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## Grafting of Methacrylamide onto Cotton Yarn Part I: Tensile Strength

Kh. M. Mostafa

Department of Textile, National Institute for Standards, El-Haram,  
P.O. Box 136 Giza, El-Giza, Egypt

**Abstract:** Methacrylamide (MAam) as a reactive monomer was directly grafted onto cotton yarns using a  $\text{KMnO}_4$ - $\text{HNO}_3$  redox system by chemical initiation technique. The major factors affecting polymerization of MAam, such as  $\text{KMnO}_4$ , nitric acid and MAam concentration as well as the reaction time (duration) and temperature of the polymerization were studied. This was done to establish the optimum conditions of grafting. It was found from the results that the graft yield is higher under the following conditions: using 0.07 N potassium permanganate as initiator, 80 meq  $\text{L}^{-1}$ , nitric acid; 1 g, methacrylamide, reaction time, 60 min and polymerization temperature, 60°C, when using a material to liquor ratio of 1:50. On the other hand, the tensile strength of poly (MAam)-cotton yarn grafts copolymer having 18.55% graft yield exhibits a higher value than ungrafted cotton yarn. While, increasing the graft yields over 18.55% lead to a decrease in tensile strength of the grafted yarn.

**Key words:** Cotton yarns, MAam, grafting, tensile strength

### INTRODUCTION

There has been considerable interest in recent years in the development of carbohydrate polymers with the capacity of creating effective functional groups for potential end use. A number of such materials have been prepared by grafting different vinyl monomers onto starch<sup>[1-7]</sup> and cellulose<sup>[8-14]</sup>. Of the chemical initiators used for the synthesis, the Mn (IV) ion in the presence of an activator has proved to be an efficient initiator<sup>[1,2]</sup>. The present study was undertaken with a view to develop improved conditions for vinyl graft co polymerization onto cotton yarns as well as studying the tensile strength of cotton yarn before and after grafting with respect to an increase in the initiator concentration in absence and presence of monomer. The up to date literature survey shows that it has been a very little work done on grafting on cotton yarns to examine such property<sup>[15,16]</sup>.

### MATERIALS AND METHODS

Cotton yarns (kindly supplied by Misr Company for Spinning and weaving, El-Mehala El-Kobra). Potassium permanganate, nitric acid, methacrylamide, sodium carbonate, ethanol and nonionic wetting agent were of pure grade chemicals.

### Treatment of cotton yarn with Potassium Permanganate:

Two grams of cotton yarn was immersed for 30 min at 50°C in 100 mL  $\text{KMnO}_4$  solution (0.01- 0.15 N) in a conical flask with a continuous shaking to ensure the homogeneity of  $\text{MnO}_2$  deposition all over the cotton yarn. After this treatment the yarn was thoroughly washed with distilled water several times to remove excess  $\text{KMnO}_4$  solution. It was then squeezed between two filter papers before being introduced into the polymerization solution.

### Graft polymerization procedure:

The graft polymerization reaction was carried out as follows: The potassium permanganate treated samples was introduced into a reaction flask containing different concentrations of nitric acid (10-150 meq  $\text{L}^{-1}$ ) and methacrylamide (0.5-3 g based on weight of substrate). A material to liquor ratio of 1:50 was used. The flask content was kept in a thermostatic water bath at different temperatures (30-80°C) for different durations (10-90 min). Nitrogen gas was purged into the reaction mixture to avoid the presence of oxygen and the flask content was shaken immediately and occasionally during the reaction. After the desired reaction time, the sample was removed and washed with cold water several times. The sample was then squeezed and dried in an electric oven at 105°C for 2 h and cooled over  $\text{P}_2\text{O}_5$  in desiccators. It was found experimentally

that, washing grafted cotton yarn with cold water 4-6 times is quite enough to remove the homopolymer (poly methacrylamide). Estimating the nitrogen% by a well-known Kjeldahal method of the grafted sample after each wash till constant nitrogen% evidences.

