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## Preparation and Characterization of Sodium Alginate-g-Polyacrylamide Copolymer

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**Abstract** Grafting of vinyl monomers onto an alginate backbone can enhance the scope of its industrial applications. In this study, the graft copolymerization of acrylamide onto sodium alginate initiated by ceric ion-allyl alcohol redox pair was studied in aqueous media. The sodium alginate-g-polyacrylamide copolymer was characterized: mechanical, morphology and thermogravimetric properties. The graft copolymerization reactions showed optimal graft yield at 50 oC with calculated activation energy of 7.35kcal/mol for the copolymerization reaction. The graft yield showed an initial increase and thereafter, a negative dependence on allyl alcohol concentrations. The Pg/Pgo ratios (1.13-1.68) were greater than unity for all polymerization reactions. The copolymer presents a decrease in tensile strength with a corresponding greater elongation and extension compared to sodium alginate. The scanning electron micrograph shows evenly distribution of grafted polyacrylamide on the sodium alginate matrix. Thermal studies showed a greater thermal stability of the graft copolymer. From this study, ceric ion-allyl alcohol redox pair was an effective initiator for graft copolymerization of the vinyl monomer onto sodium alginate in aqueous media with enhanced properties of the copolymer.

**Keywords** graft, polyacrylamide, percentage yield, redox pair, alcohol.

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### 1. Introduction

Polymers form a very important class of materials with their uses cutting across different sphere of life, notably: rubber, packaging materials, biomedical, flocculants, mulch films, and adhesives tapes [1]. Alginate a natural polymer, has many useful properties, such as viscosity control, stabilization of suspensions, emulsions and foams, improved freeze /thaw stability, film formation, rheology control [2]. Alginate is renewable, biodegradable and safe. However, it is prone to enzymatic degradation and exhibits limitation in controlled release technology [1]. Besides, alginate as a polysaccharide occurs in a large amount in nature, and can be extracted primarily from brown algae [3, 4].

Alginate graft copolymers are becoming increasingly important because of their potential application in industry. The wide range of available vinyl and other monomers suggests that grafting of these monomers onto the alginate backbone could broaden the applications of the copolymer, as desired properties could be introduced following the graft copolymerization reaction. Grafting as a tool for achieving desired properties of polymeric derivative has continued to attract considerable attention [5]. Ceric ion in redox pair with a number of readily oxidizable organic compounds can initiate the graft copolymerization of vinyl monomers onto cellulosic and non-cellulosic backbones. The mechanisms of graft reaction by such redox system are little understood. However, grafting reaction involves the copolymerisation of a monomer via an active site on a polymer backbone [6]. The development of sodium



alginate and konkoli gum grafted-polyacrylamide blend membrane [7], showed that the graft yield is depended on initiator (ceric ammonium nitrate) concentration and graft copolymerization temperature. Hydrophilic itaconic acid was grafted onto sodium alginate using ceric as the initiator [2], the effect of temperature (between 20oC and 60oC), and the graft yield observed, increased with temperature from 20oC to 30oC and then decreases thereafter. The study of flocculating characterization of graft copolymers of polyacrylamide and various polysaccharides such as guar gum, starch, and xanthan gum has shown that the copolymers derivatives has superior flocculating properties than polyacrylamide [8]. This study is to graft acrylamide onto sodium alginate initiated by ceric ion in the presence of allyl alcohol and characterized the copolymer.

## 2. Experimental

### 2.1. Materials

The reagents used were prepared from analar-grade chemicals using distilled water: sodium alginate from (Surechem Products Ltd) U.K. England, acrylamide, (SISCO Research Lab.) Bombay India, other reagents: ceric ammonium nitrate, allyl alcohol, sodium nitrate, N-N' -dimethylformamide, glacial acetic acid, methanol, sodium hydroxide, acetone were used as supplied without further purification.

