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## Synthesis and optimization of polyacrylamide and gum arabic graft copolymer

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### ABSTRACT

Graft copolymerization of polyacrylamide onto gum arabic was carried out in aqueous medium at room temperature (30 °C) using various initiator (ceric ion) and monomer (acrylamide) concentrations. The extent of graft copolymer formation was determined in terms of percentage graft yield. The results obtained showed that the percentage yield of the graft copolymer is a function of both the initiator and monomer concentrations. The grafted copolymer was characterized by infrared (IR) spectroscopy. The IR spectral data for pure Gum Arabic (GA) and that of Gum Arabic-grafted Polyacrylamide (GA-g-PAAM) indicate that grafting actually occurred. The successful grafting of polyacrylamide onto gum arabic will enhance the search for materials transformation through chemical derivatization with attendant expansion of their spectra of application.

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**Keywords:** Graft copolymerization, polyacrylamide, monomer, gum arabic, Chemical derivatization.

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### INTRODUCTION

A chemist *inter alia* is someone who takes common, readily available and inexpensive materials from the surroundings and transforms them into amazing products for the alleviation of human misery, discovery of new products or better alternatives to existing ones and the promotion of scientific research in general. In order to keep pace with contemporary trends in scientific research, we attempted to graft polyacrylamide a documented flocculant (Tripatly and Singh, 2001) onto gum arabic, a natural polysaccharide. The choice of grafting polyacrylamide onto gum arabic was not random but a meticulous exercise. This was in connection with the importance and growing concern and curiosity on water soluble

polymers of high molecular weight which have a multiplicity of industrial uses in such domains as paper manufacture, waste water treatment, enhanced oil recovery, drag reduction and mineral beneficiation (Okieimen, 2004). Gum arabic refers to the gum exudates from *Acacia senegal* tree species and is the prime source of gum arabic (Osman et al., 1993 and Menzies et al., 1996). Gum arabic is a highly complex polysaccharide with an equally complex molecular structure. Intensive studies carried out on the molecular organization of gum arabic reveal that gum arabic is a polysaccharide whose backbone chain consists of  $\beta$ -(1-3) linked galactose residues with branches linked through the 1, 6

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positions and then arabinose, rhamnose and glucuronic acid located in the ramified side chains (Anderson et al., 1990; Eagles et al., 1993; Osman et al., 1993; Idris et al., 1998). The galactose residues in the backbone chain as well as the molecular species in the ramified side chains such as arabinose, rhamnose and glucuronic acid, contain pendant hydroxyl (-OH) groups which contain non-bonding electrons, easy to ionize using electron loving species or oxidizing agents such as ceric ions and hence create reactive sites for graft polymerization reactions to commence (Cesàro et al., 1992). The grafting reaction alone has far-reaching effects on the chemistry of gum arabic because it can alter or impart novel properties to the gum arabic such as flocculation and sorption propensities. Gum arabic is a documented food additive (Baldwin et al., 1998; Williams and Philips, 2000) and the industries that make use of gum arabic include confectionaries, bakeries, beverages, pharmaceuticals, cosmetics and textile industries. The additional properties of flocculation and sorption to gum arabic enhanced by the grafting reactions present a wide range of applications making research in the area imperative. Some successes have been reported on grafting polyacrylamide onto some materials of polysaccharide origin, such as the grafting of polyacrylamide onto sodium aginate by Tripathy and Singh (2001) and the grafting of polyacrylamide onto "Konkoli" gum (Barminas, 2004 and Osemeahon et al., 2008). These grafting reactions and related characterization were not experimented on other polysaccharide materials of known chemistry including gum arabic. It was in the light of this plethora of shortcomings and potential advantages inherent in this research that we set to investigate the grafting of polyacrylamide onto gum arabic and its characterization with a view to making useful suggestions on alternative uses of gum arabic, its products and further research.

## MATERIALS AND METHODS

### Materials

Gum arabic (GA) which constitutes the prime raw material was purchased from Kano city – Nigeria. Ceric ammonium nitrate (CAN), acrylamide (AM), acetone, hydroquinone, ethanol, acetic acid and methanol were purchased from BDH laboratories and used as supplied.

