

SYNTHESIS OF 2-HYDROXY ETHYL METHACRYLATE GRAFTED COTTON FIBERS AND THEIR FASTNESS PROPERTIES

MEHLİKA PULAT* and FATMA NURALIN**

*Gazi University, Science Faculty, Chemistry Department, Teknikokullar, Ankara, Turkey

**Gazi University, Ankara Vocational Highschool, Ankara, Turkey

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In this study, 2-hydroxy ethyl methacrylate (HEMA) monomer was grafted onto cotton fibers, using a benzoyl peroxide (BPO) initiator. The effects of grafting temperature, grafting time, monomer and initiator concentrations on grafting yield (GY) and grafting efficiency (GE) percentages were investigated and the optimum grafting conditions were determined. Maximum GY value was obtained as 47.6%. From swelling tests, it was observed that GY positively affected the swelling percentages of grafted fibers. SEM analyses of grafted and ungrafted fibers were performed in order to characterize fiber morphology. The dyed fibers were subjected to fastness tests and higher fastness ratings were observed for grafted fibers, compared to ungrafted samples.

Keywords: cotton fibers, 2-hydroxy ethyl methacrylate (HEMA), grafting, swelling test, fastness

INTRODUCTION

Cotton is a widely used natural, healthy, hygroscopic and cheap textile material. Nearly 94% of its chemical structure consists of cellulose molecules. Cotton with improved physical and chemical properties is highly demanded in textile industry. As modification of synthetic and natural polymers via graft copolymerization is a commonly used method, several reports already exist on the modification of cotton in the literature.¹⁻⁴

Vinyl monomers are easily purchased chemicals, which can be used in many reactions, like polymerization and copolymerization. Some physical properties of natural and synthetic products can be improved by modifying them with these kinds of monomers.⁵⁻⁷ Vinyl monomers, such as acrylic acid (AA), acrylonitrile and methyl methacrylate, are convenient monomers for graft copolymerization of cellulose fibers and fabrics. Hygroscopic and dyeability properties of cotton can be modified by this method.⁸

Graft copolymerization of vinyl monomers onto natural polymers, using free radical initiation, is regarded as a very fascinating research field with many future industrial possibi-

lities. This technique enables the production of new polymer materials with desired properties, which are based on chemical combinations of natural and synthetic polymers. In this context, there has been a growing interest in chemical modification of natural fibers via graft copolymerization for biomedical, industrial, and textiles applications.⁹ Depending on the chemical structure of the grafting monomer, the graft copolymers could be produced as hydrophilic or hydrophobic, exhibiting improved elasticity, water absorption, ion-exchange capability, heat resistance and resistance to microbiological attack. Such copolymers have found wide application in textile and biomedical applications.¹⁰⁻¹³

The grafting of vinyl monomers onto cellulose and its derivatives is generally considered to involve three steps: (a) the generation of reactive sites on the substrate polymer, (b) the addition of monomer to the substrate, and (c) the propagation reaction of that monomer.¹⁴ Reactive sites on the cellulose backbone are generated by either physical or chemical initiation methods. Besides potassium persulfate, ceric ions, azobisisobutyronitrile and benzoyl peroxide

(BPO) are quite frequently used as initiators, although there are some studies based on UV irradiation and γ -radiation. Reports on graft polymerization of vinyl monomers, such as acrylic acrylate (AA), acrylamide (AAm) and acrylonitrile monomers onto cellulose using both chemical and radiation methods are available in the literature.¹⁵⁻²⁰

Our previous study was focused on the grafting of some vinyl monomers, such as AA, AAm, crotonic acid (CA) and itaconic acid (IA), on cotton fibers.²¹ In the present study, we aimed to investigate the grafting efficiency of 2-hydroxy ethyl methacrylate (HEMA) onto cotton fibers and the fastness properties of the grafted samples. The effects of grafting temperature (T), grafting time (t), monomer [M] and initiator [I] concentrations on grafting percentages were studied and optimum grafting conditions were determined. Besides swelling tests and SEM analysis of grafted and ungrafted cotton fibers, dyeing procedure and fastness tests were also performed.