### 2.2. Preparation of Sodium alginate-g-polyacrylamide

The graft copolymerization reaction was based on the method describe [5]. 1.0 g of Sodium alginate was dissolved in 26.5 ml distilled water contained in 500 ml flask; 10 ml of allyl alcohol was added. Ceric ammonium nitrate (CAN) at varying concentration, ranging from  $4.16 \times 10^{-3}$  –  $33.32 \times 10^{-3}$  M was then added, the flask was then allowed to stand for 10 min. (pre-oxidation time) before the addition of 0.23M of acrylamide monomer. The reaction was terminated after 3 h by the addition of excess distilled water. The viscous polymer was then precipitated by the addition of 50 ml acetone to remove free polyacrylamide chains. Sodium alginate-g-polyacrylamide was filtered and dried with the aid of a vacuum pump using a pre-weighed sintered glass type 3.

### 2.3. Purification of the copolymer

The graft copolymer was place in a 250 ml flask, 100 ml of solvent (N,N-dimethylformamide and acetic acid, (1:1) was added and stirred (250 rpm) at 40oC for 4 h. The mixture was filtered with Buchner funnel. The residue was washed with solvent (N,N-dimethylformamide and acetic acid, (1:1) twice. The copolymer was stabilized in methanol for 12 h, and dried in a vacuum oven. [8].

### 2.4 Determination of graft percentage

The percentage graft and percentage efficiency determined from the equations:

$$\% \text{Graft} = [(W2 - W1) / W1] \times 100$$

$$\% \text{Efficiency} = [(W2 - W1) / W3] \times 100$$

Where W1, W2, and W3 are the weight of the substrate, the graft copolymer and monomer respectively.

#### Characterization

The copolymer was characterized for Tensile, Morphology, and Thermogravimetric properties.

### 2.5 Determination of tensile properties of copolymer

Copolymer samples were kept in a dessicator (containing silica gel) for 72h. Tensile properties were determined from stress-strain curves, with an Instron Tensile Test Machine (Model M500-25KN), at a strain rate of 10mm/min using rectangular specimens (dimensions: 25mm × 20mm × 1mm) at room temperature ( $25 \pm 2$ oC). Readings for three samples from each sample was taken. The values reported are the mean and standard deviation respectively.

### 2.6 Scanning Electron Microscope analysis

The SEM analysis of the sample was carried out by placing the sample on a sample stop coated with colloidal graphite (conducting material) and then, transferred to a sample holder. The sample was coated in the SEM coating



device using Argon gas and thereafter ran using SEM instrument. The surface morphology of the samples was determined at different dimensions between 500 – 2200X.

### 2.7 Thermogravimetric analysis

Thermogravimetric analysis of the grafted samples was carried out with a PerkinElmer TGA 4000 (Netherlands) thermal analyzer. The sample was ramped up to a temperature of 950oC, with a starting point at 30oC under dry nitrogen gas, at a heating rate of 10.00oC/min.

## 3. Results and Discussion

The effect of ceric ion concentration on percentage grafting of acrylamide onto sodium alginate in the presence of allyl alcohol is presented in Figure 1. In the concentration range of, 4.17 – 33.32 x10<sup>-3</sup>M, there is an optimal graft yield of 250% at 25.0 x 10<sup>-3</sup>M Ceric beyond which, the graft yield decreases. A similar trend has been reported [7, 9, 10]. The increase in the graft yield with ceric ion concentration may be ascribed to increase in the number of macro-radical on the sodium alginate substrate. Increased ceric ion concentration may results to preponderance of polyacrylamide chains and a concomitant decrease in graft yield [11].

