Studies on guargum-graft-acrylamide: Characterization and polyvalent metal ion binding

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Abstract
Guargum is a water soluble natural polymer of industrial use. But it has poor biodegradation resistance. To improve biodegradation resistance, polyacrylamide side chains can be grafted on guargum. Ceric ion initiation method can be adopted for grafting. Material obtained in this process (G-g-Am) is used for DSC and TGA studies. Results have been compared with results of thermal analysis for polyacrylamide and guargum. % Residue values are giving evidence of grafting of polyacrylamide chains on guargum. It has been already reported that – COO− group from side chain of G-g-Am takes part in binding polyvalent metal ion. In this present investigation, involvement about backbone which is furnished by guargum for G-g-Am, has been studied in binding polyvalent metal ion by IR spectral study.

Keywords: Guargum, Polyacrylamide, Guargum-graft-acrylamide, Thermogravimetric analysis, Differential scanning calorimetric analysis, IR spectra.

1. Introduction
Guargum is the most commonly used water soluble natural polymer in industrial practice [1] and its structure is relatively known (fig.1). Major drawback of guargum is its poor biodegradation resistance. When guargum is grafted with polyacrylamide side chains, resulting graft copolymer (G-g-Am) becomes considerable biodegradation resistant and efficient flocculent for metallic ions [2]. Guargum-graft-acrylamide can be prepared by the ceric ion initiation method. In this method aqueous solution of guargum is used and acrylamide monomer is used. Grafting is done by ceric ion initiation method [2], using nitrogen atmosphere. Material obtained can be studied by thermal analysis to understand whether grafting has taken place or not. In this present investigation, DSC and TGA analysis are done with G-g-Am, guargum and polyacrylamide and strong evidences of grafting of polyacrylamide chains on guargum are obtained. So this work highlights ease of characterization of G-g-Am. When an aqueous solution of G-g-Am is mixed with Y (NO3)3 solution or Ba (NO3)2 solution or Cu (NO3)2 solution and pH of the mixture is raised, a distinct mass separates or a distinct precipitate like mass appeared. IR spectral study with yttrium ion bound guargum-graft-acrylamide (G-g-Am-Y3+), barium ion bound guargum-graft-acrylamide (G-g-Am-Ba2+) and cupric ion bound guargum-graft-acrylamide (G-g-Am-Cu2+) have been done thoroughly. Only involvement of – COOH group, obtained by inadvertent hydrolysis during storage or preparation of G-g-Am, has been understood and reported earlier [3]. In this present investigation, involvement of backbone in binding polyvalent metal ion has been reported. It has been found that for binding Cu2+, involvement of –CONH2 group along with –COO− group has a role. In binding Y3+ and Ba2+, involvement of –OH group from backbone has a role. So this work highlights insight of binding of polyvalent metal ion by G-g-Am.

2. Materials and Methods
2.1 G-g-am
Guargum-graft-acrylamide obtained from the Rheological Laboratory of Materials Science Centre of I.I.T., Kharagpur, has been used in this work. In this present investigation characterization of the material has been done along with study of polyvalent metal ion binding. ESCA (fig.2) study with the material has been done and from ESCA study it was
possible to understand the presence of approximately 68 atom% carbon, 22 atom% oxygen and 11 atom% nitrogen [4].

2.2 Metal nitrate solutions
Cu (NO$_3$)$_2$ solution and Y (NO$_3$)$_3$ solution can be prepared by dissolving CuO or Y$_2$O$_3$ in nitric acid. Ba (NO$_3$)$_2$ solution can be prepared by dissolving Ba (NO$_3$)$_2$ in distilled water.

2.3 G-g-Am-Na$^+$
Aqueous solution of G-g-Am is mixed with NaOH solution and the mixture is immediately poured into methanol for precipitation. Precipitate is washed with water for some time. Then it is kept in the oven for drying for IR spectral study.

2.4 G-g-Am-Y$^{3+}$
Aqueous solution of G-g-Am when is mixed with Y (NO$_3$)$_3$ solution and pH is raised by ammonium hydroxide (pH ≈ 9.5) [6], a white mass appeared which is washed with water for some time and then with methanol for some time. Then it is kept in the oven for drying for IR spectral study.

2.5 G-g-Am-Ba$^{2+}$
Aqueous solution of G-g-Am when is mixed with Ba (NO$_3$)$_2$ solution and pH is raised (pH ≈ 12.5) by adding sodium hydroxide solution, a white precipitate appears which is washed with water for some time and then with methanol for some time. Then it is kept in the oven for drying for IR spectral study.

2.6 G-g-Am-Cu$^{2+}$
Aqueous solution of G-g-Am when is mixed with Cu (NO$_3$)$_2$ solution and pH is raised (pH ≈ 6) by adding ammonium hydroxide solution, a mass separates which is washed with water for some time and then with methanol for some time and then is kept in the oven for drying for IR spectral study.

2.7 IR spectra
The IR spectra have been registered between 4000-200 cm$^{-1}$ with a Perkin-Elmer model 883 spectrometer using potassium bromide pallet.

