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Graft Copolymerization of Acrylamide and Methylmethacrylate onto Cellulose Fibres: Influence of Initiator in Gel Formation

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ABSTRACT

Acrylamide and methylmethacrylate monomers were grafted onto bleached cellulosic fibres using $K_2S_2O_8$ and a redox system of $K_2S_2O_8$ - $Na_2S_2O_5$ as initiators at room temperature while varying time, monomer concentration and concentration of initiator. The study have shown that percentage grafting increases as the concentration of monomers, concentration of initiators and graft time were increased. The study also confirms the selectivity of initiators for monomers. For example, using $K_2S_2O_8$ as initiator, acrylamide attained a maximum percentage graft of 42.4% at 7.4×10^{-2} mol dm^{-3} initiator concentration; further increase in initiator concentration lead to the formation of a gel. On the other hand, the maximum percent graft for methylmethacrylate using the same initiator was 29.8% at initiator concentration of 14.8×10^{-2} mol dm^{-3} . Similarly, using a redox system of $K_2S_2O_8$ - $Na_2S_2O_5$, acrylamide attained a maximum percentage graft of 23.7% at the maximum concentration of initiator tested while methylmethacrylate attained a maximum percentage graft of 70.2% at the same initiator concentration.

Key words: Cellulose, grafting, acrylamide, methylmethacrylate, gel formation

INTRODUCTION

Grafting of polar water soluble vinyl monomers onto the surface of hydrocarbon polymers can impart new properties to the material. According to Salam (2005), chemical modification of vinyl monomers onto jute and cotton fibres have received considerable interest in recent years. According to the report, certain unfavorable textile properties such as high stiffness, very low elasticity and susceptibility toward sunlight have tremendously limited their use. Grafting of vinyl monomers onto cellulosic fibres is an attempt at minimizing this undesirability and hence to enhance their effectiveness for intensified textile use. For example, grafting of acrylonitrile onto jute fibres gave a fibre with improved extensibility and light fastness; also grafting of hydrophobic styrene monomer onto cotton fibres yielded a graft copolymer of improved resistance to wetting (Trived and Mehta, 1973).

Graft copolymerization of vinyl monomers has been attempted during recent years using chemical initiators (Ogiwara and Kubota, 1973; Eromosele, 1994a, b; Eromosele and Ahmed, 1996; Nwufu and Ishaku, 2000a, b; Eromosele and Solomon, 2000; Aminu and Nwufu, 2004).

Among the methods of initiation, chemical method of initiation of grafting involving oxidizing agents such as $KMnO_4$, $Na_2S_2O_3$, $K_2S_2O_8$ and $KHSO_5$ are promising from the economic point of view and are quite selective in nature.

The present report highlights the graft copolymerization of acrylamide (AA) and methylmethacrylate (MMA) monomers onto bleached cellulose fibres using $K_2S_2O_8$ and $K_2S_2O_8/Na_2S_2O_5$ system as initiators. The effect of monomer concentration, time and initiator on percentage graft as well as the role of initiator in the formation of gel during grafting is reported.

MATERIALS AND METHODS

The stem of *Dracaena arborea* used for this work was pulped at the Federal Institute of Industrial Research, Oshodi (FIIRO), Lagos, Nigeria. Acrylamide, methylmethacrylate (MMA) and $Na_2S_2O_5$ were supplied by BDH Ltd while $K_2S_2O_8$ was supplied by M and B.

Pulp bleaching: Twenty gram of the pulp fibre was bleached by soaking completely in 6% hydrogen peroxide and heated for 1 h before transferring into distilled water and washed thoroughly. The fibre was thereafter soaked in 0.5 mol dm^{-3} NaOH for 30 min to remove residual lignin. It was then washed in distilled water and dried to a constant weight.

Experimental

Effect of monomer concentration: The effect of monomer concentration was studied in 250 cm^3 pyrex conical flask. One gram of the dried fibre was allowed to soak in 50 mL of distilled water for 30 min after, which various concentrations of monomer (acrylamide or methylmethacrylate) ranging from $0.28\text{-}0.70 \text{ mol dm}^{-3}$ were separately added to each flask. A constant initiator of $0.037 \text{ mol dm}^{-3}$ was used in the case of $K_2S_2O_8$ and $0.045 \text{ mol dm}^{-3}$ in the case of $K_2S_2O_8\text{-}Na_2S_2O_5$ redox system for a time of 2 h. The resultant grafted fibre was filtered and dried to a constant weight and the percent graft determined by mass balance.