**Determination of MnO<sub>2</sub> quantity onto cotton yarn:** The amount of MnO<sub>2</sub> deposited onto cotton yarn was determined by adding 10 mL 0.1 N oxalic acid and 10 mL 2 N sulphuric acid to the cotton yarn treated with permanganate in a conical flask. The mixture was gently heated to about 60°C and then titrated against a KMnO<sub>4</sub> solution of 0.01 N.

$$V \cdot 0.1 \cdot 100$$

The amount of MnO<sub>2</sub> deposited =  $\frac{\text{-----}}{W}$  meq/100 g sample

Where, V is the volume of KMnO<sub>4</sub> equivalent to the MnO<sub>2</sub> in the sample and W is the weight of the sample used.

**Estimation of the graft yield:** Graft yield of poly (MAam)-cotton yarn graft copolymer was estimated by measuring the nitrogen% by Kjeldahal method<sup>[17]</sup> and was determined as follows:

$$\text{Graft Yield (\%)} = (\text{Nitrogen\%} \times 6.07)$$

**Testing**

**Tensile strength:** It was measured according to ASTM procedure D-2256-66T.

**N.B.:** Tensile strength was measured three times for each sample and their standard deviation was calculated.

**RESULTS AND DISCUSSION**

Effect of potassium permanganate concentration on the amount of MnO<sub>2</sub> Deposited Cotton yarn was treated with different concentrations (0.01-0.15 N) of KMnO<sub>4</sub> solution as described in the Experimental section. The cotton samples treated with KMnO<sub>4</sub> were monitored for MnO<sub>2</sub> deposited over them.

Figure 1 shows the relation between the amount of MnO<sub>2</sub> deposited onto the cotton yarn sample and the KMnO<sub>4</sub> concentration. The data shows that the MnO<sub>2</sub> deposit increases by increasing the KMnO<sub>4</sub> concentration up to 0.07 N. Above this concentration no marked increase was observed and the amount of MnO<sub>2</sub> deposited is almost the same over a range of KMnO<sub>4</sub> concentration of 0.1-0.15 N.

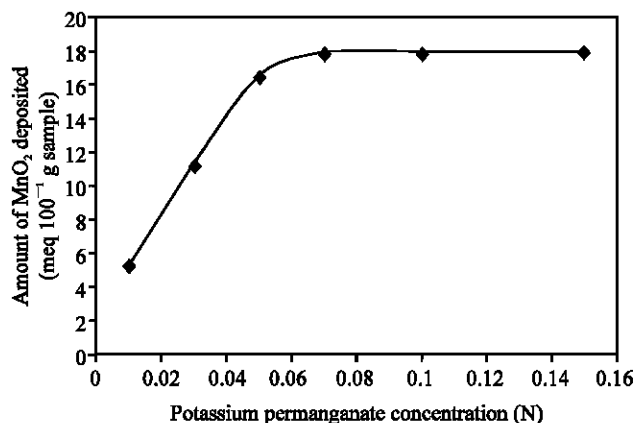


Fig. 1: Effect of potassium permanganate concentrations on the amount of MnO<sub>2</sub> deposited onto cotton yarns, Reaction conditions: Cotton yarn, 2 g; Treatment time, 30 min; treatment temperature, 50°C; nonionic wetting agent, 0.1%; material to liquor ratio, 1:50

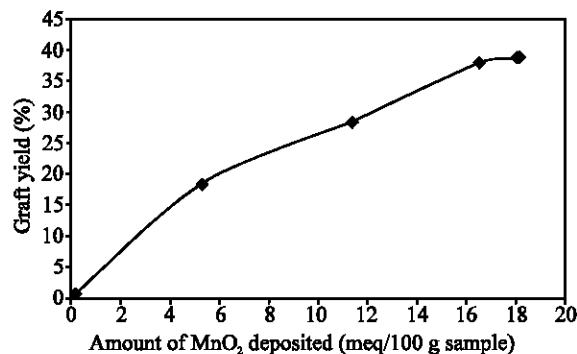
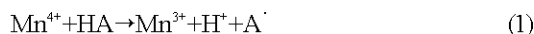