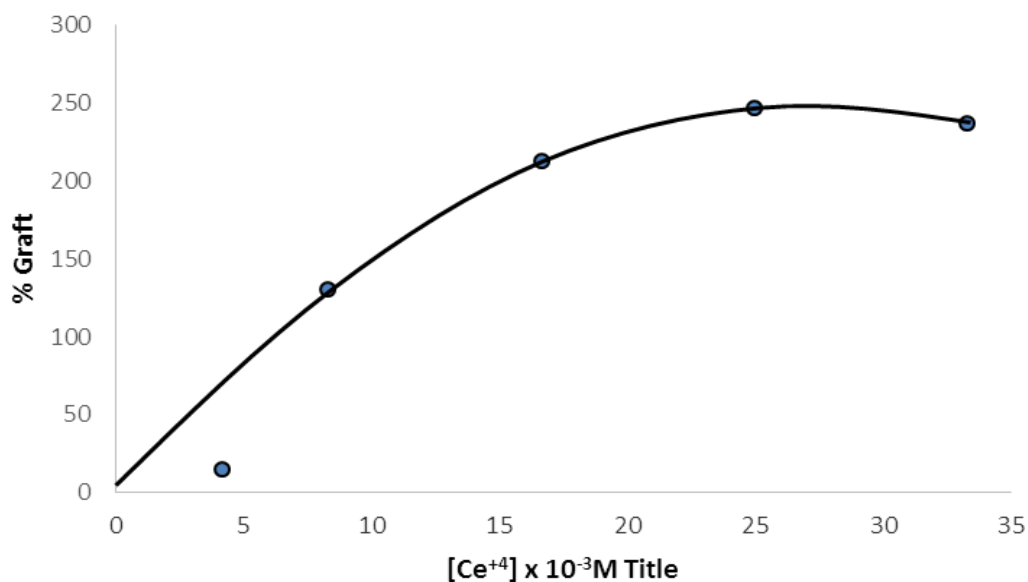


Figure 1: Effect of Cerium ion concentration on graft yield

The effect of temperature on graft copolymerization of acrylamide on to sodium alginate by ceric ion-allyl alcohol redox pairs is shown in Figure 2. Over the temperature range 30 – 60oC, the graft yield increased initially with time and decreased after optimal values. At the initial time of 30 minutes, the graft yield increased with temperature in the range, 30 -50oC and decreased thereafter, the corresponding activation energy for the graft reaction derived from the Arrhenius plot as shown in Figure 3 was 7.35kcalmol<sup>-1</sup>. Reduction in graft yield at higher temperature may be attributed to increased homopolymer formation and partly to termination of graft reaction by allyl alcohol radical species.