EXPERIMENTAL

Fiber preparation

Combed cotton fibers (20/1) were obtained from the Turkish textile company Floksel Textile Co. Cotton fibers were used after treatment.^{10,22} The hanks of the fiber sample, of about 300 cm total lengths, were boiled briskly in 500 mL of NaOH (Merck) solution (0.08%), containing 0.1 g of nonionic Triton X surfactant (Aldrich) for 3 min. The sample was then washed successively with hot water, cold water, 1.0% of HCl (Merck) solution, and finally with cold water until it was acid-free. The scoured cellulose thus obtained was dried at room temperature in a current of dust-free air.

Grafting procedure

Graft copolymerization procedure was performed according to the literature.²⁻³ BPO (Aldrich) was used as an original initiator for HEMA (Aldrich) grafting onto cotton fiber. To determine the effect of temperature on grafting yield, we investigated the polymerization reaction by varying the temperature between 30 and 60 °C, while we held the polymerization time and monomer and initiator concentrations constant. Appropriate amounts of fabric were placed into round-bottom polymerization tubes containing 0.5 mL of BPO–acetone solution. The tubes were put into a water bath at a constant temperature. After thermal equilibrium was reached, 4.5 mL of a HEMA–water solution was added into the polymerization tubes, and the polymerization reaction was performed for 2 h. Final concentrations of HEMA

and BPO in the reaction tube were of 0.25 M and 8.0×10^{-2} M, respectively. After polymerization, the treated fibers were taken out. The residual solvent, monomer and homopolymer were removed from the fibers by thoroughly washing with hot and cold water. The treated fibers were dried at 40 °C in a vacuum oven for 48 h and weighed. The grafting yields (GY) and grafting efficiency (GE) percents were calculated based on the weight of cotton fibers using the following equations:^{14,23}

$$GY (\%) = \frac{m - m_0}{m_0} \times 100 \quad (1)$$

$$GE (\%) = \frac{m - m_0}{w_m} \times 100 \quad (2)$$

where m_0 is the initial weight of cotton fiber before grafting, m is the weight of the grafted cotton fiber and w_m is the weight of the monomer used for grafting. All measurements were performed in triplicate.

To determine the effect of time, [M] and [I] on GY, we repeated the procedure, by varying t from 15 to 240 min; [M] from 0.05–2.0 M and [I] from 1.0×10^{-2} to 1.0×10^{-1} M. GY and GE values were calculated from Equations 1 and 2.

Swelling tests and SEM analysis of grafted and ungrafted cotton fibers

Swelling percentage values (S%) were determined from the equation given below, where m_w is the mass of the swollen fibers in distilled water at room temperature to a constant weight and m_d is the mass of the same fibers dried eventually at 40 °C for 48 h.^{21,23,24}

$$S (\%) = \frac{m_w - m_d}{m_d} \times 100 \quad (3)$$

SEM micrographs of grafted and ungrafted fibers were taken to observe the grafting performance, by using a JEOL model JSM 840A SEM. The conductivity was supplied by coating the samples with gold-palladium of 200 Å.

Dyeing

The commercial-grade reactive dye (Sumifix Brill.Supra Red GF 150%, CI:Red 223, Sumitomo Chemical Co. Ltd., Japan) was used as received. Reactive type dyes are widely used for industrial dyeing of cotton textile materials. Reactive dyeing of grafted and ungrafted cotton fibers was carried out using a liquid/cotton ratio of 1:50. The dye was weighed (2% on the basis of fiber sample weight) and added into the bath at 40 °C. The sample was introduced into the bath and held for 15 min; then the temperature was raised slowly to 60 °C. The dyeing was continued for 60 min, during which 40 g/mL of NaCl was added; the pH of the dye bath was kept in the range of 10–11 by using Na_2CO_3 . The dyed cotton samples were taken out of the bath and thoroughly washed with cold and then with hot distilled water. The samples were boiled in 1% of soap solution for 30 min,

then washed thoroughly with distilled water and dried in air.²⁵

Fastness testing

The weather and the rubbing fastness tests were performed by using the Xenon Arc Lamp Method (Atlas, Electric Type, Turkey) and the Crock Meter Method (Atlas, Electric Type, Turkey), respectively. The color fastness was determined according to International Standards; the specific tests used were ISO 105 C06/C1S (washing fastness), ISO 105 X12 (rubbing fastness) and ISO 105-B04 (weather fastness). The weather fastness tests were assessed according to the international blue scale (1-8), the rubbing and washing fastness tests were assessed according to the international grey scale (1-5), where scales 8 and 5, respectively, rank the best, while 1 is the most inferior. All measurements were performed in triplicate.

