

Full Length Research Paper

Development of sodium alginate and konkoli gum-grafted-polyacrylamide blend membrane: optimization of grafting conditions

Osemeahon, S. A.* , Barminas T.J., Aliyu, B. A. and Nkafamiya, I. I.

Department of Chemistry, Federal University of Technology, P.M.B 2076, Yola, Nigeria.

Accepted 18 March, 2008

This experiment is a continuation of our effort to develop a blend membrane of sodium alginate and “konkoli” gum-g-polyacrylamide (KG-g-PAAm) for bioremediation of wastewater. The effect of graft reaction conditions on the percentage graft yield in the graft copolymerization was investigated. It was observed that grafting parameters such as acrylamide (AM), ceric ammonium nitrate (CAN), “konkoli” gum (KG), temperature and reaction time have remarkable influence on the percentage graft yield of the graft copolymer. The percentage graft yield initially increased and then decreased for all the parameters investigated. Optimum percentage graft yield of 83, 85, 86, 84 and 84 were obtained by varying AM, CAN, temperature, reaction time and KG, respectively. This result present the optimum grafting conditions required for copolymerization of AM onto KG.

Key words: Membrane, grafting, conditions, yield.

INTRODUCTION

‘Konkoli’ seed gum (KG) from *Maesopsis eminii* plants is widely used as thickeners in soup and other traditional baked food products in Nigeria, primarily because of its high viscosity, binding and swelling propensity (Osemeahon, 2003; Barminas and Eromosele, 2002). In Nigeria, this plant grows wild in the east, south and middle belt of the country (Osemeahon, 2003; Aliyu, 2002). Its shoots greenish flowers around April and May and bear fruits which gets matured around August and September as they become publish black containing a very hard seed. The seeds are normally removed from the dried fruits and ground into fine powder and may be constituted in hot or cold water and used in the preparation of soups and other traditional baked foods (Osemeahon, 2003).

The need for improved membrane composition as super absorbent polymers using available polymeric materials has been the subject of extensive research (Lee and Lin, 2000; Hegazy et al., 2001). Superabsorbent polymers are important because of their excellent characteristics, wide applications in many fields, such as

horticulture, gel actuators, water blocking tapes, medicine. In addition, the studies are included charac for drug delivery systems and absorbent pads (Barminas et al., 2005). These swollen polymeric networks have also found wide applications in different technological areas, such as, materials for contact lenses and protein separation, matrices for cell encapsulation and tissue engineering, matrices for cell encapsulation and tissue engineering and devices for controlled release of pharmaceutically active proteins (Hennik and Nostrum, 2002; Hoffman, 2002). In these applications, water absorbency and retention are crucial.

Grafting of natural polymers such as water-soluble polysaccharides containing various functional groups is of considerable interest for modification of the polymer structure. Such modifications have led to the preparation and characterization of grafted and blend membranes for prevaporation process (Toti et al., 2002) and as polymeric flocculants (Tripathy and Singh, 2001). One of the most valued properties of these modified products is their absorbency and dehydration behaviour (Lee and Lin, 2000). KG is a seed galactomannan (Barminas and Eromosele, 2002) even though hydrophilic and exhibits high swelling capacity, it may be practically unsuitable as a scavenger in wastewater treatment (Barminas et al., 2005) and hence the need for its modification.

*Corresponding author. Email: sundayosemeahon@yahoo.com.

In our last experiments (Osemeahon, 2003 and Barminas et al., 2005), we reported the successful grafting of acrylamide onto KG and blending of the KG-g-PAAm with sodium alginate to develop sodium alginate and KG-g-PAAm blend membrane. Preliminary investigation on the swelling properties of the grafted membrane in aqueous medium was also reported (Barminas et al., 2005). However, the percentage graft yield (21%) obtained from the graft reaction was relatively low when compared to the 98% graft yield obtained from a similar experiment involving the grafting of acrylamide onto Guar gum reported earlier by Toti et al. (2002). In this experiment, we set out to investigate the grafting conditions of AM onto KG with the aim of optimizing the percentage graft yield.

MATERIALS AND METHODS

Materials

Acrylamide, ceric ammonium nitrate, acetone and methanol were of BDH analytical grade and were used as supplied.

