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Studies on barium ion binding by polymer

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Abstract

Polycrylamide is a water soluble polymer used in paper industry. Aqueous solution of polyacrylamide binds Y^{3+} and Cu^{2+} when pH is raised. In this present investigation binding of Ba^{2+} ion by industrial polycrylamide sample (PAm) has been understood by TGA, DTA, DSC analysis, IR Spectral analysis, SEM study and by EDS study. When aqueous solution of PAm is mixed with barium nitrate solution & pH is raised by adding 60% NaOH solution, a deep white layer separates on standing which is treated with MeOH to get barium ion bound Polymer (PAm- Ba^{2+}). DTA thermogram for PAm shows an endotherm near about at $270^{\circ}C$ which indicates acid anhydride formation or imide formation indicating presence of $-COOH$ group in industrial polyacrylamide sample. Similar endothermic peak at $270^{\circ}C$ is almost absent in the DTA thermogram for barium ion bound polymer (PAm Ba^{2+}) which indicates involvement of $-COOH$ group of PAm in binding Ba^{2+} at high pH. This is further supported by IR spectra, TG analysis, DSC analysis, SEM study and EDS study.

Keywords: polyacrylamide, barium ion binding ceramic oxide, differential thermal analysis, scanning electron microscopy, spectral analysis.

1. Introduction

Guargum-*graft*-acrylamide (G-g-Am) is a water soluble graft copolymer [1]. It has good biodegradation resistance and is an efficient flocculent for metallic ions [1, 2]. G-g-Am binds Y^{3+} , Ba^{2+} and Cu^{2+} at different pH range and has been already reported [1-3]. It has been also reported that guar sample can bind Y^{3+} , Ba^{2+} and Cu^{2+} [4, 5] and polyacrylamide sample can bind Y^{3+} and Cu^{2+} [4]. Whether polyacrylamide can bind Ba^{2+} or not that has been checked in this present investigation. DTA, TGA, DSC analysis, IR spectral analysis, SEM study and EDS study have been carried out in this present investigation to understand that $-COOH$ group from industrial polyacrylamide sample (PAm) has role to bind Ba^{2+} ion. Earlier it has been found that $-OH$ group from guar sample takes part in binding Ba^{2+} [5] but alcoholic $-OH$ group is absent in polyacrylamide. In guargum-*graft*- acrylamide (G-g-Am), alcoholic $-OH$ groups are present in the backbone of G-g-Am which take part in binding Y^{3+} , Ba^{2+} & Cu^{2+} [6, 7]. This present work helps to understand that polyacrylamide side chains of G-g-Am can help to bind polyvalent metal ion.

2. Materials and Methods

2.1 Barium nitrate solution

Barium nitrate solution has been prepared by dissolving barium nitrate in distilled water to get a saturated solution.

2.2 Industrial polyacrylamide sample (PAm)

Polyacrylamide used in this work is obtained from the paper industry: ITC Limited, Paper Boards & Specialty Papers Division, Unit: Tribeni, P.O. Chandrahati, Hooghly, West Bengal, India. Molecular weight of the polymer is high. Brand name of the material is Maxfloc C11. It was supplied from Thermax Company.

2.3 Barium ion bound polymer (PAm - Ba^{2+})

50ml approximately 1wt% polyacrylamide sample is mixed with approximately 4 ml $Ba(NO_3)_2$ solution in a beaker and stirred. Mixture becomes white. 10 ml 60% NaOH solution added and stirred. Mixture is allowed to stand for 30 mins. Upper part of the mixture is more white than the bottom part. 15 ml MeOH is added and allowed to stand for 10 mins. A tighter white mass separates. Mass is collected by a glass rod and kept in 5 ml MeOH in a small beaker.