RESULTS AND DISCUSSION

Effect of temperature

The effect of temperature on graft polymerization of cotton fibers was studied within the range of 30-60 °C. As the temperature was increased, the GY also gradually increased, reached to a maximum value and then decreased (Figure 1). Maximum GY was calculated as 47.6% at 50 °C. The initial increase in GY may be attributed to the increase of the mobility and diffusion rate of the monomer and initiator molecules. The decrease in GY at higher temperatures was due to the favored chain-termination reactions and the increase in homopolymer formation. Similar results were also reported in chemically initiated graft copolymerizations of various vinyl monomers on natural and synthetic fibers.^{2-4,6,14}

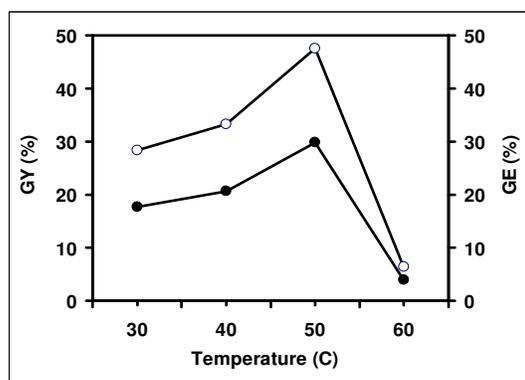


Figure 1: Effect of temperature on GY (o) and GE (●) (t = 2 h, [M] = 0.25 M, [I] = 8.0 x 10⁻² M)

As might have been expected, GY and GE curves were similar to each other. The maximum GE value was calculated as 29.8%, using the grafting conditions of [M] = 0.25 M, [I] = 8.0 x 10⁻² M, t = 2 h and 50 °C.

Effect of polymerization time

The effect of polymerization time on GY was investigated by changing the time (from 15 to 240 min) at constant temperature, [M] and [I]. As shown in Figure 2, GY initially increased with time and then reached a saturation grafting value nearly after 2 h. The maximum GY value was obtained as 47.6%. This behavior could be attributed to the depletion in both monomer and initiator concentrations, as well as to the changes in the composition of the system as the reaction proceeded.²⁶ A similar trend was obtained for the GE curve. The GY values reported by several researchers who worked on grafting of cotton fibers with vinyl polymer were of about 20%. So this is a high value in comparison with the GY results given in the literature.¹⁵

Effect of monomer and initiator concentration

The effect of [M] on GY was studied by varying its concentration between 0.05 M and 2.0 M at constant temperature, time and [I]. As may be noted from the results presented in Figure 3, GY increased first with increasing [M], reached a maximum and then decreased. As [M] increased, the diffusion of monomer molecules into the fiber structure also increased, leading to a higher GY. The decrease in GY can be explained by the enhancement of homopolymer formation at high monomer concentrations. It was observed that the maximum GY value was obtained at 0.25 M HEMA concentration.

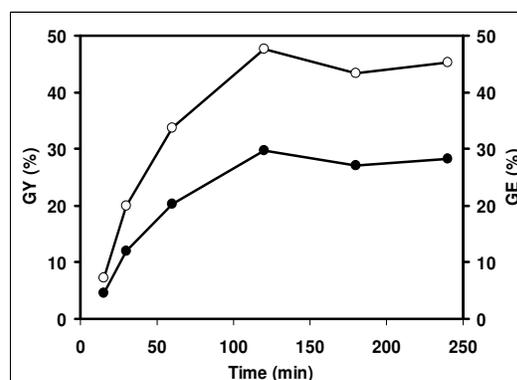


Figure 2: Variation of GY (o) and GE (●) with polymerization time (T = 50 °C, [M] = 0.25 M, [I] = 8.0 x 10⁻² M)

