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Electroinitiated Graft Copolymerization of Acrylic Monomer onto the Natural Fibre

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ABSTRACT

The electroinitiated graft copolymerization of acrylamide onto natural fibre, muga silk in the solution of NH_4NO_3 and H_2O_2 in N, N- dimethylformamide was carried out using copper electrodes. The extent of grafting depends upon the impressed current level, reaction time, monomer concentration and H_2O_2 concentration. The mechanism of grafting copolymerization is suggested and the kinetics of the reaction is derived.

Keywords: *Muga Silk, Acrylamide, Grafting, Electoinitiated Polymerization.*

Introduction

The graft copolmerization from natural fibres, such as cotton, silk and wool, may Change their physico-chemical properties [1,2]. However, graft copolymerization by the electrochemical techniques appears to be scanty in the literature [3,4]. Previously, the Fe(II)/ H_2O_2 redox system was used for preparation graft copolymers onto natural fibres. Present work describes the formation of graft copolymers from muga silk with acrylamide in the system consisting of H_2O_2 and Cu-electrodes as in previous work [5].

Experimental Methods

Materials

N, N-dimethylformamide (DMF) was purified by fractional distillation. Acrylamide (AA), $NaNO_3$, and H_2O_2 were of analytical grade and used without further purification.

Polymerization Methods

A solution of known quantities of AA, NH_4NO_3 and H_2O_2 was prepared in DMF. The solution was taken into an H- type fritted electrolytic cell which accommodates the copper electrodes (area: $0.82 \times 2.6\ cm^2$). The known quantity of muga- silk was wounded around the anode and the solution was kept for 24 hours at 25°C without supplying any current. No increase in weight of the fibre was noticed after drying. On the other hand, when current was passed through the freshly prepared solution the increased in weight of the silk fibers was observed indicating the formation of graft copolymers. Knowing the constant dry weight of the original fibre sample (M1), dry weight of the grafted (M2) and weight of homopolymers (M3), the add- on (in %), grafting ratio and grafting efficiency, were calculated [6-7].

Add on (in %) = $\frac{M2-M1}{M2} \times 100$

Grafting Ratio = $\frac{M2-M1}{M1} \times 100$

Grafting Efficiency, % = $\frac{M2-M1}{[M2-M1]\times M3} \times 100$

Results and Discussion

During electrolysis, the graft copolymerization was observed in the anode compartment. The effect of current density, reaction time, monomer concentration and H_2O_2 concentration on the add-on percentage, grafting ratio and grafting efficiency were investigated to get the optimum conditions for grafting. The effect of the current density on the add-on percentage is shown in table 1. It is evident that add-on percentage increases with impressed currents and finally becomes more or less constant.

Table 1

Effect of current on Grafting Ratio and Grafting Efficiency in the anodic Grafting on silk (1.0 g) with Acrylamide (AA) (2.82 mol. $L^{-1)}$ in dimethylformamide (DMF) Solution of NH_4NO_3 (0.30 mol. L^{-1}) at Cu- electrodes. H_2O_2 concentration = 4.16×10^{-3} mol. L^{-1}; Electrolysis time=120 min. Anolyte vol.= 12.5 mL at 25°C.

Current (mA)	Weight of Grafted Fibres (g)	Increase in Weight (g)	Weight of Ungrafted Poly (AA) (g)	Grafting Ratio (%)	Grafting Efficiency (%)
10	1.187	0.187	1.087	18.7	17.2
15	1.290	0.290	1.090	29.0	21.0
20	1.365	0.365	1.125	36.5	24.5
25	1.408	0.408	1.224	40.8	25.0
30	1.428	0.428	1.244	42.8	25.6
40	1.443	0.443	1.280	44.3	25.7

The variations of add-on percentage with polymerization time is shown in **figure 1** which shows that at constant current of 30 mA and at constant H_2O_2 concentration ($4.16\times 10^{-3\ \text{mol.}}$ L^{-1}), the add-on percentage increases with time, tending to level off at longer durations of polymerization.

