

## Studies on polyvalent metal ion bound guar gum-graft-acrylamide to explore nature of ion binding

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**Abstract :** Guar gum-graft-acrylamide has been found to be a flocculent for metallic ions. From guar gum-graft-acrylamide three new materials : yttrium ion bound guar gum-graft-acrylamide, barium ion bound guar gum-graft-acrylamide and cupric ion bound guar gum-graft-acrylamide have been synthesized. To understand nature of ion binding, pH titration, conductometric titration, transmission electron microscopic (TEM) study and transmission electron diffraction (TED) study have been carried out. TEM images and TED patterns indicate macrostructures for these materials may not be same.

**Keywords :** Graft copolymer, polyvalent metal ion, transmission electron microscope, microstructure, ceramic oxide.

### Introduction

Guar gum is a water soluble natural polymer in industrial practice<sup>1</sup>. Its structure is well known (Fig. 1). Major drawback of guar gum is its poor biodegradation resis-

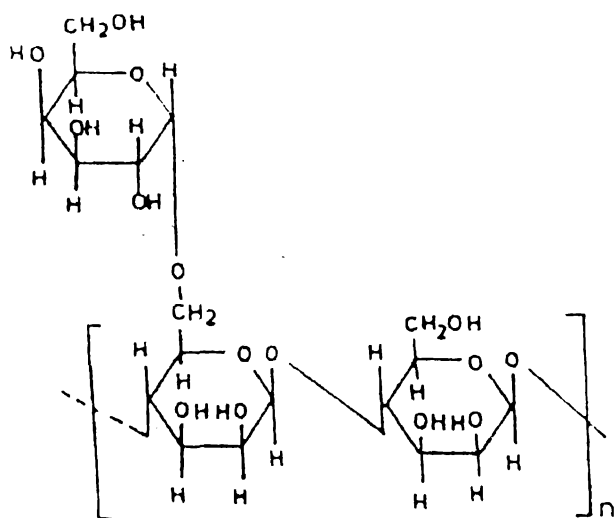


Fig. 1. Structure of guar gum.

tance. When guar gum is grafted with polyacrylamide side chains, resulting graft copolymer (G-g-Am) becomes considerable biodegradation resistant and efficient flocculent for metallic ions<sup>2</sup>. When aqueous solution of G-g-Am is mixed with  $Y(NO_3)_3$  solution or  $Ba(NO_3)_2$  solution or

$Cu(NO_3)_2$  solution and pH of the mixture is raised, a distinct mass separates or a distinct precipitate like mass appeared<sup>3-5</sup>. pH titration has been carried out to understand pH range for achieving these materials : G-g-Am- $Y^{3+}$  (yttrium ion bound guar gum-graftacrylamide), G-g-Am- $Ba^{2+}$  and G-g-Am- $Cu^{2+}$ . Conductometric titration has been carried out to understand nature of ion binding. Transmission electron microscopic (TEM) images have been studied to understand difference in microstructure for different polyvalent metal ions. Transmission electron diffraction (TED) study has been carried out taking these materials to understand whether any structural regularity is present in these materials or not<sup>6</sup>. Recently  $Y_1Ba_2Cu_3O_{7-x}$  superconductor has been prepared by polymeric precursor technique<sup>7</sup>. This motivated research on ion binding behaviour of modified natural polymer.

### Materials and methods :

#### (i) Guar gum-graft-acrylamide :

Guar gum-graft-acrylamide (G-g-Am) is a material obtained using guar gum by ceric ion initiation method and is achieved from Rheological Laboratory of Materials Science Centre of IIT, Kharagpur, India<sup>2</sup>. GM<sub>3</sub> grade of graft copolymer is used for study<sup>2</sup>. ESCA study with the material has been done. In XPS (X-ray photoelectron spectroscopy), the energy of the incident photon is so great that electrons are ejected from inner cores of atoms. As a first approximation, core ionization energies are insensitive to the bonds between atoms because they

are too tightly bound to be greatly affected. So core ionization energies are characteristics of the individual atoms rather than the overall molecule. Electron spectroscopy for chemical analysis (ESCA) is the alternative name which is limited to study of surface layers. G-g-Am was analyzed by ESCA. A sample of the stock shows ESCA plot as shown in Fig. 2. Peak closer to 280 eV binding energy can be assigned to carbon. Peak closer to 382 eV binding energy can be attributed to nitrogen and peak closer to 500 eV binding energy can be assigned to oxygen. From peaks, it was possible to understand that it contains approximately 68 atom% carbon, 22 atom% oxygen and 11 atom% nitrogen<sup>8</sup>.