### Preparation of gum arabic

Gum arabic (grade one *Acacia senegal*) dried exudates were purchased in powdered form from farmers in Kano-Nigeria, weighed and then stored at room temperature (30 °C) for subsequent use in the research.

### Graft copolymerization of acrylamide and gum arabic

The synthesis of the characterized grafted copolymer was preceded by optimization experiments from which most suitable concentrations of the initiator (CAN) and the monomer (AM) were obtained and used. This was done in order to proffer the best reaction conditions to the synthesis of the earmarked graft copolymer.

The polymeric product (GA-g-PAAM) was synthesized by the ceric-induced solution polymerization method (Tripathy and Singh, 2001; Osemeahon et al., 2008). The polymerization reaction was carried out at room temperature (30 °C). Gum arabic solution (2%) was prepared by weighing out 2 g of the gum arabic using a sensitive electronic balance (AB204) and dissolving the mass in a 100 ml volumetric flask. This 2% solution was then transferred into a 250 ml beaker that was used as the reaction vessel. Then CAN (0.164 g) which is equivalent to  $3.0 \times 10^{-3}$  M Ceric ammonium nitrate  $[\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6]$  was weighed and added to 100 ml of 2% GA solution and a time lapse of 20 minutes was allowed for the initiator to interact with the polysaccharide functional groups in the GA solution after stirring and thus paving the way to grafting reactions

(Tripathy and Singh, 2001). Similarly, AM (1.422 g) equivalent to 0.20 M  $\text{CH}_2=\text{CHCONH}_2$  was added to the GA solution and stirred thoroughly for 30 minutes. The graft copolymerization reaction was then allowed to proceed for six hours and the reaction was terminated using 2 ml of 5% hydroquinone solution. After termination, the graft copolymer was precipitated using excess acetone. The precipitated grafted product was filtered and then submerged in pure acetone for one hour in order to get rid of any hazardous remnants of acrylamide monomer units from the newly synthesized product and thus rendering the product non-deleterious to its earmarked industrial applications.

#### Further purification of graft copolymer

At the end of the graft copolymerization reaction, there exist in the reaction mixture the graft copolymer (GA-g-PAAM), homopolymer of polyacrylamide, residual monomers of acrylamide, impurities and other contaminants. The purification process involves the extraction of occluded polyacrylamide from the graft copolymer (Tripathy and Singh, 2001). This was carried out by solvent extraction using ethanol and methanol in succession. The grafted product previously submerged in acetone was submerged in ethanol for 30 minutes and then methanol for one hour and further washed with methanol five times. The grafted copolymer was then removed and dried, weighed, percentage yield calculated and then kept for subsequent uses.

#### Determination of grafting percentage

The extent of graft copolymer formation can be obtained from the percent graft copolymer yield. The graft percentage was determined with aid of an equation described by Osemeahon et al. (2008);

$$\% \text{ Graft} = \left( \frac{W_2 - W_1}{W_1} \right) \times 100$$

Where  $W_1$  is the weight of ungrafted GA and  $W_2$  is the weight of grafted GA.

The percentage conversion which is also an indication of process efficiency was computed by taking recourse to an equation described by Tripathy and Singh (2001).

$$\% \text{ Conversion} = \frac{(GA - g - PAAM, wt) - (Polysacwt)}{(\text{Weight of acrylamide})} \times 100$$

The grafting efficiency obtained through percentage conversion or graft percentage was optimized by appropriate adjustment of reaction conditions.

#### Infrared spectroscopic analysis of the graft copolymer

In order to ascertain the copolymer grafting reaction, the IR spectra of pure gum arabic (GA) and the grafted product (GA-g-PAAM) were measured. Powdered samples of the products were scanned from  $4000 \text{ cm}^{-1}$  to  $600 \text{ cm}^{-1}$ . The IR spectra were taken with the aid of the Fourier Transform Infrared Spectrophotometer (SHIMADZU FTIR-8400S) and the results were subsequently interpreted.