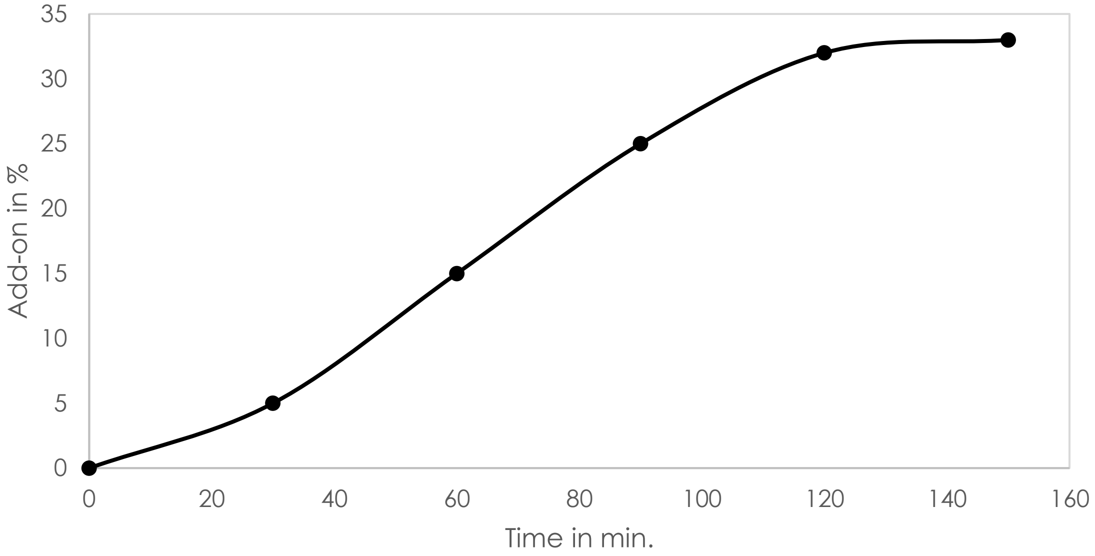

Figure 1. Dependence of add-on percentage on the time of electrolysis in the anodic grafting of silk fibres (1.0 g) in the solution of AA (2.80 mol. L^{-1}) in DMF solutions of NH_4NO_3 (0.30 mol. L^{-1}) and H_2O_2 (4.16× $10^{-3\ mol.}$ L^{-1}), at Cu-electrodes at 25°C. Anolyte vol.= 12.5 mL at 25°C The effect of the monomer concentration on the add-on percentage is shown in figure 2. It is clear that an increase in the concentration of AA causes an enhancement in the add-on percentage.

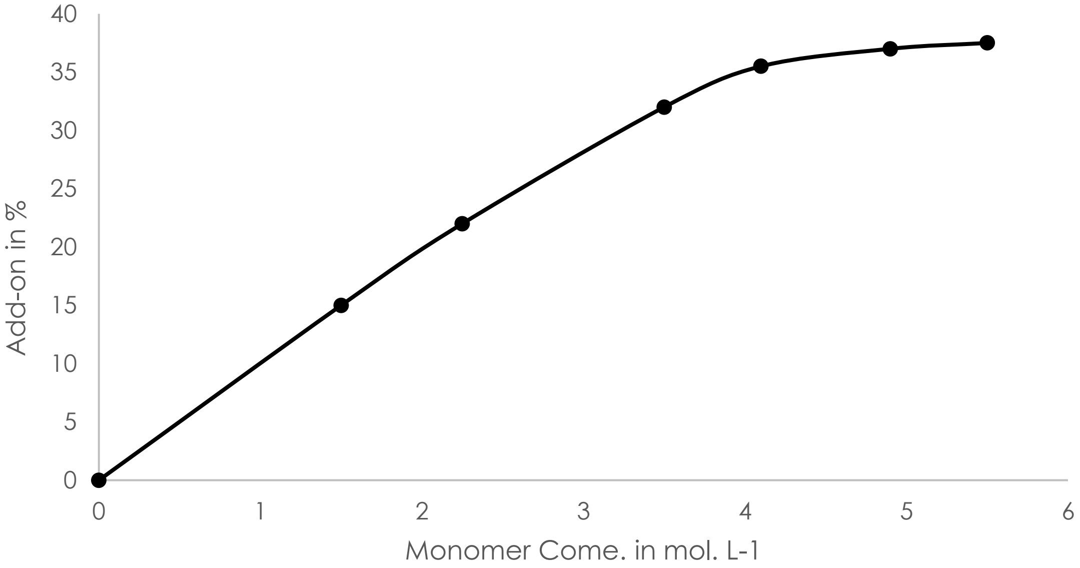

Figure 2. Dependence of add-on percentage on monomer concentration in the anodic grafting of silk fibres (1.0 g) in the solution of NH_4NO_3 (0.30 mol. $L^{-1)}$, and H_2O_2 (4.16× $10^{-3\ mol.}$ L^{-1}at Cu- electrodes. Current =30mA; Electrolysis time=120 min.; Anolyte vol. = 12.5mL at 25°C.