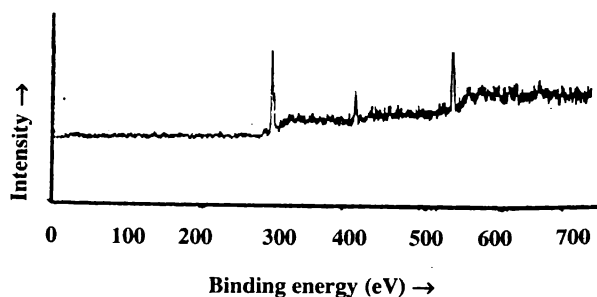


Fig. 2. ESCA plot for a sample of the stock.

(ii) *Metal nitrate solutions :*

$\text{Cu}(\text{NO}_3)_2$  solution and  $\text{Y}(\text{NO}_3)_3$  solution can be prepared by dissolving  $\text{CuO}$  or  $\text{Y}_2\text{O}_3$  in small amount of concentrated nitric acid and then making the volume upto the mark of volumetric flask by distilled water to get 0.5 M solution.  $\text{Ba}(\text{NO}_3)_2$  solution can be prepared by dissolving  $\text{Ba}(\text{NO}_3)_2$  in distilled water.

(iii) *pH titration :*

Beckman model G pH meter has been used for pH titration. For pH titration, sodium hydroxide solution is added from the burette.

(iv) *Conductometric titration :*

For conductometric titration, a dip-type cell (cell constant 1.1) containing platinised platinum electrode has been used for conductometric titration. Sodium hydroxide solution is added from the burette.

(v) *TEM and TED :*

For transmission electron microscopic (TEM) images and transmission electron diffraction (TED) patterns,

PHILIPS CM-12 transmission electron microscope and 100 KV electrons have been used. For G-g-Am, few drops of aqueous solution of G-g-Am are placed on a small thin sheet of aluminium. Another small thin sheet of aluminium is placed over the first one. Two sheets are then pressed carefully by placing the assembly in between two glass plates. The system has been kept for two days putting a small weight over the top plate, for drying the polymer film in between two aluminium sheets. Then weight is removed and it is placed in concentrated solution of NaOH. Aluminium sheets dissolve in concentrated NaOH solution and film of very small thickness for G-g-Am is collected on a microscopic grid and washed quickly with dil. HCl and then with distilled water for sometimes. Then it is dried in vacuum.

For G-g-Am- $\text{Y}^{3+}$  G-g-Am- $\text{Ba}^{2+}$  and G-g-Am- $\text{Cu}^{2+}$ , films are collected on microscopic grid similarly by using mixture of aqueous G-g-Am and respective metal nitrate solution instead of using aqueous G-g-Am alone as in the previous case. Films for G-g-Am- $\text{Y}^{3+}$ , G-g-Am- $\text{Ba}^{2+}$  and G-g-Am- $\text{Cu}^{2+}$  are washed with distilled water for many times and dried in vacuum along with microscopic grids. Films are examined for TEM images and for TED patterns by the transmission electron microscope. Images are recorded on Kodak electron image films.

