major factors that 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 the extent of contribution of any factor may be different. However, the functional group incorporated by grafting and its ability to interact with metal ion may playa more important role in the determination of selectivity and quantum of metal ion uptake.

3.6.2 Sorption Behavior of Xanthan Gum and its Graft Copolymer

The metal ion sorption studies have been carried out on a graft copolymer of different compositions (which has been synthesized by varying the concentration of monomer) by taking its 0.020 gm in 10 ml of metal ion solution of known concentration and kept undisturbed for 24 h. For the metal ion sorption studies, five metal ions have been chosen (Cu, Zn, Ni, Pb and Hg) and the amount of metal ion uptake has been calculated by titrating the remaining metal ions (all the solutions are made in triple distilled water). The results were summarized in Table 6. The data revealed that the graft copolymer shows better metal ion uptake behavior than the substrate (Xanthan gum).

The effect of percent grafting on sorption behavior of the graft copolymer has been studied in terms of percent ion uptake (Pu), partition coefficient (Kd) and retention capacity (Qr). From Table 6 it was clear that these parameters have a direct relationship with percent grafting. It might be due to the increase in percent grafting; the concentration of N,N′-dimethyl acrylamide was also increased and the pendent groups of N,N′-dimethyl acrylamide can hold more metal ions.

4 Conclusions

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

5 References

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Table 6. Absorption of metal ion on Xanthan gum and its graft copolymer

			Percent uptake (Pu)					Partition coefficient (Kd)					Retention capacity (Qr)				
Sample	[DMA] × 10^2mol dm^{-3}	%G	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	13.0	3.5	2.2	0.6	1.9	1.5	0.4
A	8.3	72	19.9	5.7	18.1	12.9	2.9	123.9	30.4	110.5	74.2	14.9	9.7	2.6	9.1	7.4	1.5
B	12.5	77	20.8	6.1	18.5	13.1	3.2	131.2	32.3	113.3	75.4	16.5	10.1	2.8	9.3	7.5	1.6
C	16.6	105	22.3	6.5	19.4	14.3	3.9	142.9	34.9	120.5	83.4	20.5	10.8	3.0	9.8	8.2	2.0
D	20	129	23.0	7.1	21.9	15.0	4.6	149.4	37.8	139.9	88.5	24.3	11.2	3.2	11.0	8.6	2.3
E	25	122	22.5	6.7	21.1	14.8	4.3	145	36.1	133.1	86.8	22.4	10.9	3.1	10.6	8.5	2.1

Where XOH: Xanthan gum and A, B, C, D, E = Graft copolymer.

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