Effect of time: In time studies, the fibre weight was maintained at 1 g, the concentrations of initiators were kept constant at $0.037 \text{ mol dm}^{-3}$ for $K_2S_2O_8$ and $0.045 \text{ mol dm}^{-3}$ for $K_2S_2O_8\text{-}Na_2S_2O_5$, while, the concentration of acrylamide and methylmethacrylate were kept at 0.7 mol dm^{-3} . The reaction time was kept at 60-240 min.

Effect of initiator concentration: In studying the effect of initiator concentration, all other factors were kept constant for example, time was 2 h, monomer concentrations were 0.7 mol dm^{-3} for acrylamide (AA) and methylmethacrylate (MMA), respectively. The concentration of $K_2S_2O_8$ ranged between $0.037\text{-}0.148 \text{ mol dm}^{-3}$ while that of $K_2S_2O_8\text{-}Na_2S_2O_5$ redox system ranged from $0.045\text{-}0.159 \text{ mol dm}^{-3}$ at a 1:1 ratio.

In all cases, percentage graft and graft efficiency were calculated as:

$$\text{Graft (\%)} = \frac{W_2 - W_1}{W_1}$$

While:

$$\text{Grafting efficiency} = \frac{W_2 - W_1}{W_3}$$

Where:

W_1 = Initial weight of dry fibre

W_2 = Dry weight of grafted fibre

W_3 = Concentration of monomer used

RESULTS AND DISCUSSION

Effect of increase in monomer concentration: The studies have shown that as the concentration of monomers increases, the graft yield and efficiency also increased. This agrees with the findings reported by Nwufo and Ishiaku (2000a) as well as that of Ghosh and Dev (1996). This can be explained by the fact that as the concentration of monomers increases, more and more of the monomers become available for attachment to the initiated backbone hence the steady increase in percentage graft. This is supported by the polymer equation ($r_p = K_p [M](2fk_d[I]/kt)^{1/2}$), which states that the rate of propagation is proportional to the monomer concentration. For acrylamide (AA), percentage graft increased from 5.3-12.4 when $K_2S_2O_8$ was used as the initiator and from 8.2-17.4 when a redox system of $Na_2S_2O_5$ - $K_2S_2O_8$ was used. On the other hand, methylmethacrylate (MMA) had the highest percentage graft of 17.4% when $K_2S_2O_8$ was used as initiator and 58.3% when $Na_2S_2O_5$ - $K_2S_2O_8$ was used as initiator. This result clearly shows a higher percentage graft when redox system is used than when a single initiator is used. This increase in percentage graft with redox system can be attributed to a multiple initiation of the cellulose which can either take place at the oxygen or at the carbon. This view is supported by Okieimen and Uroghide (1990) as well as Samal *et al.* (1987). The results are shown in Fig. 1 and 2, respectively.

Effect of increasing time on percentage graft: For both the acrylamide and methylmethacrylate, the percentage graft and graft efficiency increased with increase in time. This is due to increase in grafting sites with time as well as favorable reaction environment such as

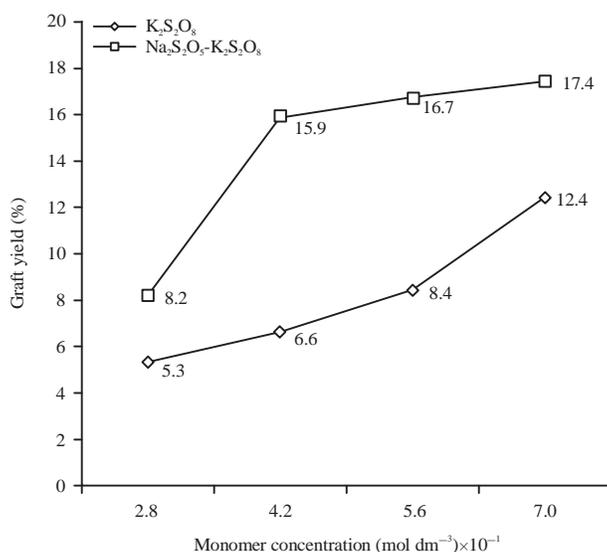


Fig. 1: Effect of concentration of acrylamide monomer on the graft yield using $K_2S_2O_8$ and $K_2S_2O_8/Na_2S_2O_5$ initiators