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Another 5 ml MeOH is added to the main bulk, allowed to stand for 5 mins and white mass obtained. Mass is collected by glass rod and kept into MeOH in that small beaker. After sometime, methyl alcohol is removed by decantation and washed with methyl alcohol for some time and then it is washed with 10 ml distilled water for 3 times and finally with 3 ml methyl alcohol. Then it is dried in an oven for IR experiment, thermal analysis & microscopic study.

2.4 DTA and TGA

For simultaneous DTA and TG analysis, Pyris Diamond TGA/DTA instrument has been used. Name of the company is Perkin Elmer. Simultaneous DTA and TGA have been carried out in presence of air upto 600°C using samples as shown in Table -1.

Table 1: Sample size for simultaneous DTA and TGA

| Sample | Approximate amount |
|--|--------------------|
| Industrial polyacrylamide (PAm) | 10.24 milligrams |
| Barium ion bound polymer (PAm-Ba ²⁺) | 12.28 milligrams |

Alumina crucible used for DTA and TGA. Heating rate used: 10⁰ C/ min.

2.5 DSC

Differential scanning calorimetric analysis has been carried out using PYRIS Diamond DSC instrument. Name of the company is Perkin Elmer. DSC analysis has been carried out using sample size as shown in Table -2.

Table 2: Sample size for DSC analysis

| Sample | Approximate amount |
|--|--------------------|
| Industrial polyacrylamide sample (PAm) | 5.44 milligrams |
| Barium ion bound polymer (PAm – Ba ²⁺) | 5.46 milligrams |

For DSC, sample is kept in aluminium crucible and an aluminium lid is fitted tightly by applying pressure. Atmosphere is nitrogen atmosphere and experiment has been carried out upto 600⁰ C. heating rate used: 10⁰ C/min.

2.6 IR

IR spectral analysis has been carried out using FTIR instrument (Model: NICOLET 6700 FT- IR) Name of the company is Thermo Fisher SCIENTIFIC. Spectral range covered is 4000 Cm⁻¹ to 500 Cm⁻¹. KBr pallet technique has been used for IR spectral analysis.

2.7 SEM

Scanning Electron Microscopic (SEM) study has been carried out using FESEM instrument [Model name: MERLIN (Column → GEMINI. 2)]. Name of the company is CARL ZEISS. SEM experiments have been carried using gold – palladium alloy coated samples. Coating has been done by sputtering technique. Instrument used for coating is Quorum (No. → Q150RES). EDS (Energy Dispersive Spectroscopy) study for PAm – Ba²⁺ has been carried out using AMETEK (MATERIALS DIVISION). Name of the company is EDAX.

3. Results and Discussion

3.1 DTA, TGA & DSC

DTA, TGA and DTG plots for industrial polyacrylamide sample (PAm) and for barium ion bound polymer (PAm-Ba²⁺) are shown in fig.1 and fig.2 respectively. DTA plot for PAm & DTA plot PAm –Ba²⁺ are different. There is an endothermic peak near about at 270⁰C in the DTA thermogram for PAm. This can be attributed to acid anhydride formation or imide formation involving –COOH group [1]. When acid anhydride or imide is formed, H₂O will be splitted and hence there will be weight loss. In TGA for PAm, there is considerable weight loss in this temperature range. This is further evidence by the achievement of endothermic peak near about at 267⁰C in DSC thermogram for PAm (fig.3). Surprisingly, similar endothermic peak in DTA thermogram for PAm –Ba²⁺ (fig.2) at 270⁰C is absent. This can be attributed to involvement of–COOH group of PAm in binding Ba²⁺ ion to get PAm- Ba²⁺ sample. So free –COOH groups are lacking to show absence of similar endothermic peak due to acid anhydride formation or imide formation for PAm-Ba²⁺ at 270⁰C. This is further evidence by lack of strong endothermic peak at 267⁰C in the DSC thermogram for PAm-Ba²⁺ (fig.3).