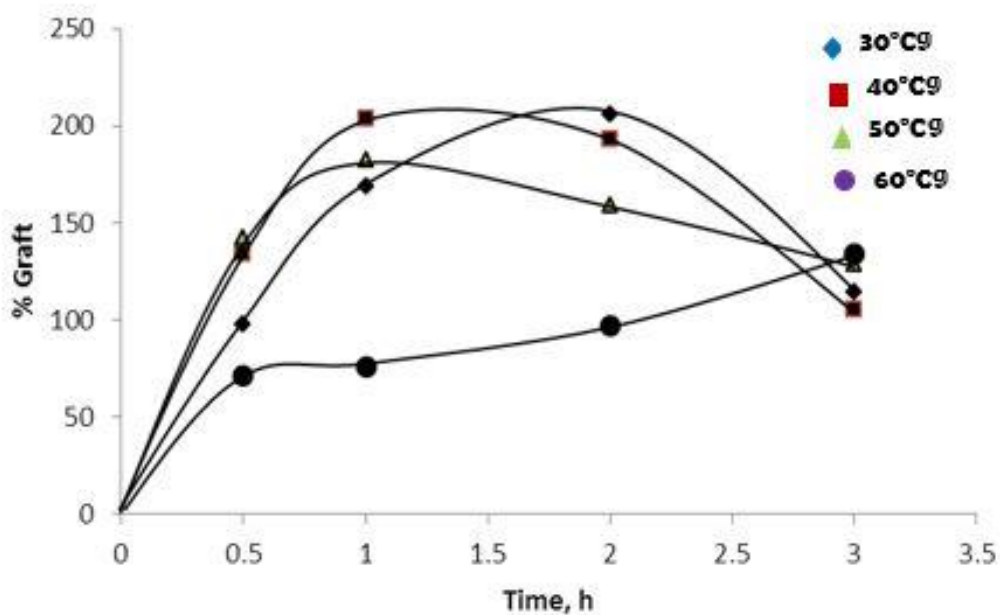


Figure 2: Effect of temperature on sodium alginate-g-polyacrylamide graft yield

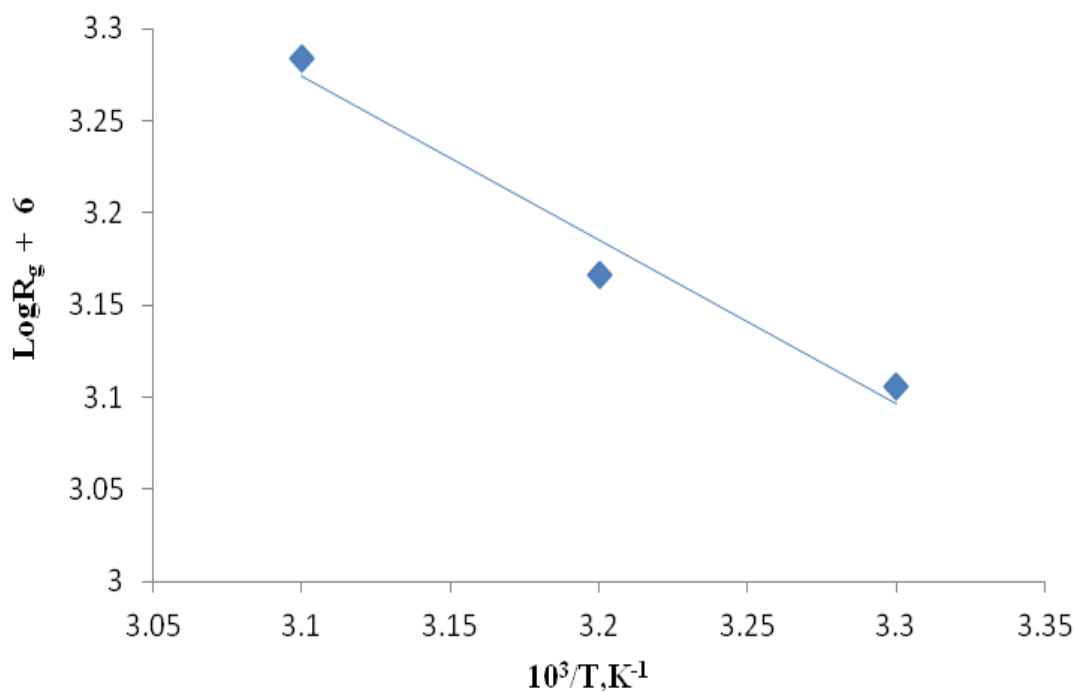


Figure 3: Arrhenius plot for grafting acrylamide on sodium alginate

Effects of allyl alcohol on the grafting yield (pg) and yield ratio (pg/pgo) of acrylamide onto sodium alginate is represented in Tables 1 and 2 respectively. The effect of allyl alcohol shows an optimal value, at  $1.22 \times 10^3 M$



concentration beyond which there was decreased in graft yield. This was consistent with the corresponding decreased in grafting ratio at higher concentrations. A plausible explanation to this occurrence may be due to termination of growing grafting onto polyacrylamide chains by allyl alcohol radical species.

**Table 1:** Effect of Allyl alcohol on graft yield for sodium alginate-g-polyacrylamide

Na.Alg (g)	Allyl alcohol x 10 <sup>3</sup> (M)	[Ce <sup>+4</sup> ] (mol x 10 <sup>3</sup> )	Graft yield (%)
1	0.00	16.67	74.6
1	1.22	16.67	124.86
1	2.44	16.67	120.13
1	4.88	16.67	93.18
1	7.32	16.67	83.93

**Table 2:** Effect of allyl alcohol on percentage graft yield ratio sodium alginate-g-polyacrylamide

Na.Alg (g)	Allyl alcohol x 10 <sup>3</sup> (M)	[Ce <sup>+4</sup> ] (mol x 10 <sup>3</sup> )	Graft yield (%)