The Konkoli (*Maesopsis eminii*) dry seed was decoated and milled into powder. This was then sieved through a 100 μm sieve screen to obtain fine powder and packaged in a polyethylene bag for use. This crude sample was used as KG without extraction and purification.

Synthesis of graft copolymer

Konkoli-g-polyacrylamide (KG-g-PAAm) was synthesized by reacting KG with acrylamide (AM) at 60°C using ceric ammonium nitrate (CAN) as an initiator following the method described by Toti and Aminabhavi (2002). An initiator containing 2.5×10^{-3} mol of CAN was employed and solution polymerization method was used. The grafted copolymer obtained at the end of 6h was precipitated in excess acetone. This was further purified by filtration and washing with a mixture of water and methanol (7:3 by volume), to remove the homopolymer formed. The solid mass was then air dried at room temperature (30°C) for 24 h. The percentage graft yield was then calculated from the relation:

$$\% \text{ Graft} = [(W_2 - W_1) / W_1] \times 100$$

Where W_1 and W_2 are weight of KG and grafted KG respectively. The above procedure was repeated at different initiator concentrations, monomer concentration, temperatures, reaction time and KG concentrations.

RESULTS AND DISCUSSION

Synthesis of graft copolymer

A graft copolymer, KG-g-PAAm was synthesized by ceric-ion-induced polymerization method. The mechanism of ceric ion action involves the formation of a chelate complex (Barminas et al., 2005). It has been established by the works of Niu and Volesky (2000) that the chelate complex is formed between the -OH groups of KG. This decomposes to generate free radical sites on the polysaccharide backbone. The grafting of the acrylamide

monomer occurs at these active free-radical sites on the backbone of KG (Barminas et al., 2005). The grafting reaction of acrylamide onto KG may be represented in Figure 1 as suggested by Barminas et al. (2005).

Effect of monomer concentration

The effect of monomer (acrylamide) on the percentage graft yield of KG-g-PAAm is shown in Figure 2. The percentage graft increases initially over the monomer range of 1.0 to $16.0 \text{M} \times 10^{-6}$ and then decreases. The percentage graft at the optimum monomer concentration of 16.0×10^{-6} is 83%. The apparent acceleration in the graft yield may be attributed to the gel effect, resulting from an enhanced solubility of polyacrylamide in the monomer (Eromosele and Hamagadu, 1993). This would consequently increase the viscosity of the reaction medium and reduce rate of termination by the coupling of the growing polymer chains.

The decrease in the graft yield at a monomer concentration higher than 16.0×10^{-6} may be due to an enhanced homopolymer formation by chain transfer to monomer (Eromosele, 1991)

Effect of initiator concentration

Figure 3 represent the effect of initiator (ceric ammonium nitrate) concentration on the copolymer graft yield. At very low concentration 2.19×10^{-4} , the graft yields increases to an optimum value of 85%. Further increases in concentration of CAN led to a reduction in yield. The initial increase may be ascribing to an increase in the concentration of free radicals in the system (Barminas et al., 2005; Eromosele and Hamagadu, 1993). At a critical initiator concentration of 10.95×10^{-4} M, there is a possibility of termination reaction of grafted polymeric radicals (Eromosele 1994; Barminas et al., 2005).

Effect of temperature

The effect of temperature on the graft copolymerization was investigated over the range of 30 - 90°C. The result as presented in Figure 4 indicates initial increases in graft yield up to 60°C and then followed by a gradual decrease in yield above 60°C. The percentage graft increase overall, with temperature in the range of 30 - 60°C is consistent with an expected increase in swellability of the polysaccharide (KG) and enhanced rate of diffusion of the monomer to the radical sites on the KG and on the graft polymer (Barminas et al., 2005; Eromosele, 1994; Sartore et al., 2002).