3.2 IR

IR spectra for PAm & for PAm-Ba²⁺ are shown in fig.4 and fig.5 respectively. IR spectra for PAm shows peak at about 3430 Cm⁻¹ which can be attributed to ν_{NH} (stretch) of – CONH₂ group. Peak at about 1649 Cm⁻¹ in the IR spectra for PAm can be attributed to ν_{C=O} of –CONH₂ group. Peak position for ν_{NH} (stretch) has been slightly increased in IR spectra for PAm-Ba²⁺. This may be due to breaking of few hydrogen bonds. Most interesting point to note in the IR spectra for PAm is the presence of a strong peak at about 925 Cm⁻¹ which can be attributed to bending vibration of –OH group of –COOH. Similar strong peak at 952 Cm⁻¹ is absent in the IR spectra for PAm-Ba²⁺. This is an important evidence of involvement of –COOH group of PAm in binding Ba²⁺ to get –COOM. So IR spectra is supporting result of thermal analysis.

3.3 SEM

SEM images for industrial polyacrylamide (PAm) and for barium ion bound polymer (PAm-Ba²⁺) are shown in fig.6 and fig.7 respectively. Industrial polyacrylamide sample shows skeletal image at 3000x magnification. Industrial polyacrylamide sample dissolves in water. When aqueous solution of industrial polyacrylamide is mixed with barium nitrate solution and pH of the mixture is raised by adding 60% NaOH, a deep white layer separated on standing. After treating nonsolvent (MeOH), the mass has been washed with MeOH and water respectively. SEM image for PAm-Ba²⁺ (fig.7) shows lack of skeletal image and image is much more uniform. This is probably due to welding of polymeric chains by Ba²⁺ ions in PAm-Ba²⁺ sample. This is further supported by EDS study for PAm –Ba²⁺ (fig.8). Bulk EDS study for PAm – Ba²⁺ indicates presence of barium in barium ion bound polymer (PAm–Ba²⁺) (Table -3).

Table 3: Bulk EDS study for PAm- Ba²⁺.

| Element | Weight % | Atomic % | Net Int. | Error % | Kratio | Z | R | A | F |
|---------|----------|----------|----------|---------|--------|------|------|------|---|
| C K | 13.18 | 16.63 | 18.29 | 10.09 | 0.11 | 1.05 | 0.98 | 0.76 | 1 |
| N K | 12.96 | 14.02 | 12.01 | 16.27 | 0.09 | 1.02 | 0.99 | 0.69 | 1 |
| O K | 73.17 | 69.28 | 122.28 | 7.47 | 0.51 | 0.99 | 1 | 0.71 | 1 |
| BaM | 0.68 | 0.08 | 0.09 | 23.95 | 0.01 | 0.55 | 1.33 | 1.54 | 1 |

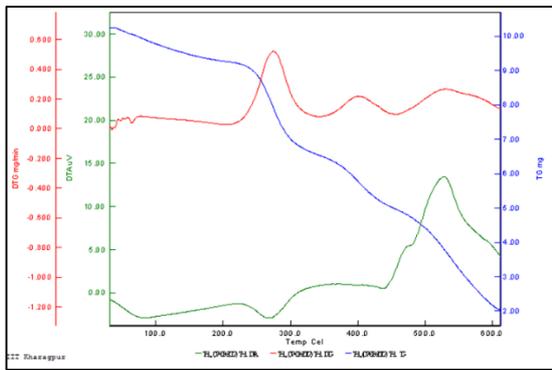


Fig 1: DTA, TGA and DTG plots for industrial polyacrylamide sample (PAM).

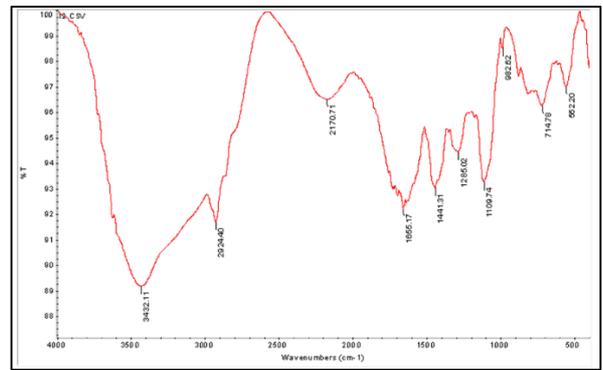


Fig 5: IR spectra for barium ion bound polymer (PAM-Ba²⁺).