1	0.00	16.67	-
1	1.22	16.67	1.68
1	2.44	16.67	1.62
1	4.88	16.67	1.25
1	7.32	16.67	1.13

**Table 3:** Mechanical properties of sodium alginate and polyacrylamide grafted alginate

Copolymer Sample	Tensile Strength (MPa)	Elongation @break (%)	Extension (mm)
Na Alg	54.62 ± 3.8	12.75 ± 5.7	1.14 ± 0.05
Na.Alg-g-PAM	42.18 ± 2.4	18.06 ± 4.1	2.51 ± 0.12

The mechanical properties of sodium alginate and polyacrylamide grafted copolymer are presented in table 3 above. The copolymer shows a decrease in tensile strength, but increase in both elongation at break and extension when compared to the pristine sodium alginate. The decrease in tensile strength may be attributed to the perturbation of the sodium alginate crystalline structure by polyacrylamide chains, which in turn increases the volume space within the copolymer matrix thereby conferring more flexibility on the copolymer chains. Enhanced flexibility of the later is consistent with observed increased elongation and extension of the copolymer. The tensile strength of sodium alginate and sodium alginate-g-polyacrylamide, 54.62±3.8 MPa and 42.18±2.4 MPa respectively are comparable to the corresponding values, 58.30±5.8 MPa and 47.40±4.9 for sodium alginate and sodium alginate-g-polyacrylonitrile hydrogels respectively [12].