## RESULTS AND DISCUSSION

#### Effect of initiator concentration on percentage graft yield

Figure 1 depicts the effect of initiator concentration on graft copolymer yield. From Figure 1, the percentage yield of the grafted copolymer increases somewhat linearly with concentration of CAN to a maximum and then further increase in the initiator concentration leads to a drop in the percentage conversion. The optimum concentration of CAN that gave the highest percentage conversion (70%) was  $3.0 \times 10^{-3} \text{ M}$ . The relatively high percentage yield may be attributable to two factors, the first being the complete and homogeneous dissolution of gum arabic with attendant exposure of the constituent numerous functional groups to graft copolymerization reactions and secondly, this significant yield may be attributable to the complete decomposition of the initiator molecules into ionic species of high charge density capable of

creating free radical reactive sites on the polysaccharide backbone through redox processes. Jideonwo and Okieimen (2006) suggested that the CAN concentration at which maximum graft level occurs represents the reduction equivalent of the backbone polysaccharide. Consequently, grafting buds off at the activated sites on the GA backbone with monomeric units of acrylamide (Tripathy and Singh, 2001).

The gradual increase in % conversion with increase in CAN concentration is due to the fact that more reactive sites are created on the GA backbone by the initiator ions as their concentration increases, which lead to more effective grafting reactions. Meanwhile, the drop in % conversion at higher concentrations of CAN is explained by the plausible formation of a complex of ceric in the backbone polymer which instead blocks potential sites for grafting and this is due to the solubility of GA in water. Hence, the accessibility of the backbone polymer to the reactants which depend on its state of aggregation and degree of swelling is an important factor regulating the degree of graft copolymer formation (Jideonwo and Okieimen, 2006).

#### **Effect of monomer concentration on percentage graft yield**

Figure 2 illustrates the dependence of percentage yield on the concentration of acrylamide at constant CAN concentration. The results show an initial increase in the percentage yield with acrylamide concentration reaches a maximum and then decreases with further increase in AM concentration. The percentage graft level increases initially with monomer concentration due to unsaturation of free radical reactive sites on the polysaccharide backbone and more available growing radicals from the grafting points. The highest value of % yield obtained was 60% and this corresponds to a point where the free radical sites on the backbone are saturated and the available monomers are just enough to sustain

the growing grafted chains. Further increase in the concentration of acrylamide, gives rise to excess acrylamide monomer species in the reaction medium, which leads to homopolymer formation by acrylamide molecules and thus resulting to a net drop in percentage yield of the grafted polymeric product (Jideonwo and Okieimen, 2006). The highest percentage yield of the grafted product was obtained when 0.20 M acrylamide was used.

#### **Grafting evidence portrayed by IR analysis**

The IR spectra of pure GA and that of the grafted copolymeric product (GA-g-PAAM) are shown in Figures 3 and 4 respectively. From the IR spectra of gum arabic, a broad peak was observed at 3437.26  $\text{cm}^{-1}$  which falls in the range of -OH vibrations (Tripathy and Singh, 2001 and Osemeahon, 2003). Intense peaks also appeared at 1437.02  $\text{cm}^{-1}$  corresponding to the absorption of -COOH groups. Two broad peaks featured at 1042.60  $\text{cm}^{-1}$  and 1112  $\text{cm}^{-1}$  are probably due to -C-O groups and two sharp peaks were observed at 2923.22  $\text{cm}^{-1}$  and 2853.78  $\text{cm}^{-1}$  attributable to the presence of aliphatic -C-H groups (Mendham et al., 2006; Morrison and Boyd, 2007).

Meanwhile the IR spectra of the grafted polymeric product displayed alien features not typical of pure gum arabic spectra which lent credence to the expected occurrence of the grafting reaction. Some of these features included the following:

- The appearance of a peak at 2361.91  $\text{cm}^{-1}$  in GA-g-PAAM spectra which is absent in gum arabic spectra and represents the nitrile group (-C $\equiv$ N) (Christian, 2007). The appearance of the -C $\equiv$ N groups may proceed from the oxidation of amine groups in acrylamide and suggests grafting.