## Results and discussion

(i) *pH titration curves :*

pH titration curves for G-g-Am- $\text{Y}^{3+}$ , G-g-Am- $\text{Ba}^{2+}$  and G-g-Am- $\text{Cu}^{2+}$  have been shown in Figs. 3, 4 and 5

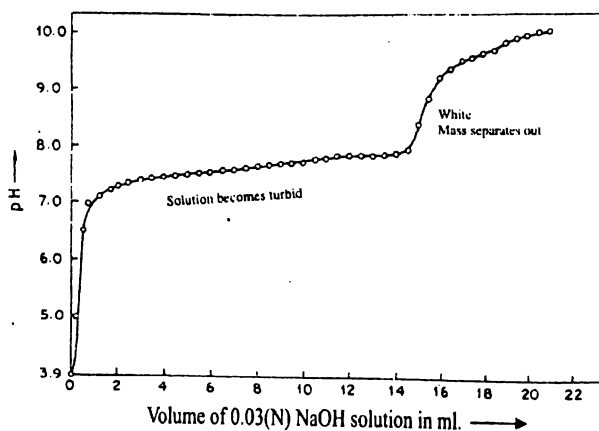


Fig. 3. pH titration curve for a mixture of aqueous G-g-Am,  $\text{Y}(\text{NO}_3)_2$  solution and  $\text{HNO}_3$ , when titrated against NaOH solution.

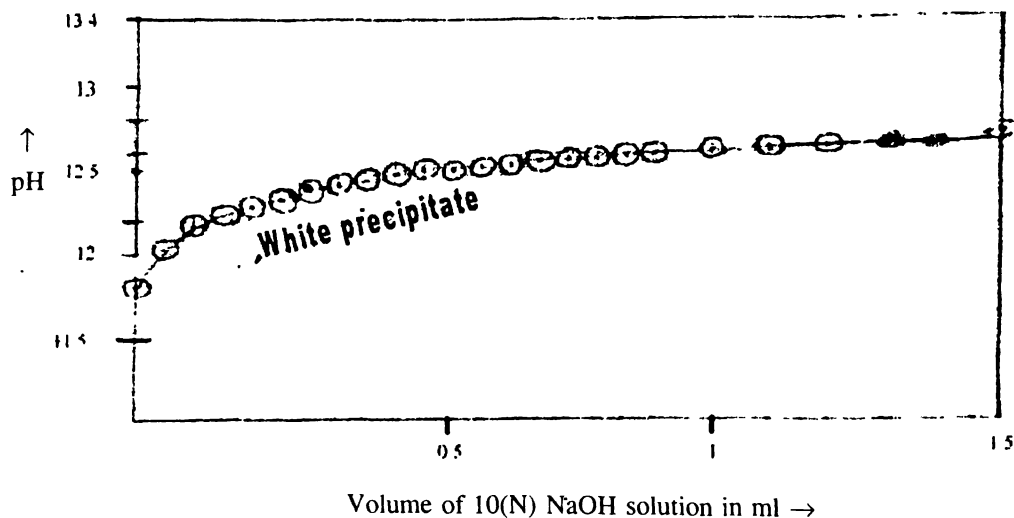


Fig. 4. pH titration curve for a mixture of aqueous G-g-Am and  $\text{Ba}(\text{NO}_3)_2$  solution when titrated against NaOH solution.

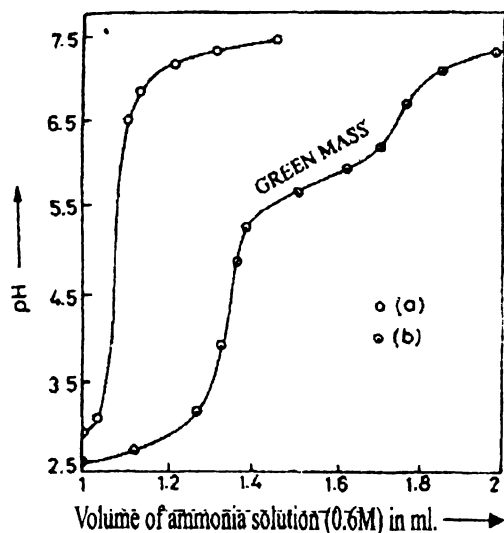


Fig. 5. pH titration curve for (a) a mixture of aqueous G-g-Am solution and  $\text{HNO}_3$  and (b) a mixture of aqueous G-g-Am,  $\text{Cu}(\text{NO}_3)_2$  solution and  $\text{HNO}_3$ , when titrated against ammonia solution.