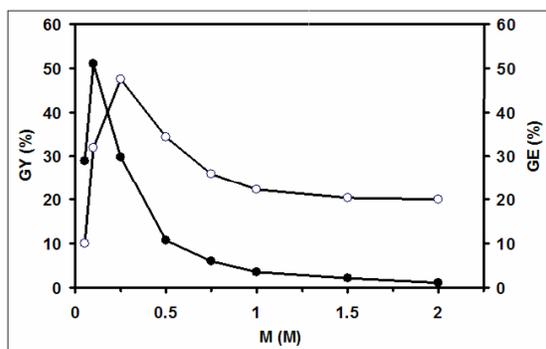


Figure 3: Variation of GY (o) and GE (●) with monomer concentration ($T = 50\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$, $[I] = 8.0 \times 10^{-2}\text{ M}$)

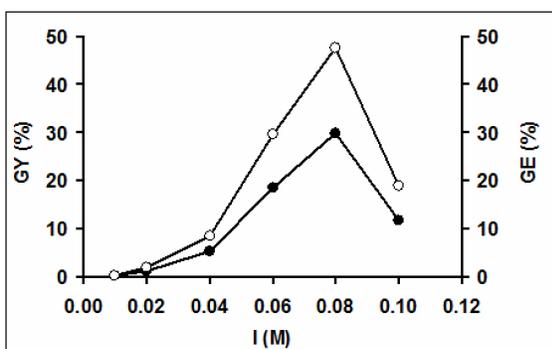


Figure 4: Variation of GY (o) and GE (●) with initiator concentration ($T = 50\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$, $[M] = 0.25\text{ M}$)

Table 1
Optimal grafting conditions, maximum GY and S% values of cotton fibers grafted with particular vinyl monomers

Grafted monomer	T (min)	T ($^{\circ}\text{C}$)	[M] (M)	[I] (M)	GY (%)	S (%)
HEMA	120	50	0.25	0.08	47.6	432
AA*	60	60	2.5	0.08	23.8	502
AAm*	60	70	1.0	0.04	20.8	290
CA*	60	60	1.5	0.10	12.9	499
IA*	60	70	1.0	0.10	15.9	510

*Values reported by M. Pulat and C. Isakoca²¹

GE values displayed a similar trend to that of GY. GE increased by increasing HEMA concentration until a maximum value was attained, and then decreased. Two different values were obtained when the experimental data were used in Equations 1 and 2. Maximum GE value of 51.2% was reached at 0.10 M HEMA concentration and maximum GY value of 47.6% was obtained at 0.25 M of HEMA concentration. GE value is a kind of an indicator that shows the maximum production value, using a minimum monomer amount. With respect to the monomer amount consumed for the grafting reaction, GE values seem more significant than GY values. According to definitions, the obtained GY values were higher than those of GE, resulted for minimal monomer concentration. From the comparison of GY-GE values in Figure 3, it is seen that a lower monomer amount causes more grafting. Similar results are presented in the literature.⁹⁻¹¹ In such a case, 0.10 M of HEMA concentration could be suggested as a more convenient grafting concentration than 0.25 M.

Figure 4 represents the effect of initiator concentration on GY and GE. Evidently, the grafting percentages increased significantly as the

BPO concentration increased, and a further increase in BPO concentration decreased the GY and GE. Free radicals occurred as a result of BPO decomposition, taking place in various reactions in polymerization media. The increase in BPO concentration increases the probability of both hydrogen abstraction from the cellulose backbone and chain transfer reactions of PHEMA homopolymers with cellulose. So, the GY and GE increase in both cases. However, the excessive increase in BPO concentration causes the formation of free radical species via decomposition of BPO ($\text{C}_6\text{H}_5\text{COO}^{\bullet}$ and/or $\text{C}_6\text{H}_5^{\bullet}$). These free radicals react with cellulose macroradicals and growing polymer chains, resulting in termination or combination reactions; consequently, grafting yield decreases.^{2,14-21}