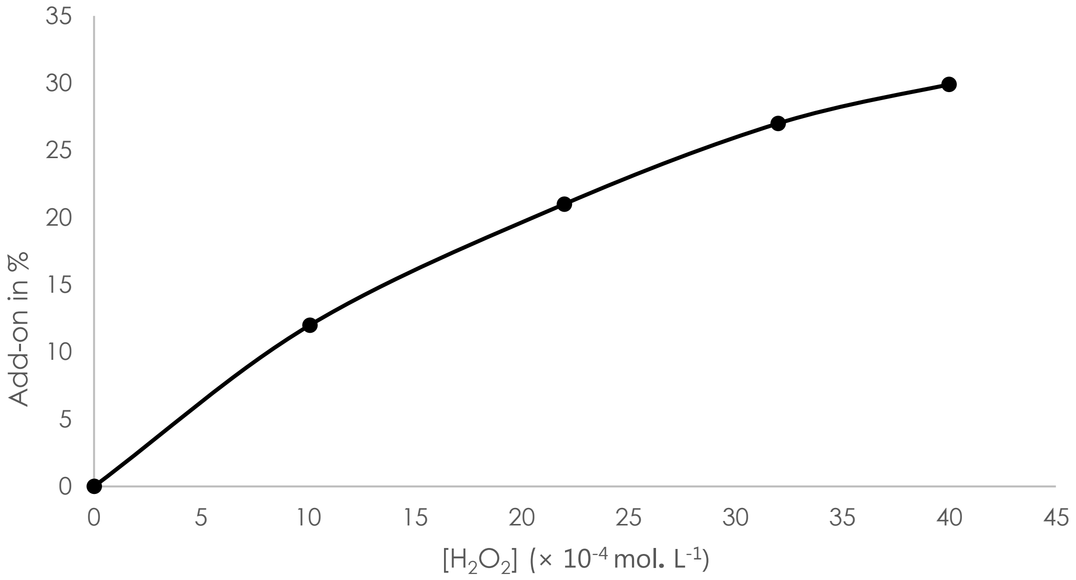

Figure 3. Effect of H_2O_2 concentration add-on percentage in the anodic grafting of silk fibres (1.0 g) with AA (2.82 mol. L^{-1}) in DMF solutions of NH_4NO_3 (0.30 mol. L^{-1}) at Cu-electrodes at 30 mA. Electrolysis time=120 min.; Anolyte vol.= 12.5 mL at 25°C.

Figure 3 shows the effect of H_2O_2 concentration on the add-on percentage at 25°C. It is evident that add-on percentage also increases with increase in concentration of H_2O_2.

Mechanism and Kinetics

The mechanism of electroinitiated grafting of AA onto the silk fibres is based on the generation of Cu^+ ions sacrificial dissolution of Cu anode [3], Cu^+ ions generated in the situ, reacts with H_2O_2 present in the anolyte to yield a hydroxyl radical, which reacts with silk to produce active centres in it. The following reaction schemes are suggested for the electroinitiated grafting [5].

$Cu \rightarrow Cu^+ + e^-$

$Cu^+ + H_2O_2 \rightarrow Cu^{2+} + OH^- + OH\cdot$

$S\text{-}OH + OH^- \rightarrow S\text{-}O\cdot + H_2O$

$S\text{-}O\cdot + M \rightarrow SOM\cdot$ (initiation)
(K_i)

$SOM\cdot + M \rightarrow SOMM\cdot$
(K_p)

$SOM\cdot + nM \rightarrow SOM_{n+2}M\cdot$
(K_t)

$SOMM^{\bullet} + nM \rightarrow$ graft copolymer

$SOM_{n1}M^{\bullet} + SOM_{n2}M^{\bullet} \rightarrow SOM_{n1+n2+2}$ or graft copolymer (Termination)

Here, K_{i}, K_p and k_t are the rate constants of the respective steps.

The rate of initiation of chain radicals may be given as

$$R_i = K_i\,[SO^{\bullet}]\,[M] = k_i \cdot \frac{I}{FV} \qquad \text{(i)}$$

The rate of propagation is given as

$$\frac{-d[M]}{dt} = R_p = K_p\,[SOM^{\bullet}]\,[M] \qquad \text{(ii)}$$

The rate of termination is given as

$$\frac{-d[M^{\bullet}]}{dt} = R_i = 2K_t\,[SOM^{\bullet}]^2 \qquad \text{(iii)}$$

$$\text{Or, } [SOM^{\bullet}] = \left(\frac{ki}{2kt} \cdot \frac{1}{FV}\right)^{1/2} \qquad \text{(iv)}$$

From equation (ii),

$$[SOM^{\bullet}] = \frac{Rp}{2Kp[M]}$$

Substituting this value in equation (iv)

$$\frac{Rp}{2Kp[M]} = \left(\frac{Ki}{2Kt} \bullet \frac{I}{FV}\right)^{1/2}$$

$$\text{So, } R_p = Kp \bullet \left(\frac{Ki}{Kt}\right)^{1/2} \left(\frac{I}{2FV}\right)^{1/2} [M]$$

Thus, the rate of graft copolymerization is proportional to the square root of current impressed in ampere and first power of monomer concentration.

Conclusion

The physio-chemical properties of such grafted fibre may change. Therefore, the moisture absorption capacity, tensile strength, torsional torque etc. of such grafted fibres may be change as per our desire.

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