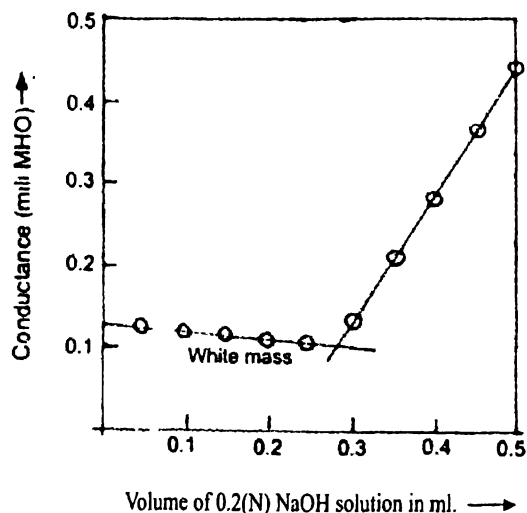


Fig. 6. Conductometric titration curve for a mixture of aqueous G-g-Am and  $\text{Y}(\text{NO}_3)_2$  solution when titrated against NaOH solution.

respectively. pH titration curve for mixture of  $\text{Cu}(\text{NO}_3)_2$  solution and aqueous G-g-Am shows formation of a distinct green mass instead of pale blue  $\text{Cu}(\text{OH})_2$ , at pH 6. Similarly white distinct mass separates for the mixture of  $\text{Y}(\text{NO}_3)_3$  solution and aqueous G-g-Am at pH 9.5 and for the mixture of  $\text{Ba}(\text{NO}_3)_2$  solution and aqueous G-g-Am at pH 12.5.

(ii) Conductometric titration :

Conductometric titration curves for G-g-Am- $\text{Y}^{3+}$ , G-

g-Am- $\text{Ba}^{2+}$  and G-g-Am- $\text{Cu}^{2+}$ , are shown in Figs. 6, 7 and 8 respectively. In case of G-g-Am- $\text{Cu}^{2+}$ , initial addition of NaOH decreases conductance due to consumption of  $\text{H}^+$  from  $\text{HNO}_3$  in the mixture by  $\text{OH}^-$ . Then conductance remains almost constant probably due to expulsion of  $\text{H}^+$  by polymer to bind polyvalent metal ion and consumption of this  $\text{H}^+$  by  $\text{OH}^-$  of added NaOH. After that conductance increases due to excess NaOH. In case of G-g-Am- $\text{Ba}^{2+}$ , initial decrease in conductance is due to consumption of  $\text{H}^+$  ions of  $\text{HNO}_3$  by  $\text{OH}^-$  of NaOH and

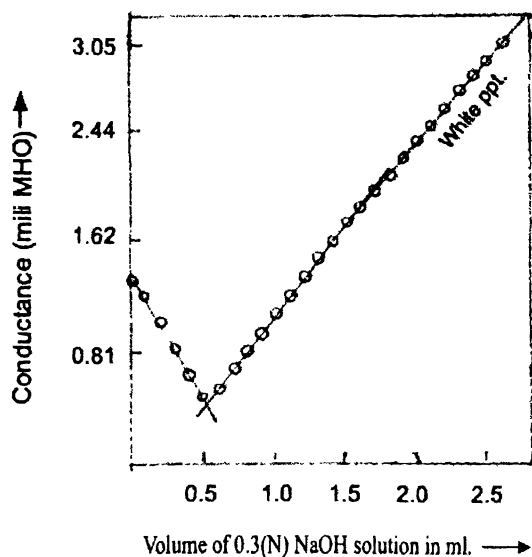


Fig. 7. Conductometric titration curve for a mixture of aqueous G-g-Am,  $\text{Ba}(\text{NO}_3)_2$  solution and  $\text{HNO}_3$ , when titrated against NaOH solution.