Fig. 2: Graft yield of poly (MAam)-cotton yarn graft copolymer as a function of the amount of MnO<sub>2</sub> deposited, Reaction conditions: Cotton yarn, 2 g; Methacrylamide, 1 g; HNO<sub>3</sub>, 80 meq L<sup>-1</sup>; Time, 60 min; Temperature, 60°C; material to liquor ratio, 1:50

It is logical to assume that MnO<sub>2</sub> particles are deposited uniformly all over the cotton cellulose and are located at certain sites, most probably at the hydroxyl group of cotton cellulose. Once the accessible hydroxyl groups are occupied by MnO<sub>2</sub> particles, extra deposition of MnO<sub>2</sub> will be difficult and, if deposited, the particles will be easily removed during washing. This would explain why the amount of MnO<sub>2</sub> deposited onto the cotton sample remains constant at higher concentrations of KMnO<sub>4</sub>, especially above 0.07 N.

**Tentative mechanism of grafting:** Cotton yarn was turned to a brownish, dark brownish or even black color when it

was treated with  $\text{KMnO}_4$  solution, depending on the concentration of the  $\text{KMnO}_4$  solution used as described above. In the presence of an acid used  $\text{HNO}_3$  (HR), primary radical species formation occurs as a result of the action of an acid on the  $\text{MnO}_2$  deposited as follows:

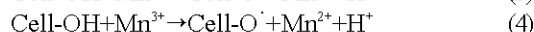
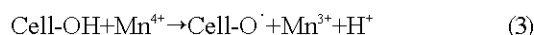


Once the free radical species ( $\text{A}^{\cdot}$ ) are formed, they produce cellulose macroradicals via direct abstraction of hydrogen atom from cellulose molecules. This reaction may be represented as follows:

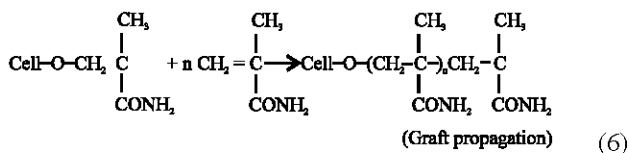
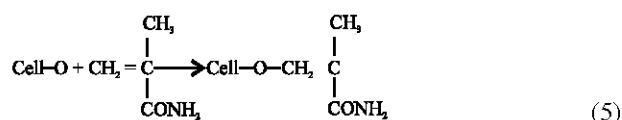


Where,  $\text{Cell-OH}$  represents the cotton cellulose molecule.

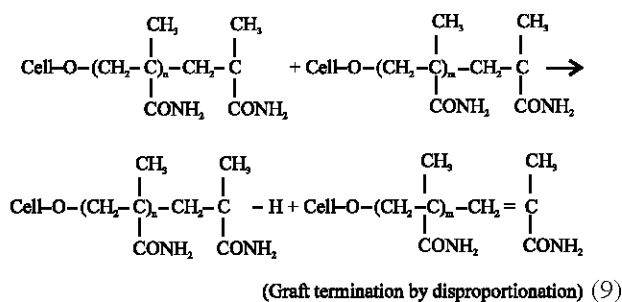
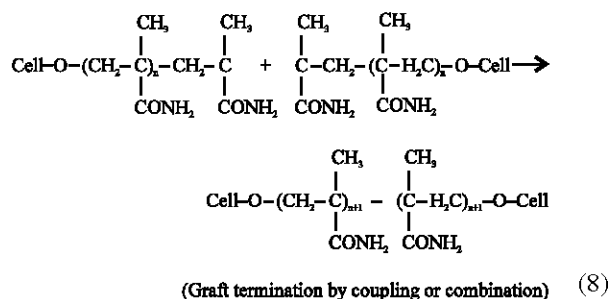
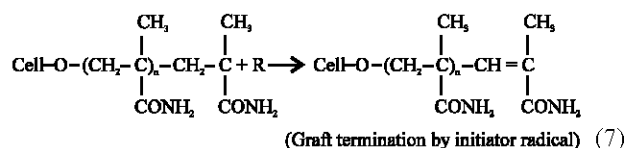
Cotton cellulose macro radicals may also be formed by direct attack of  $\text{Mn}^{4+}$  or  $\text{Mn}^{3+}$  ions on the cellulose molecule via abstraction of the hydrogen atom.