- The lowering, broadening and shifting of the absorption to higher wavelengths of the peak at 1041.6  $\text{cm}^{-1}$  in gum arabic spectra to 1026.16  $\text{cm}^{-1}$  in GA-g-PAAM spectra indicating the formation of ether linkages whose absorption peaks fall

within the range 1000 – 1150  $\text{cm}^{-1}$  (Mendham et al., 2006). This is also a strong indication of the occurrence of grafting reactions.

- The more intense and sharper peak in the gum arabic spectra at 1437.02  $\text{cm}^{-1}$  for  $-\text{COOH}$  groups shifted to less intense and broader peaks at 1448.97  $\text{cm}^{-1}$  in GA-g-PAAM spectra is in the neighborhood of  $-\text{C-N}$  vibrations in amines and amides (Bailey, 1995) and suggests grafting.

- The relatively sharp peak at 3437.26  $\text{cm}^{-1}$  in gum arabic spectra shifted to a broader peak at lower wavelengths at 3467.16  $\text{cm}^{-1}$  in

GA-g-PAAM spectra corresponding to  $-\text{N-H}$  bonds absorption bands. This suggests the replacement of  $-\text{OH}$  groups by  $-\text{NH}$  groups in the process of grafting. Assuming an utter obliteration of acrylamide monomer species and homopolyacrylamide chains from the grafted copolymer, during the purification process, the appearance of peaks at 2361.91, 3467.16, 1448.59 and 1026.16  $\text{cm}^{-1}$  in the graft copolymer is good enough evidence for grafting.

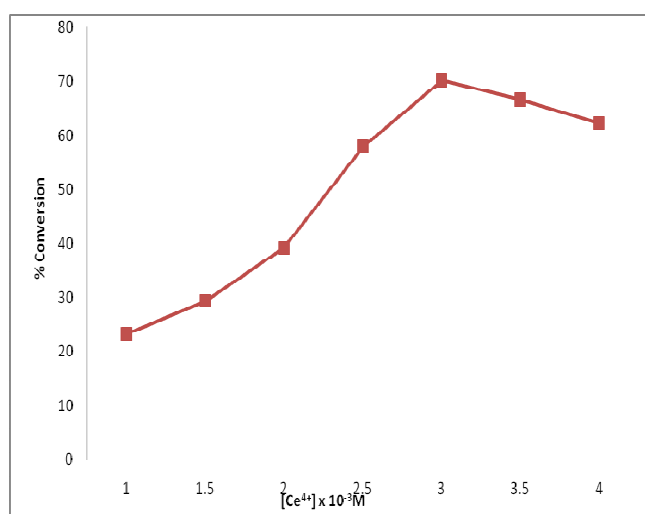


Figure 1: Effect of initiator concentration on percentage graft yield.

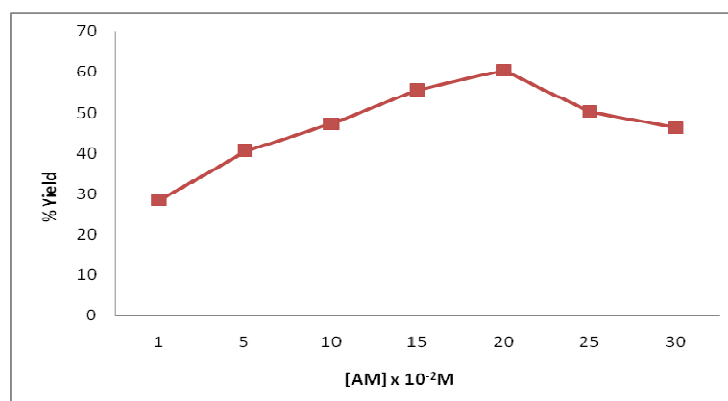


Figure 2: Effect of monomer concentration on graft yield.