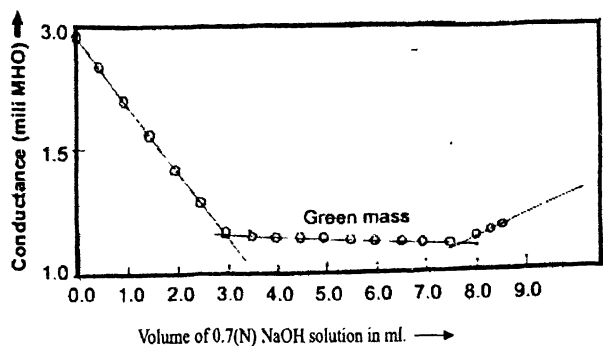


Fig. 8. Conductometric titration curve for a mixture of aqueous G-g-Am and  $\text{Cu}(\text{NO}_3)_2$  solution, when titrated against NaOH solution.

then conductance increases gradually due to binding of bigger  $\text{Ba}^{2+}$  from solution and increase in concentration of smaller  $\text{Na}^+$  ions from NaOH. In case of G-g-Am- $\text{Y}^{3+}$ , conductance remains almost constant, probably due to expulsion of large number of  $\text{H}^+$  ions for binding  $\text{Y}^{3+}$  by G-g-Am and consumption of these  $\text{H}^+$  ions by large number of  $\text{OH}^-$  ions. Then conductance increases due to excess NaOH.

This indicates, some functional groups of G-g-Am are responsible for binding polyvalent metal ion by G-g-Am when pH is raised. Probably this functional group is acidic functional group.

(iii) TEM :

TEM image for G-g-Am- $\text{Y}^{3+}$  (Fig. 10) shows porous structure. Probably polyvalent metal ion is welding polymeric chains. Similar porous structure is absent in TEM image for G-g-Am (Fig. 9), in TEM image for G-g-Am- $\text{Ba}^{2+}$  (Fig. 11) and in TEM image for G-g-Am- $\text{Cu}^{2+}$

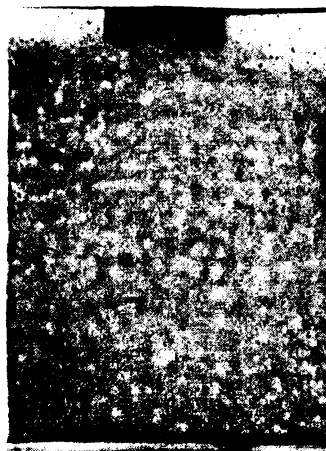


Fig. 9. TEM image for G-g-Am.

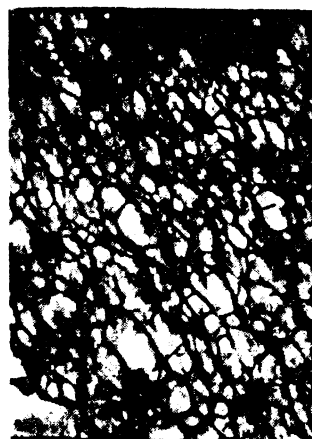


Fig. 10. TEM image for G-g-Am- $\text{Y}^{3+}$ .

(Fig. 12). TEM images are indicating microstructures for G-g-Am- $\text{Y}^{3+}$ , G-g-Am- $\text{Ba}^{2+}$  and G-g-Am- $\text{Cu}^{2+}$  may not be identical.

(iv) TED :

TED patterns for G-g-Am, G-g-Am- $\text{Y}^{3+}$ , G-g-Am- $\text{Ba}^{2+}$  and G-g-Am- $\text{Cu}^{2+}$  are shown in Figs. 13-16 respectively. TED pattern for G-g-Am shows regular spots indicating structural regularity. This structural regularity



Fig. 11. TEM image for G-g-Am-Ba<sup>2+</sup>.

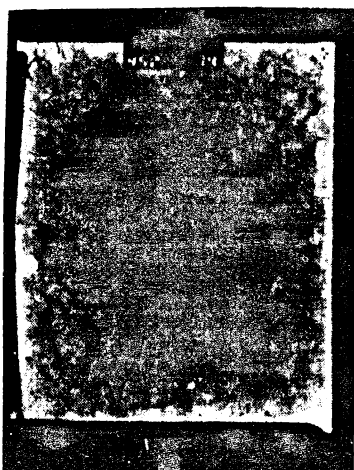


Fig. 12. TEM image for G-g-Am-Cu<sup>2+</sup>.