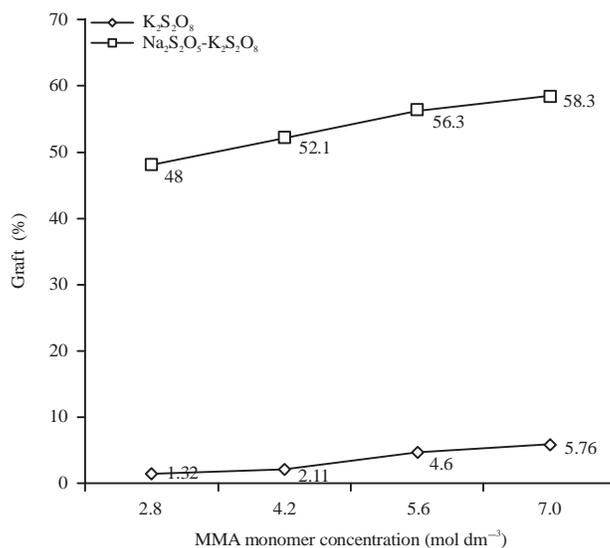


Fig. 2: Effect of concentration of methylmethacrylate (MMA) monomers on the graft yield using K₂S₂O₈ and K₂S₂O₈/Na₂S₂O₅ initiators

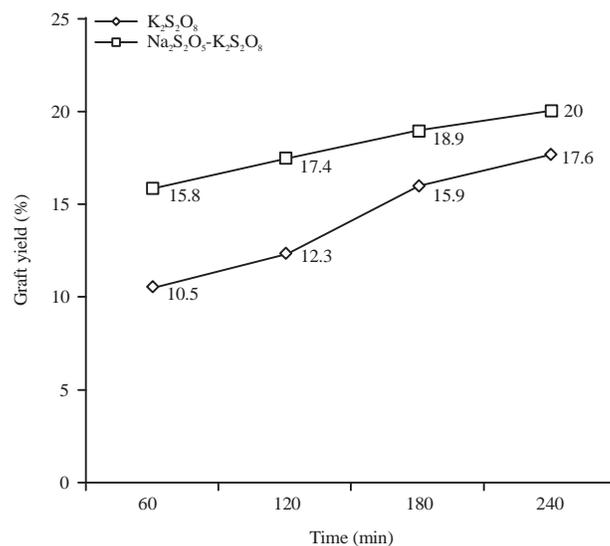


Fig. 3: Effect of time on the graft yield of 0.7 mol dm⁻³ acrylamide using K₂S₂O₈ and K₂S₂O₈/Na₂S₂O₅ initiators

viscosity and monomer solubility that allows the monomer molecules to reach the grafting sites on the cellulose. The MMA attains a maximum percentage graft of 62.7 with Na₂S₂O₅-K₂S₂O₈ and 13.1 when K₂S₂O₈ is used as initiator. On the other hand, AA attains its maximum percentage graft of 20.0 with the redox initiator and 17.6 with the single initiator. According to Liu *et al.* (1993) and Kantouch *et al.* (1972), a reduction in percentage graft and graft efficiency is bound to occur when the monomer and initiator concentration starts decreasing with time. These findings are shown in Fig. 3 and 4, respectively.

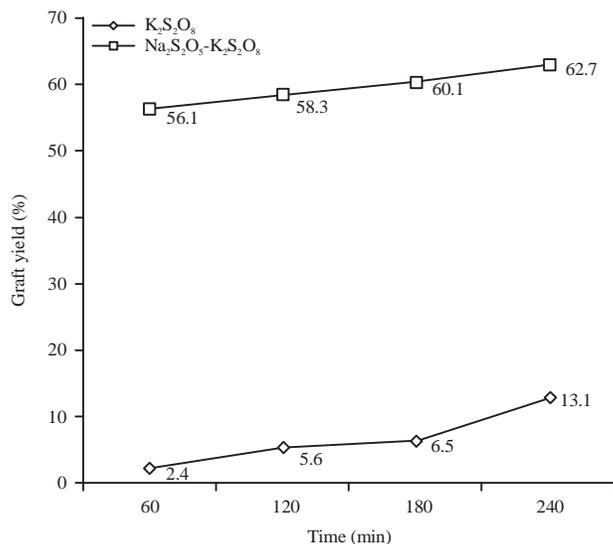


Fig. 4: Effect of time on the graft yield of 0.7 mol dm^{-3} MMA using $K_2S_2O_8$ and $K_2S_2O_8/Na_2S_2O_5$ initiators

Effect of type and concentration of initiator: From the studies, when the concentration of initiators were held constant while varying other factors, there was a remarkable improvement in the percentage graft when redox system of $Na_2S_2O_5-K_2S_2O_8$ was used compared to the single $K_2S_2O_8$ initiator. For instance, using the single initiator a maximum percentage graft of 12.4% was attained while the redox system attained 17.4% on acrylamide, while these values with respect to MMA were 5.76 and 58.3%, respectively. Researches have opined that the increase in percentage graft when redox system is used as initiator is due to multiple initiation by the redox system compared to the single initiator hence the improved grafting brought about by several available sites for attachment of monomers (Eromosele, 1994a; Eromosele and Ahmed, 1996; Shukla and Sharma, 1987). According to Misra *et al.* (1987), for hydroxyl fitted polymers such as cellulose, initiation can occur at the oxygen and at the carbon. The result also shows that the redox initiator had a stronger affinity or selectivity for MMA than AA given the higher yields recorded with respect to MMA than AA.