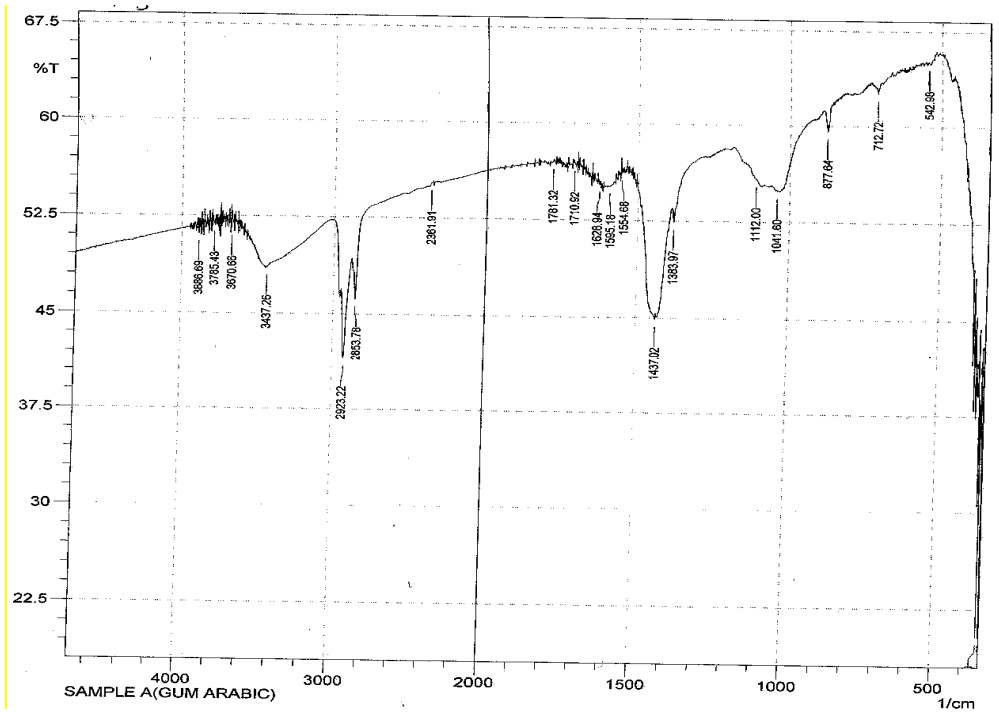


Figure 3: IR Spectra of Gum Arabic.

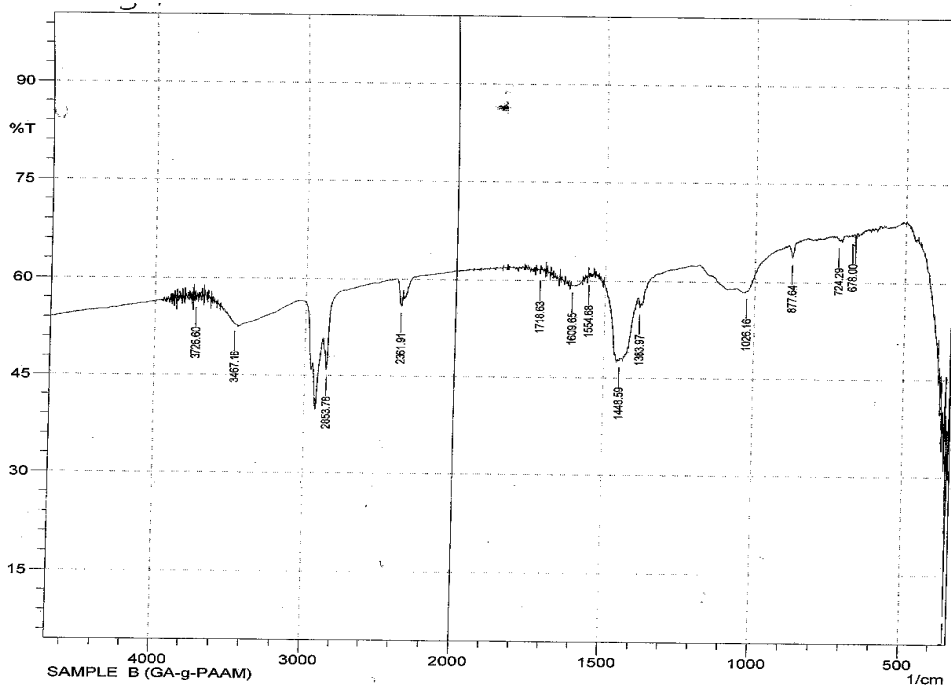


Figure 4: IR spectra of GA-g-PAAM.