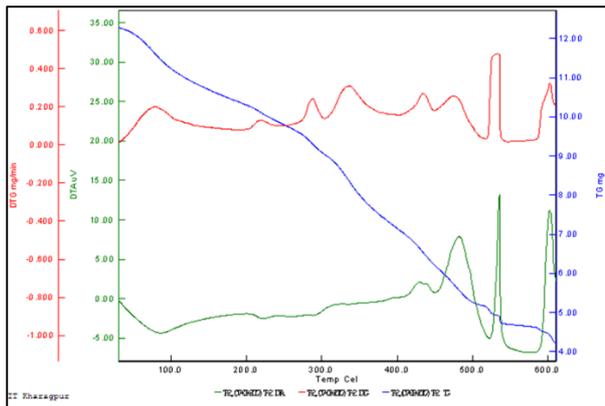


Fig 2: DTA, TGA and DTG plots for barium ion bound polymer (PAM-Ba²⁺).

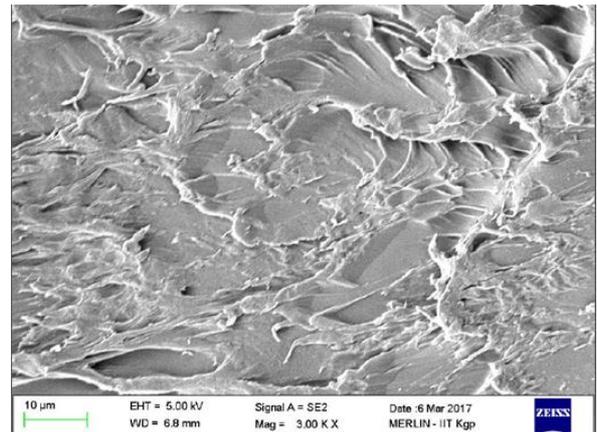


Fig 6: SEM image for industrial polyacrylamide sample.

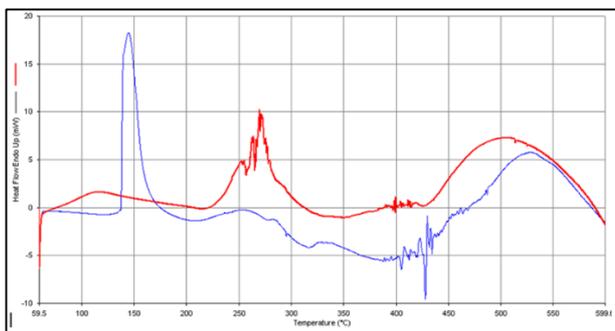


Fig 3: DSC plots for industrial polyacrylamide sample (red curve) and barium ion bound polymer (PAM-Ba²⁺) (blue curve)

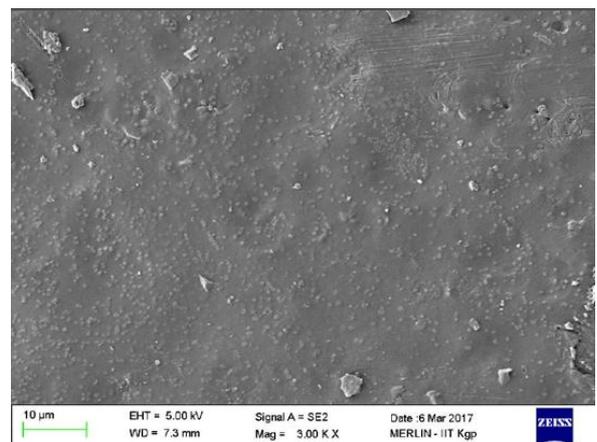


Fig 7: SEM image for barium ion bound polymer.