Effect of time

The time conversion curve of the graft copolymerization

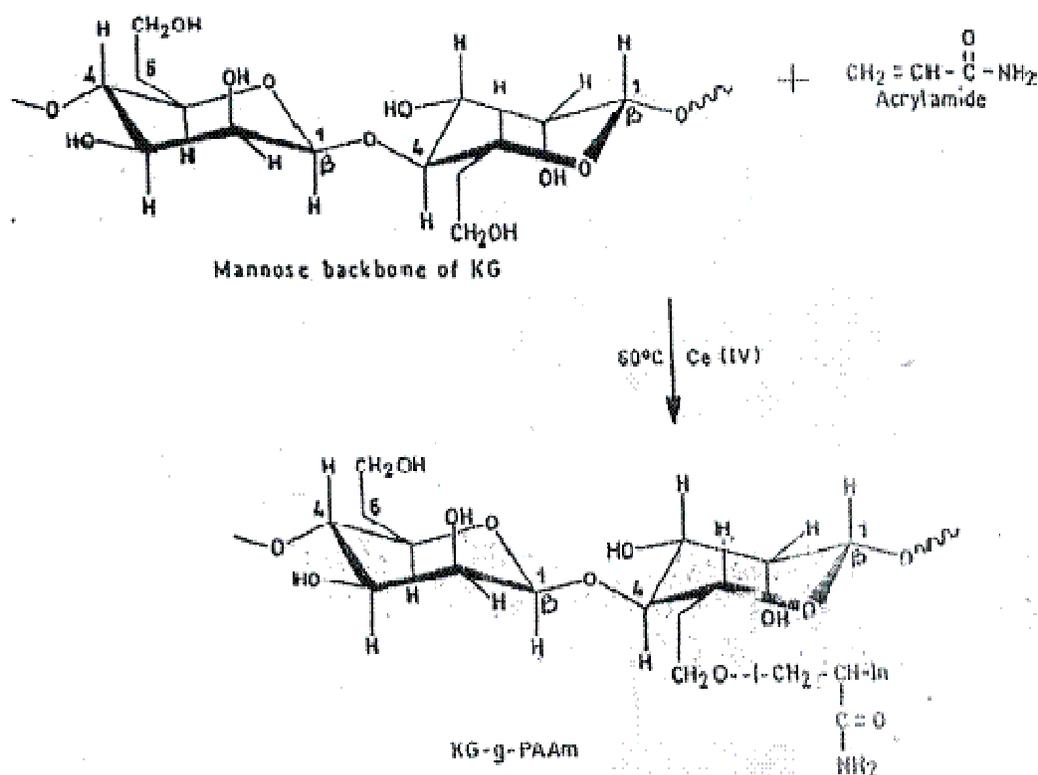


Figure 1. Grafting reaction of acrylamide onto KG.

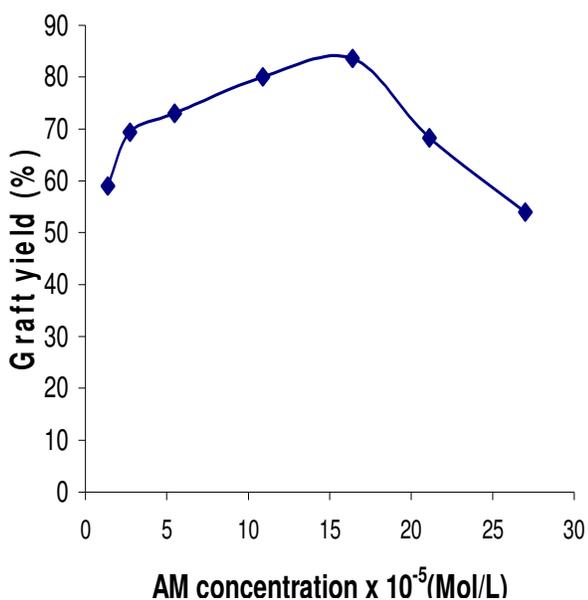


Figure 2. Effect of monomer concentration on graft yield (Initiator = 2.5×10^{-3} mol/L, temperature = 60°C , time = 6 h, KG = 1%, w/v)

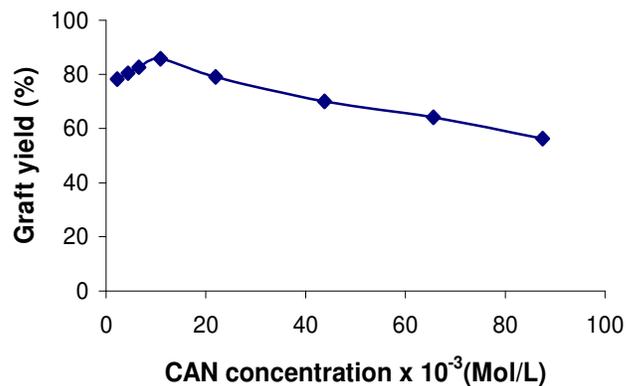


Figure 3. Effect of initiator concentration on graft yield (AM = 0.105 mol/L, temperature = 60°C , time = 6 h, KG = 1%, w/v).