The surface morphologies of sodium alginate and sodium alginate-g-polyacrylamide copolymer are presented in Figures 4 and 5 respectively. From the micrographs a large difference in the morphologies of the polymers can be seen. The ungrafted sodium alginate is distinctly different in morphology compared to the graft copolymer having irregular shape which appears smooth. For the latter, clusters of grafted polyacrylamide are evident on the surface of the alginate, an indication of graft polymerization. There is a more even distribution of polyacrylamide on the surface of alginate, understandably because the reaction medium was homogenous.



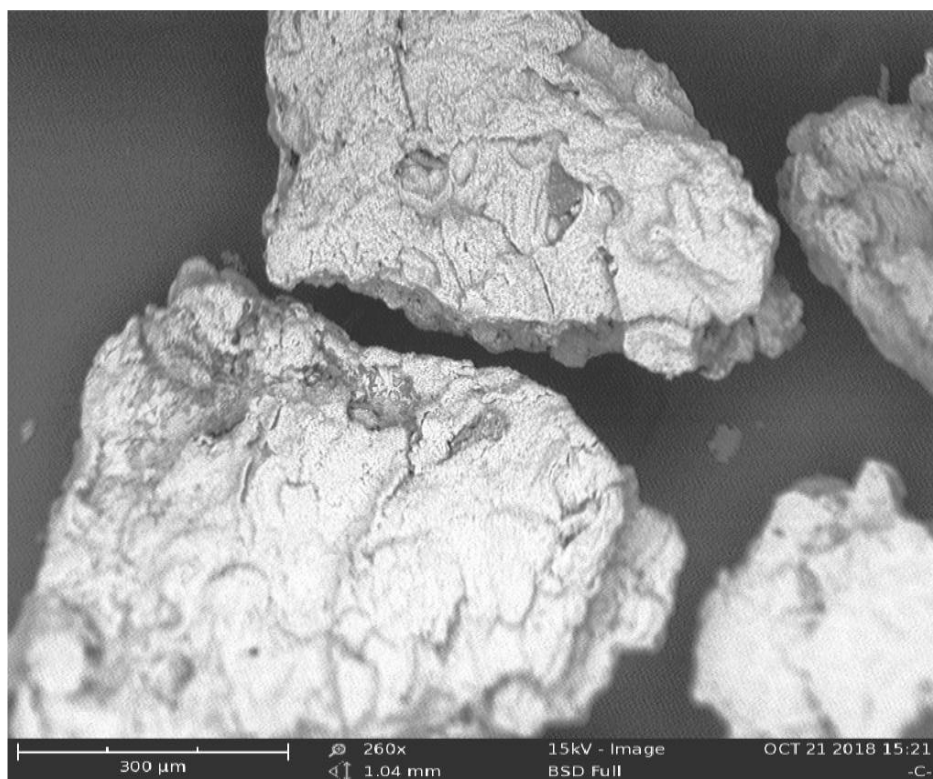


Figure 4: SEM micrograph of sodium alginate

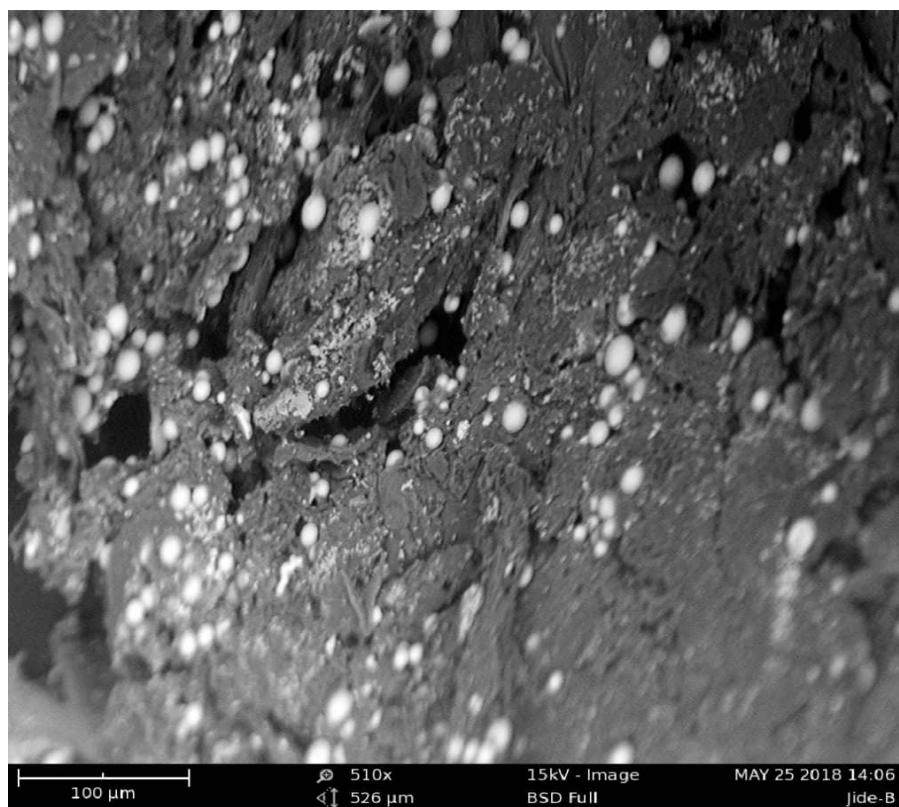


Figure 5: SEM micrograph of sodium alginate-g-polyacrylamide



The results for thermogravimetric analysis of sodium alginate and its graft copolymer with polyacrylamide are represented in table 4. From the onset degradation temperatures ( $T_0$ ), it is evident that the graft copolymer was more stable than sodium alginate having values of 231.25 and 233.34°C for sodium alginate (Na.Alg) and sodium alginate-g-polyacrylamide (Na.Alg-g-PAM) respectively. This is in agreement with higher thermal stability for potato starch-g-polyacrylonitrile compared to the ungrafted starch [13]. However, from the temperature at 10% degradation ( $T_{10\%}$ ), sodium alginate is more stable than the grafted copolymer. This may be attributed to decomposition of acrylamide within the temperature range 175 – 300°C, to yield imide group via cyclization and evolution of ammonia. [14, 15], at high degradation temperature, the presence of imide moieties in the graft copolymer enhances its stability resulting in reduced weight loss compared to sodium alginate.

**Table 4:** Thermal stability of sodium alginate and sodium alginate-g-polyacrylamide copolymer

Polymer Sample	$T_0$	$T_{10\%}$	$T_{50\%}$	$T_{max}$
Na Alg	231.25	306.30	381.25	502.01
Na.Alg-g-PAM	233.34	258.33	383.33	558.33