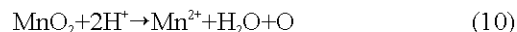
In the presence of a vinyl monomer the cellulose is added to the double bond of the vinyl monomer, resulting in a covalent bond between monomer and cellulose with creation of free radical on the monomer. i.e. a chain is initiated. Subsequent addition of monomer molecules to the initiated chain propagates the grafting reaction onto cellulose as follows:



Finally, termination of the growing grafted chain may occur via reaction with the initiator, coupling or combination and disproportionation as follows:



**Effect of  $\text{MnO}_2$  deposited on the graft yield:** Figure 2 shows the graft yield of poly (MAAm)-cotton graft copolymers versus the amount of  $\text{MnO}_2$  deposited onto cotton yarns. Obviously, the graft yields increases substantially as the  $\text{MnO}_2$  deposit increases until  $\text{MnO}_2$  concentration of 17.91 meq/100 g samples is reached and then remains constant. The enhancement in grafting by increasing the amount of  $\text{MnO}_2$  deposited up to 17.91 meq/100 g samples is due to  $\text{MnO}_2$  and free radical species participate mainly in the creation of cellulose macro radicals, which are capable of initiating grafting. On the other hand, the fact that the graft yield remains constant after 17.91 meq/100 g sample is deposited onto the cotton yarns may be attributed to: (a) a faster termination rate between two chain radicals via bimolecular collision, (b) a lower diffusion rate of monomer from the aqueous phase to the cellulose phase due to the excess amount of  $\text{MnO}_2$  deposited and © a higher oxygen production of inhibiting oxygen at a higher  $\text{MnO}_2$  concentration due to the side reaction represented by the equation shown below:



**Effect of nitric acid concentration:** Figure 3 shows the effect of the nitric acid concentration on the graft yield of poly (MAAm)-cotton yarn graft copolymers. It is clear from the Fig. that increasing nitric acid concentration up to 80 meq  $\text{L}^{-1}$  is accompanied by enhancement in the graft yield. Above this concentration, grafting decreases. The fall in the graft yield could be attributed to (a) the

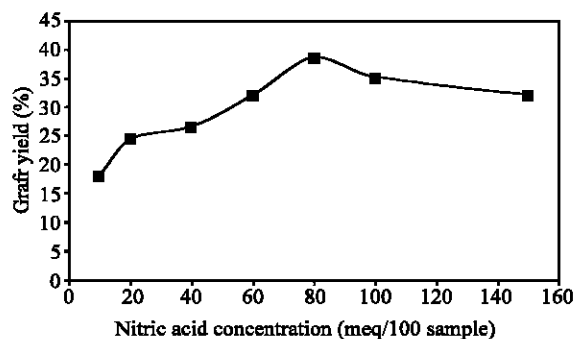


Fig. 3: Effect of changing HNO<sub>3</sub> concentration on the graft yield of poly (MAAm)-cotton yarn graft copolymer, Reaction conditions: Cotton yarn, 2 g; MnO<sub>2</sub>, 17.91 meq/100 g sample; Methacrylamide, 1 g; Time, 60 min; Temperature, 60°C; material to liquor ratio, 1:50

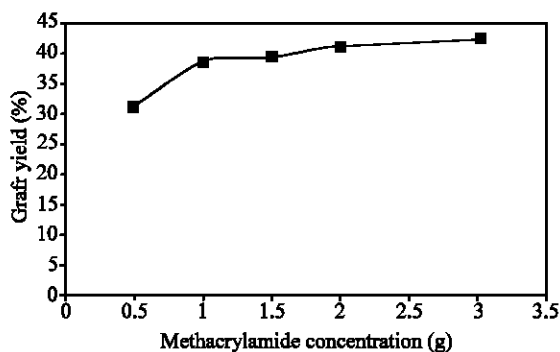


Fig. 4: Effect of changing methacrylamide concentration on the graft yield of poly (MAAm)-cotton yarn graft copolymer, Reaction conditions: Cotton yarn, 2 g; MnO<sub>2</sub>, 17.91 meq/100 g sample; HNO<sub>3</sub>, 80 meq L<sup>-1</sup>; Time, 60 min; Temperature, 60°C; material to liquor ratio, 1:50

coagulation of colloidal homopolymer in the solution and in the fiber structure increases at lower pH. This retards the diffusion of both the monomer and the initiator into the fiber phase and (b) the side reaction as shown before in equation 10 increases at a higher acid concentration. Thus, besides consuming some MnO<sub>2</sub> (required for the production of initiating species), it also leads to a constant production of inhibiting oxygen.