The prime intent of this research was to produce a graft copolymer for subsequent characterization using gum arabic and polyacrylamide. The graft copolymer synthesis was preceded by optimization reactions in which the most suitable concentrations of the initiator and monomer were determined and used in the graft copolymer synthesis (i.e. concentrations that gave highest percentage graft yield). The grafting reaction was successful as portrayed by the IR analysis.

Figure 1 shows the effect of initiator concentration on percentage graft yield. Figure 2 shows the effect of monomer concentration on percentage graft yield. Here, we observe that the percentage graft yield is simultaneously a function of initiator and monomer concentrations. The dependence of percentage or reaction rate or other parameters on concentration of reacting species has been reported by other researchers like Osemeahon et al. (2008), Chukwu et al. (2011), Olaleken and Odebunmi (2011) and also Vivekanandan and Kamaraj (2011). The outcome of this research is therefore a consolidation of trends earlier reported in the domain of biopolymers. The uniqueness of this research however lies in the fact gum arabic, a documented food additive and an emulsifier/stabilizer (Menzies et al., 1996; Baldwin et al., 1998) in various industrial processes was transformed by graft copolymerization to a new polymeric material endowed with unprecedented chemical properties such as flocculation and sorption propensities which are desirable characteristics that can be utilized in environmental sanitization and combating of aqua transmitted ailments and hence used to reinforce or supplement bioremediation of wastewaters (Osemeahon et al., 2008) especially industrial effluents amongst others. This might also blaze the trail to novel procedures of material treatment for manufacturing purposes. A good example is the carbonization of cassava (*Manihot esculenta*) for use as fillers in rubber compounding in order to enhance

processability and physiomechanical properties *inter alia* (Ugbesia et al., 2011).

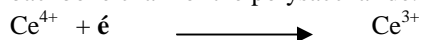
### IR analysis

Figure 3 depicts the IR spectra of gum arabic while figure 4 gives the IR spectra of the graft copolymer of gum arabic and polyacrylamide. Evidence provided by the IR spectra clearly shows that grafting actually occurred. This successful graft reaction is in conformity with earlier reported works on grafting reactions using varied polysaccharides with other species of polymeric materials like polyacrylamide and methylacrylate. Samples of such researches include the works of Tripathy and Singh (2001), Osemeahon (2003), Jideoniwo and Okieimen (2006) and Osemeahon (2008).

From the findings of this research in general, it may be worth noting that chemical derivatization (material transformation), if well harnessed, is capable of rendering unproductive materials around us productive and further diversifying the use of some useful materials or simply adding value to them with attendant up-surge in demand.

### Mechanism of ceric action

This mechanism involves the formation of a chelate complex that decomposes to generate free radical sites on the polysaccharide backbone (Tripathy and Singh, 2001; Osemeahon et al., 2008). The high charge density  $Ce^{4+}$  then interacts with the backbone galactose residues or the peripheral rhamnose and glucuronic acid residues abstracting electrons from the loosely bound non-bonding electrons of oxygen on the hydroxyl (-OH) group to be reduced to  $Ce^{3+}$  and thus creating free radical sites on the backbone chain of the polysaccharide.



The free radical sites in the presence of acrylamide monomers generate graft copolymers. When a simplistic approach is followed, a low concentration of initiator should initiate a few grafting sites which results in longer polyacrylamide grafted

chains, compared to a higher concentration of the catalyst which will initiate a large number of grafting sites and thus making the average polyacrylamide grafted chains shorter for the same acrylamide concentration.

### Conclusion

In this study we carried out the graft copolymerization of acrylamide (AM) onto gum arabic (GA) using ceric ammonium nitrate (CAN) as initiator. The evidence for grafting was demonstrated by the infrared (IR) analysis. Both initiator and monomer concentrations were found to have profound influence on the percentage yield of the graft copolymer. The flocculation properties of the graft polymeric product have been studied and will be duly reported in the next publication from this series.

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