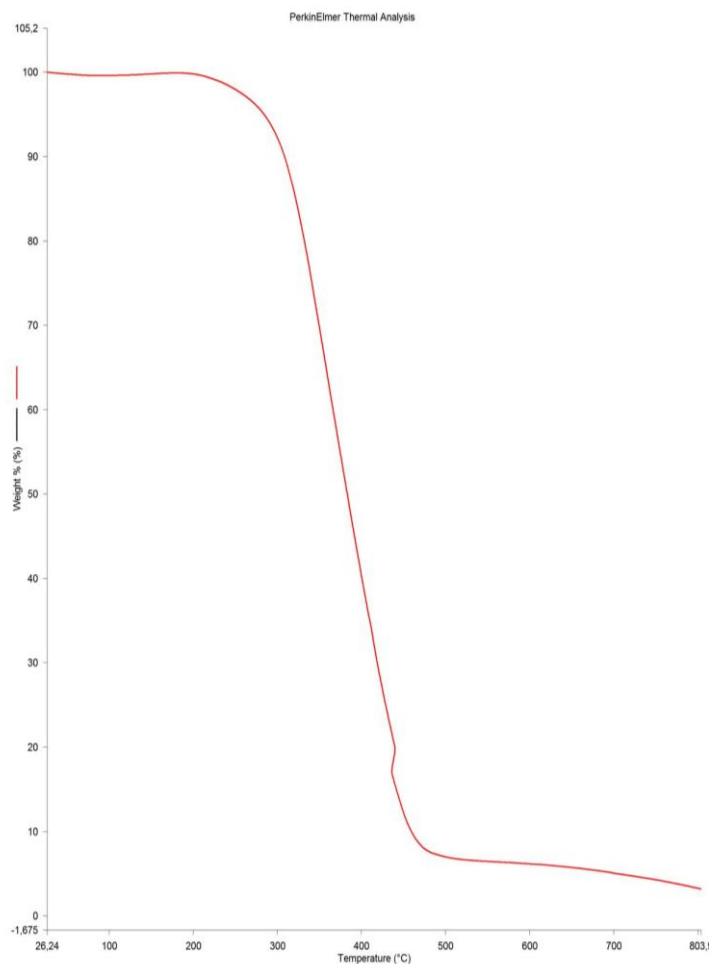


Figure 6: Thermogram for sodium alginate (Na.Alg)

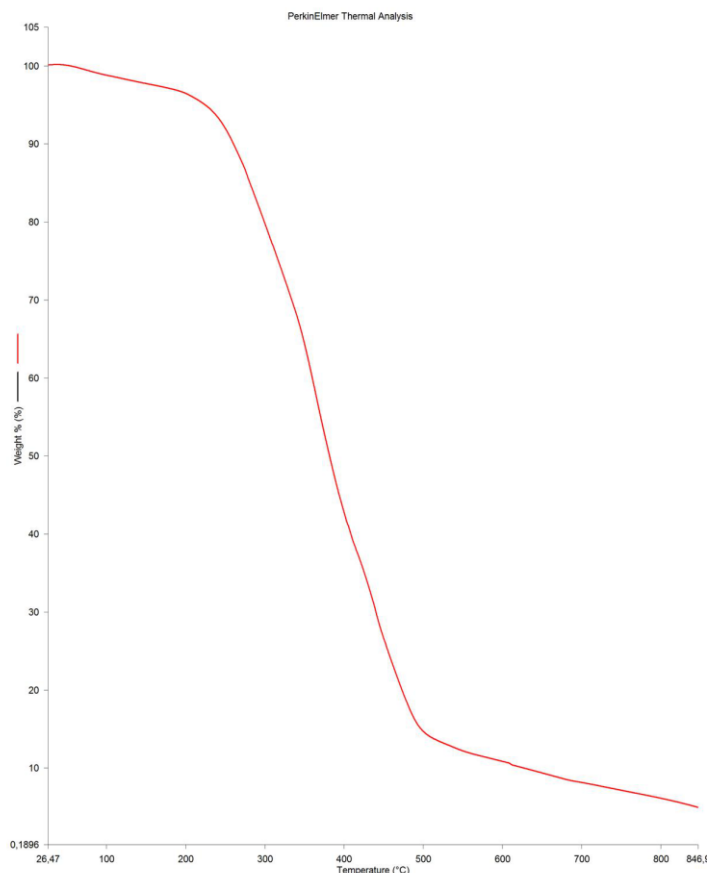


Figure 7: Thermogram for sodium alginate-g-polyacrylamide (Na.Alg-PAM)

#### 4. Conclusions

The graft copolymerization of acrylamide onto sodium alginate by ceric ion-allyl alcohol redox pair showed optimal yields in time-temperature conversion in the range 30 – 60°C. The effect of allyl alcohol on the copolymerization reaction showed an initial increase in graft yield, followed by a negative dependence as the concentration of allyl alcohol increases. The ratio of graft yields in the presence and absence of allyl alcohol  $P_g/P_{g0}$  was greater than unity. The ungrafted sodium alginate showed an irregular shape which appeared smooth. For the sodium alginate-g-polyacrylamide, the distribution of grafted polymer was even. The graft copolymer was more thermally stable compared to sodium alginate based on temperature at which degradation occurred. The grafted copolymer owing to its enhanced shear and thermal stabilities could find broad industrial applications.

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