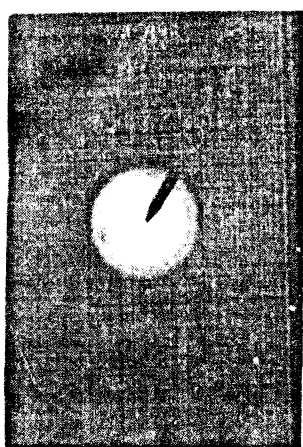


Fig. 13. TED pattern for G-g-Am.

may arise from polar-polar interaction through hydrogen bonding. But for G-g-Am-Cu<sup>2+</sup> and G-g-Am-Y<sup>3+</sup>, simi-

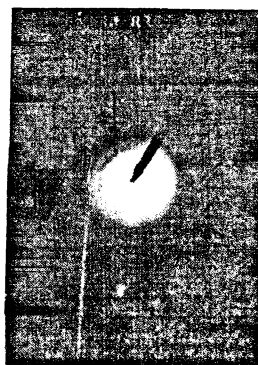


Fig. 14. TED pattern for G-g-Am-Y<sup>3+</sup>.

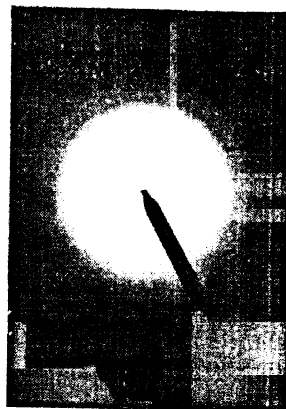


Fig. 15. TED pattern for G-g-Am-Ba<sup>2+</sup>.

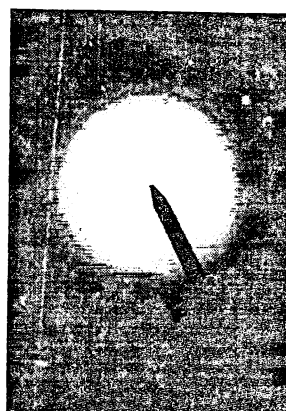


Fig. 16. TED pattern for G-g-Am-Cu<sup>2+</sup>.

lar regular spots are absent in the TED patterns. This is indicating Cu<sup>2+</sup> and Y<sup>3+</sup> are destroying a structural regularity. But for G-g-Am-Ba<sup>2+</sup>, TED pattern indicates absence of structural regularity.

**Conclusion :**

Recently preparation of ceramic oxide superconductor by polymeric precursor technique has been reported. This work may help in this regard. Use of modified natural polymer is expected to be economically favourable. This investigation indicates aqueous solution of G-g-Am helps to bind polyvalent metal ion when pH is raised. TEM images and TED patterns are indicating microstructures for G-g-Am-Y<sup>3+</sup>, G-g-Am-Ba<sup>2+</sup> and G-g-Am-Cu<sup>2+</sup> may not be identical.

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**References**

1. E. Pezron, A. Ricard, F. Lafuma and R. Audebirt, *Macromolecules*, 1988, **21**, 1121.
2. S. R. Deshmukh, P. N. Chaturvedi and R. P. Singh, *J. Appl. Polym. Sci.*, 1985, **30**, 4013.
3. A. Chattopadhyay, D. Bhattacharya and R. P. Singh, *Materials Letters*, 1993, **17**, 179.
4. A. Chattopadhyay, D. Bhattacharya and R. P. Singh, *Materials Letters*, 1995, **25**, 277.
5. A. Chattopadhyay and P. K. Nandi, *J. Tech.*, 2008, **40**, 45.
6. J. A. N. Zasadzinski, A. Chu and R. K. Prod'homme, *Macromolecules*, 1986, **19**, 2960.
7. H. K. Lee and D. Kim, *J. Appl. Phys.*, 1989, **65**, 2563.
8. C. J. Powell, *Application of Surface Science*, 1978, **1**, 186.