**Effect of monomer concentration:** Figure 4 shows the effect of MAAm concentration on the graft yield of poly (MAAm) -cotton yarn graft copolymers. The MAAm concentration used ranged from (0.5-3 g). It was seen from the Fig. that, as the concentration of MAAm increases, the graft yield also increases. This could have been associated with the higher availability of monomer

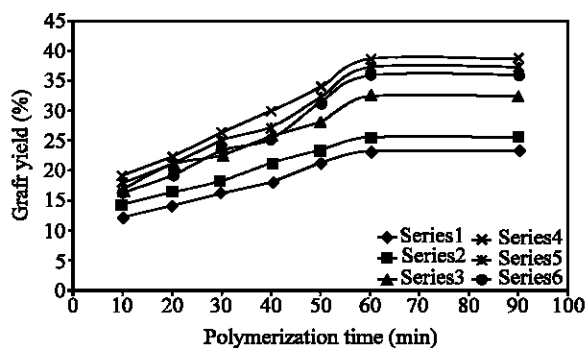


Fig. 5: Effect of changing polymerization time and temperature on the graft yield of poly (MAAm)-cotton yarn graft copolymer, Where, Series 1= 30°C, Series 2= 40°C, Series 3= 50°C, Series 4= 60°C, Series 5= 70°C, Series 6= 80°C, Reaction conditions: Cotton yarn, 2 g; MnO<sub>2</sub>, 17.91 meq/100 g sample; Methacrylamide, 1 g; HNO<sub>3</sub>, 80 meq L<sup>-1</sup>; material to liquor ratio, 1:50

molecules around the cellulose macroradicals. The latter are relatively immobile and for grafting to occur, the monomer molecules need to be in close proximity to the substrate.

**Effect of polymerization time and temperature:** Figure 5 shows the graft yield of poly (MAAm)-cotton yarns graft copolymer as a function of polymerization time at different temperatures. It is clear from the Fig. 5 that, the graft yields exhibiting an initial fast rate, which slows down with time, then levels off. This is observed regardless of the polymerization temperature used. The extent of grafting increases by raising the temperature from 30°-60°C. Increasing the temperature to 70°C and 80°C is accompanied by decreased grafting. The favorable effect of temperature (up to 60°C) on grafting could be ascribed to:

1. Higher diffusion from the aqueous phase to the cellulose phase;
2. Higher rate of initiation and propagation of the graft chain;
3. Greater swell ability of cotton fabric;
4. Better decomposition of the redox system, leading to more free radical species; and
5. Increased the mobility of the methacrylamide molecules.

On the other hand, the decrement in grafting observed at 70° and 80°C is perhaps due to the faster termination rate and greater amount of homopolymer formation at higher temperatures.

Table 1: Effect of changing  $\text{KMnO}_4$  concentration in absence of monomer on the tensile strength of cotton yarn

$\text{KMnO}_4$ conc. (N)	Tensile strength (g)
0	180±2.01
0.01	174±1.95
0.03	168±2.11
0.05	161±1.83
0.07	158±1.55
0.10	157±1.45
0.15	157±2.00

Reaction conditions: Cotton yarn, 2 g; Treatment time, 30 min; treatment temperature, 50°C; nonionic wetting agent, 0.1%; material to liquor ratio, 1:50.