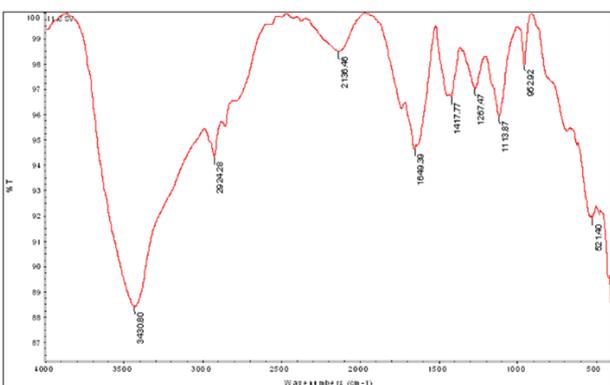


Fig 4: IR spectra for industrial polyacrylamide sample.

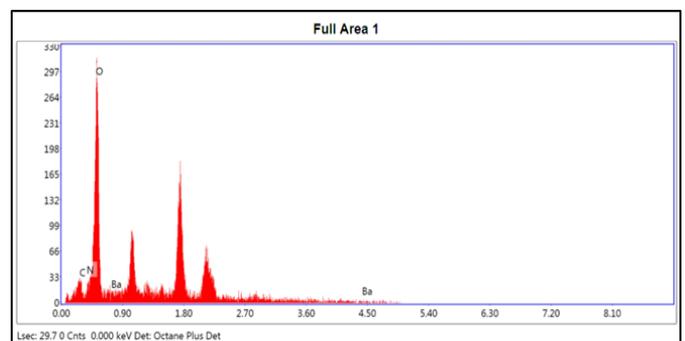


Fig 8: EDS for PAM- Ba²⁺.

4. Conclusion

$Y_1Ba_2Cu_3O_{7-x}$ (ceramic oxide) superconductor can be prepared by polymeric precursor technique [8, 9]. So ion binding by polymer is an active field of research now-a-days. This work indicates, polyacrylamide sample can bind Ba^{2+} . Earlier it has been found that guar sample can bind Y^{3+} , Ba^{2+} and Cu^{2+} . Now it is understood that polyacrylamide can also bind Y^{3+} , Ba^{2+} and Cu^{2+} . Polyacrylamide sample binds Ba^{2+} by using $-COOH$ groups. This $-COOH$ group may come by hydrolysis of some $-CONH_2$ groups during preparation or during storage of the polymer [1]. Earlier it has been found that guargum-graft-acrylamide binds polyvalent metal ion by using $-COOH$ groups which may arise due to hydrolysis of some $-CONH_2$ groups of G-g-Am during preparation of the graft copolymer by ceric ion initiation method using ceric ammonium nitrate solution [1].

5. Acknowledgement

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6. References

1. Chattopdhyay A, Bhattacharya D, Singh RP. Materials Letters, 1993; 17:179.
2. Chattopdhyay A, Bhattacharya D, Singh RP. Materials Letters, 1995; 25:277.
3. Chattopdhyay A, Nandi PK. J. of Tech. 2008; 40:45.
4. Chattopdhyay A. J. Indian Chem. Soc. 2014; 91:425.
5. Chattopdhyay A. International J. of Chem. Studies, 2016; 4(6):112.
6. Chattopdhyay A. Poster paper presented in National Symposium of Indian Chem. Soc. 2015.
7. Chattopdhyay A. International J. of Chem. Studies. 2015; 2(6):5.
8. Dunn B, Chu CT, Zhou LW, Cooper JR, Gruner G. Adv. in Ceram. Mater. 1987; 2(3B):343.
9. Chattopdhyay AJ. Indian Chem. Soc. 2012; 89:1647.