agrees with earlier report by Eromosele and Hamagadu (1993). The decrease in percentage graft yield after 2 h may be rationalized by partial hydrolysis and dissolution of the grafted polymer chains (Osemeahon, 2003)

is represented in Figure 5. The graph is characterized by initial increases in graft yield with time up to a period of 2 h after which the yield decreases with time. This result

Effect of KG concentration

The effect of KG concentration on the percentage graft

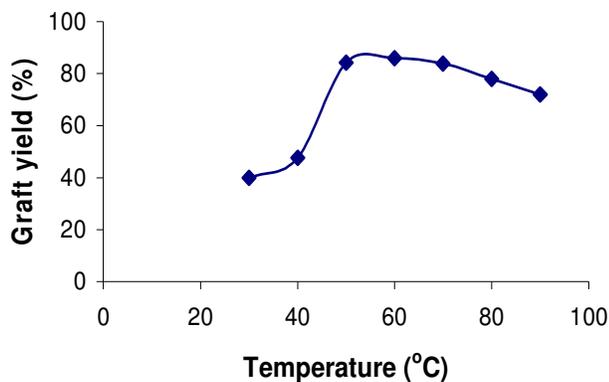


Figure 4. Effect of Temperature on graft yield (AM = 0.105 mol/L, Initiator = 2.5×10^{-3} mol/L, time = 6 h, KG = 1%, w/v).

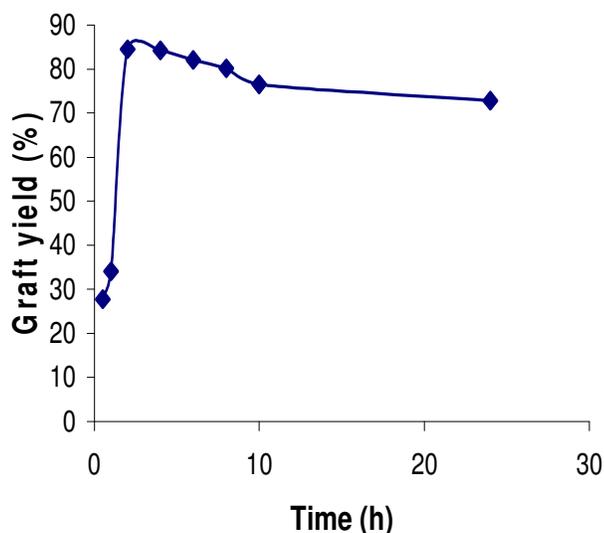


Figure 5. Effect of reaction time on the graft yield (AM = 0.105 mol/L, Initiator = 2.5×10^{-3} mol/L, temperature = 60°C, KG = 1%, w/v).

yield of Kg-g-PAAm is presented in Figure 6. It is revealed that the graft yield initially increased and then decreased. The initial increases can be rationalized by the increases in KG concentration. The observed trend at higher concentration (above 1% w/v) may be due to increase in homopolymerization. It may also be as a result of caging effect (Osemeahon, 2003).

Conclusion

In conclusion, the effect of graft conditions on the percentage graft yield in the copolymerization of AM onto KG has been investigated. It was observed that the percentage graft yield increased initially and then decreased for all the parameters investigated. Optimum percentage graft yield of 83, 85, 86 84 and 84 were obtained by vary-

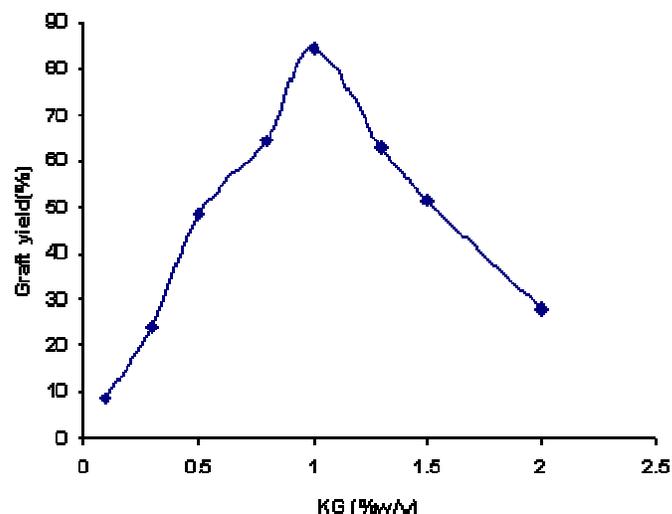


Figure 6. Effect of KG on graft yield (AM = 0.015 mol/l, Initiator = 2.5×10^{-3} mol/L, temperature = 60°C, time = 6 h).