N.B.: Tensile strength was measured three times for each sample and their standard deviation was calculated

Table 2: Effect of changing  $\text{KMnO}_4$  concentration in presence of monomer on the tensile strength of poly (MAAm)-cotton yarn graft copolymers

$\text{KMnO}_4$ conc. (N)	Graft yield (%)	Tensile strength (g)
Zero	Zero	180±2.01
0.01	18.35	189±2.52
0.03	28.40	168±2.11
0.05	37.90	161±1.85
0.07	38.60	158±1.55
0.10	38.60	157±1.41
0.15	38.60	157±1.35

Reaction conditions: Cotton yarn, 2 g; Methacrylamide, 1 g;  $\text{HNO}_3$ , 80 meq  $\text{L}^{-1}$ ; Time, 60 min; Temperature, 60°C; material to liquor ratio, 1:50.

N.B.: Tensile strength was measured three times for each sample and their standard deviation was calculated

It may be further noted that leveling off grafting as the reaction proceed could be associated with depletion in monomer and initiator concentration as the reaction proceeds.

**Tensile strength of cotton yarn before and after grafting:**

The tensile strength of cotton yarn before and after grafting was studied with respect:

1. Changing the  $\text{KMnO}_4$  concentration in absence of monomer.
2. Changing the  $\text{KMnO}_4$  concentrations in presence of monomer i.e. as the grafting proceeds.

N.B.: The tensile strength of cotton yarn before grafting was taken as a reference substrate just for comparison.

**Effect of changing  $\text{KMnO}_4$  concentration in absence of monomer on the tensile strength of cotton yarn:**

Table 1 shows the effect of changing  $\text{KMnO}_4$  concentration on the tensile strength (g) of ungrafted cotton yarn. It is seen Table 1 that, increasing the initiator concentration from 0.01-0.15 N without any monomer present in the reaction leads to a decrease in tensile strength of cotton yarns from 180 g in case of untreated cotton yarn to 157 g for that treated with 0.15 N  $\text{KMnO}_4$ .

This can be attributed to both, the oxidation of cellulose and chain rapture, because of the initiator and

the acidity of the reaction medium (15). On the other hand, the crystallinity of the fibers may be increases with increasing the initiator concentration, duo it is well known that grafting occurs on the amorphous region of cellulose as evidenced by Eichhorn<sup>[16]</sup>.

**Effect of changing  $\text{KMnO}_4$  concentration in presence of monomer on the tensile strength of poly (MAAm)-cotton yarn graft copolymers:**

Table 2 shows the effect of changing  $\text{KMnO}_4$  concentration in presence of MAAm on the tensile strength of poly (MAAm)-cotton yarn graft copolymers. By increasing the graft yields to 18.35; the tensile strength increases then decreases by further increase in the graft yield. The increase in tensile strength by increasing the graft yield up to 18.35% may be duo to the strengthen of the yarn. While on the other hand a decrease in the tensile strength by increasing the graft yields may be duo to the combined effect of oxidation via initiator and grafting with the monomer.

On the other word, when the reaction is carried out in the presence of a monomer the oxidation or depolymerization is lower than in case of cotton alone, In this case the macro cellulose radicals generated by the initiator are used to carry out the graft copolymerization of the polymer and the degradation of the cellulose are reduced. Beside, the grafting of MAAm onto the cellulose results in a reduction of the degree of crystallinity of the grafted fibers as shown before. While on the other hand, the effect of initiator concentration on the tensile strength of poly (MAAm) –grafted cotton yarn is also noted. An increase in the amount of grafted MAAm onto the cotton yarns results in a decrease of the crystallinity, because a large amount of a polymer is present on the grafted fibers (amorphous region). So, there is a noted decrease in the tensile strength as shown in tabular data presented in Table 2.

Nearly 38.6% graft yield on cotton yarn was obtained by applying the following reaction conditions:  $\text{KMnO}_4$ , 0.07 N;  $\text{HNO}_3$ , 80 meq/100 g sample; MAAm, 1 g; Temperature, 60°C; Time, 60 min when using a material to liquor ratio of 1:50. On the other hand, the tensile strength of poly (MAAm)-cotton yarn grafts copolymer having 18.55% graft yield exhibits a higher value than ungrafted cotton yarn. While, increasing the graft yields over 18.55% lead to a decrease in tensile strength of the grafted yarn.

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