2.8 Thermal Analysis
Simultaneous DSC and TGA analysis have been done using STANTON REDCROFT STA 625 simultaneous thermal analyzer in static air.

3. Results and Discussion
3.1 ESCA
ESCA study indicates approximately 11 atom% nitrogen, which indicates involvement of acrylamide to get G-g-Am.

3.2 DSC Analysis
DSC and TGA thermograms for G-g-Am, guar gum and polyacrylamide are shown in figs. 3 – 5 respectively. DSC thermograms for guar gum, polyacrylamide and G-g-Am are completely different. These are indicating G-g-Am may be the product of interaction of guar gum and polyacrylamide [5].

3.3 TGA thermograms
TGA thermograms for G-g-Am, guar gum and polyacrylamide are also different. The most interesting difference is in % residue values (Table-1). % Residue values for guar gum and polyacrylamide are much lower than that for G-g-Am. If G-g-Am is the mixture of guar gum and polyacrylamide, % residue for G-g-Am would be lower. But % residue for G-g-Am is much higher. This is indicating grafting of polyacrylamide chains on guar gum which may be the cause of increase in stability [2] regarding better biodegradation resistance.

Table 1: % Residue values for different materials:

<table>
<thead>
<tr>
<th>Material</th>
<th>% Residue from TGA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Guar gum</td>
<td>14.36</td>
</tr>
<tr>
<td>Polyacrylamide</td>
<td>8.91</td>
</tr>
<tr>
<td>G-g-Am</td>
<td>19</td>
</tr>
</tbody>
</table>

3.4 IR Spectra
IR spectra for G-g-Am, G-g-Am-Na$^+$, G-g-Am-Y$^{3+}$, G-g-Am-Ba$^{2+}$ and G-g-Am-Cu$^{2+}$ are shown in figs. 6-10 respectively. In the IR spectra for G-g-Am-Na$^+$, peak near about at 3500 cm$^{-1}$ can be attributed to $V_{N-H}$ (stretching vibration). Peak near about at 2800 cm$^{-1}$ can be attributed to $V_{O-H}$ (stretching vibration considering hydrogen bonding). Peak near about at 1600 cm$^{-1}$ can be attributed to $V_{C = O}$ (stretching vibration for amide). Peak near about at 1400 cm$^{-1}$ can be attributed to $V_{COO^-}$ (asymmetric stretch). Peak near about at 1300 cm$^{-1}$ can be attributed to $V_{COO^-(symmetric stretch)}$. Peak near about at 1000 cm$^{-1}$ can be attributed to bending vibration of –OH group. Peak near about at 800 cm$^{-1}$ may be attributed to M-O bending vibration for –COOM. In the spectra for G-g-Am-Cu$^{2+}$, the relative intensity for the peak for $V_{N-H}$ (stretching) with respect to peak for $V_{C = O}$ (amide) has been decreased along with the appearance of a sharp peak near about at 400 cm$^{-1}$. Option for this explanation is involvement of N-H group in binding Cu$^{2+}$. In the spectra for G-g-Am-Y$^{3+}$, peak for $V_{O-H}$ (stretch) is almost absent and peak for O-H bending is also almost absent. These are in support of involvement of –OH group of backbone in binding Y$^{3+}$. In the spectra for G-g-Am-Ba$^{2+}$, relative intensity of the peak for $V_{O-H}$ (stretch) has been considerably reduced and peak near about at 1000 cm$^{-1}$ ($V_{OH}$ binding) has been lowered into a strong peak towards 800 cm$^{-1}$. This is going in favour of involvement of –OH group in binding Ba$^{2+}$.
Fig 3: DSC and TGA thermograms for G-g-Am.

Fig 4: DSC and TGA thermograms for guar gum.

Fig 5: DSC and TGA thermograms for polyacrylamide.

Fig 6: IR spectra for G-g-Am.

Fig 7: IR spectra for G-g-Am-Na⁺.

Fig 8: IR spectra for G-g-Am-Y³⁺.

Fig 9: IR spectra for G-g-Am-Ba²⁺.

Fig 10: IR spectra for G-g-Am-Cu²⁺.
4. Conclusion
Guargum-graft-acrylamide is a modified natural polymer. Aqueous solution of guargum-graft-acrylamide is an efficient flocculent for metallic ions. Aqueous solution of guargum-graft-acrylamide has very high viscosity. Rheologically it may be possible to prove whether grafting of polyacrylamide chains have taken place on guargum or not. But thermal analysis is an easy tool to understand evidence of grafting in this case. IR spectra are indicating involvement of –COO of side chain in binding Y$^{3+}$, Ba$^{2+}$ and Cu$^{2+}$ by G-g-Am. Along with this, indications of involvement of –OH group of backbone in binding Y$^{3+}$ and Ba$^{2+}$ are also evident. Similarly indication of involvement of –CONH$_2$ group in binding Cu$^{2+}$ is also evident. This difference may be due to softer nature of Cu$^{2+}$ than Y$^{3+}$ or Ba$^{2+}$.

5. Acknowledgement
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6. References