ing AM, CAN, Temperature, Reaction time and KG respectively. This result present the optimum grafting conditions required for the graft copolymerization of AM onto KG and hence economic yield of KG-g-PAAm for use in the graft membrane.

REFERENCES

- Aliyu B (2002). The nutrients content of dry *Maesopsis eminii* (Konkoli) and *Citriscius linatus*(Guna). PGD Thesis, Abubakar Tafawa Balewa University, Bauchi, Nigeria, pp. 1-2.
- Barminas JT, Eromosele IC (2002). Rheological properties and potential industrial application of konkoli (*Maesopsis eminii*) seed gum. In Williams PA, Philips EO (Eds), gum and stability for the food industry. Royal Soc. Chem., UK. pp. 306-311.
- Barminas JT, Ajayi JO, Osemeahon SA (2005). Development of sodium alginate and konkoli gum-grafted-polyacrylamide blend membrane. Science forum J. Pure Appl. Sci. 8: 70-79.
- Eromosele IC (1991). Effect of Acitic acid on Polymerization of Butylcyanoacrylate by Tetrabutylammonium acetate in Tetrahydrofuran. J. Macromol. Sci. Chem., A28(3 and 4): 347-358.
- Eromosele IC, Hamagadu TJ (1993). Graft Copolymerization of Methylacrylate onto Caesarweed Fibers by the Potassium Permanganate-Toluene Redox system.
- Eromosele IC (1994). Graft copolymer of acrylonitrile onto cotton cellulose by potassium permanganateThioacetamide redox system. J. Appl. Polym. Sci., 51: 1817-1827.
- Hegazy EA, Kamal N, Kalifa NA, Mahmoud GA (2001). Separation and extraction of some heavy and toxic metal ions from their waste by grafted membranes. J. Appl. Polym. Sci., 81: 849-860.
- Hennik WE, Van Nostrum CF (2002). Novel crosslinking methods to design hydrogels. Adv. Drug Deliv. Rev., 54: 13-36.
- Hoffman AS (2002). Hydrogel for medical applications. Adv. Drug Deliv. Rev., 43: 3-12.
- Lee W, Lin G (2000). Supersorbent polymeric materials VIII. Swelling behaviour of cross linked poly (acrylate-co-tri-methyl methacrylo-ethyl ammonium iodide) in aqueous salt solutions. J. Appl. Polym. Sci., 81: 552-560.
- Niu H, Volesky B (2000). Gold cyanide biosorption with L-cysteine. J. Chem. Technol. Biotechnol, 75: 436-442.
- Osemeahon SA (2003). Sorption of metal ions in aqueous solution by grafted membranes, M. Tech. Thesis, Federal University of Technology, Yola Nigeria.

- Sartore L, Penco M, Bignotti F, Peroni I, Gil MH, Lee W, Lin G (2002). Supersorbent polymeric materials VIII. Swelling behaviour of Ramos, MA Damore A (2002). Grafting of selected presynthesized macromonomers onto various dispersion of silica particles. *J. Appl. Polym. Sci.* 85: 1287-1296.
- Toti SU, Aminabhavi (2002). Pervaporation separation of water-isopropyl alcohol mixtures with blend membranes of sodium alginate and poly(acrylamide)-grafted-Guar gum. *J. Appl. Polym. Sci.*, 85: 2014-2024.
- Toti SU, Mahadevappa Y, Kumaresk K, Soppimath TM, Aminabhavi (2002). Sorption, diffusion and pervaporation separation of water-acetic acid mixture through the blend membranes of sodium alginate and guar gum-graft poly(acrylamide). *J. Appl. Sci.*, 88: 259-277.
- Tripathy T, Singh PR (2001). Characterization of polyacrylamide-grafted sodium alginate. A novel polymeric flocculants. *J. Appl. Polym. Sci.*, 81: 3296-3308.