When other factors were held constant while varying the concentration of initiators, AA attains its maximum graft yield of 42.4% with the single initiator and could only attain a maximum yield of 23.7% with the redox system. Further increase in the concentration of the $K_2S_2O_8$ initiator leads to the formation of a gel at an initiator concentration of $0.110 \text{ mol dm}^{-3}$ with a monomer concentration of 0.7 mol dm^{-3} . Further increase in initiator concentration lead to formation of more gel confirming that the gel formation is dependent on initiator/monomer ratio. On the hand, the redox system did not form gel even at the highest concentration tested. According to Liu *et al.* (1993), sufficiently high cross link concentrations may lead to the formation of an infinite network known as a gel in which networks of chains are of unlimited extent such that all chains linked into one molecule. With MMA, the maximum graft yield obtained with single initiator was 29.8% while the value for the redox system was 70.2% with no gel formed. These findings are shown in Fig. 5 and 6.

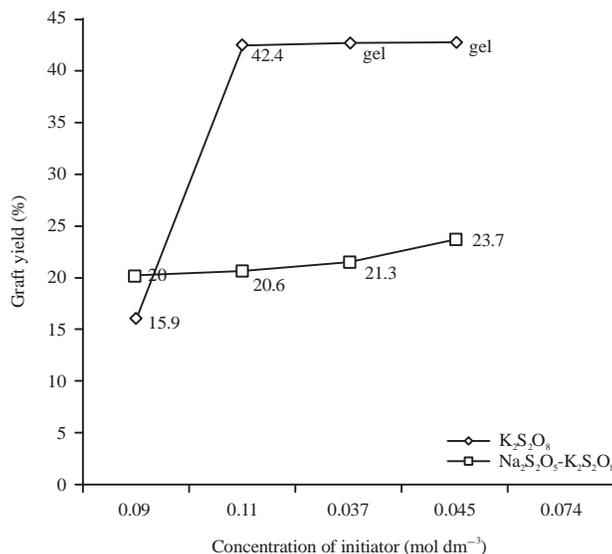


Fig. 5: Effect of initiator concentrations ($K_2S_2O_8$ and $K_2S_2O_8/Na_2S_2O_5$) on the graft yield of acrylamide

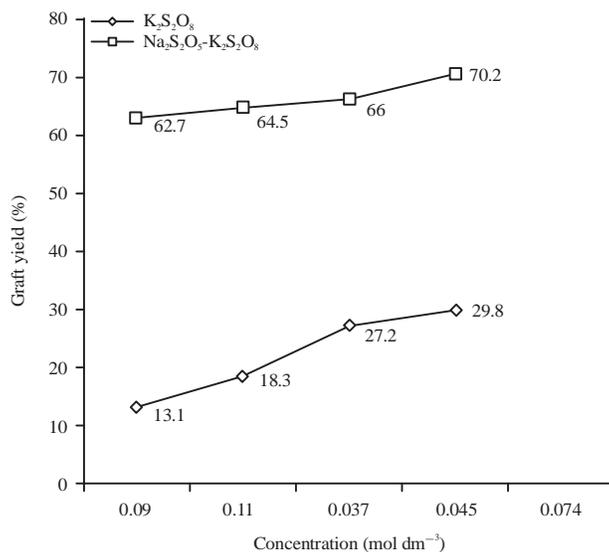


Fig. 6: Effect of initiator concentrations ($K_2S_2O_8$ and $K_2S_2O_8/Na_2S_2O_5$) on the graft yield of MMA

CONCLUSION

The studies have confirmed the selectivity of initiators for monomers in graft copolymerization. While, $K_2S_2O_8$ performed well for AA leading to the formation of gel at higher ratio of initiator to monomer, a redox system of $Na_2S_2O_5$ - $K_2S_2O_8$ had a higher affinity and therefore positively selective towards MMA in all parameters tested. The findings could serve in the selection of initiators in graft polymerization.

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