The optimum grafting conditions, maximum GY and S% values for HEMA grafted onto cotton fibers are summarized in Table 1. To compare the values, data referring to other vinyl monomers, obtained from our previous studies, are presented in the same table. Maximum GY values on cotton fibers have been reported as 1.46%-10.2% for AAm; 9.5% for IA and 1.5% for AA by other researchers.^{4,10,14} In our previous study, the GY

values found were much higher than the values given in the literature. In this study, a lower monomer amount was used and higher GY and GE values were obtained, compared to other vinyl monomers. As a result, it can be said that HEMA is a suitable grafting monomer for cotton fibers under the conditions established in this study.

Considering the graphs given in Figures 1-4, the optimum grafting conditions providing maximum GY values were determined as 0.25 M of HEMA concentration, 50 °C, 2 hours of grafting time and 0.08 M of BPO concentration

Swelling values

S% values calculated from Equation 3 are presented in Table 2. The maximum S% values (underlined in the table) belong to the samples prepared under maximum GY conditions. Swelling values of the grafted fibers increased according to GY. In general, low swelling values were obtained for the samples grafted using low [I] and [M] concentrations. The highest swelling value of grafted fiber was measured as 432% under optimum grafting conditions, 0.25 M of HEMA concentration, 50 °C, 2 hours of grafting time and 0.08 M of BPO concentration. As the measured S% value of ungrafted cotton fibers was 155%, it can be said that the swelling capacities of the grafted fibers were nearly three times higher than the capacity of the ungrafted cotton fibers.²¹ As PHEMA has an extremely hydrophilic character, grafting of cotton with this polymer caused an increase in swelling values. The comparative S% values of various vinyl-grafted cotton fibers are also presented in Table 2. Similar swelling values were observed, except for AAm grafted cotton fibers.

SEM analysis

Scanning electron micrographs of ungrafted and grafted fibers at two different magnifications are presented in Figure 5. A change in the morphology of fiber surface before and after grafting can be evidently observed. Both grafted and ungrafted cotton samples present fiber bundles (ribbon-like structure). No polymer chain, or mound is detected on the ungrafted cotton fiber surfaces (Fig. 5 a, c). Some apparent aggregates of PHEMA fibrils on the surface of grafted fibers are a good evidence for the successive grafting process (Fig. 5 b, d). The bonded PHEMA fibrils on the cotton fibers indicate that the grafting was successfully performed.

Dyeing properties

The ratings of rubbing, washing and weather fastness of the cotton fibers are presented in Table 3. The results obtained from dry rubbing fastness, washing fastness and weather fastness tests showed that the grafted and ungrafted cotton fibers appeared to have similar fastness values, with the exception of wet rubbing and washing fastness. The wet rubbing fastness value for HEMA grafted cotton fiber was 5, while the wet rubbing fastness value for ungrafted cotton fiber was 3. The washing fastness rating of the grafted sample presents better rating than that of the ungrafted sample. The results given in the table indicate that the color of HEMA grafted cotton fiber is more stable to wet rubbing and washing. Consequently, fastness results show that the ratings obtained from the fastness tests are satisfactory, if compared with the values given in the literature.²⁵

Table 2
S% values of HEMA grafted cotton fibers under specified conditions

t = 2 h, [M] = 0.25 M, [I] = 8.0 x 10 ⁻² M		T = 50 °C, [M] = 0.25 M, [I] = 8.0 x 10 ⁻² M		T = 50 °C, t = 2 h, [I] = 8.0 x 10 ⁻² M		T = 50 °C, t = 2 h, [M] = 0.25 M	
T (°C)	S%	T (min)	S%	[M] (M)	S%	[I] (M)	S%
30	293	15	176	0.05	160	0.01	158
40	360	30	220	0.10	350	0.02	155
50	<u>432</u>	60	356	0.25	<u>432</u>	0.04	160
60	178	120	<u>432</u>	0.50	358	0.06	335
		180	415	0.75	296	0.08	<u>432</u>
		240	430	1.00	235	0.10	195
				1.50	213		
				2.00	215		

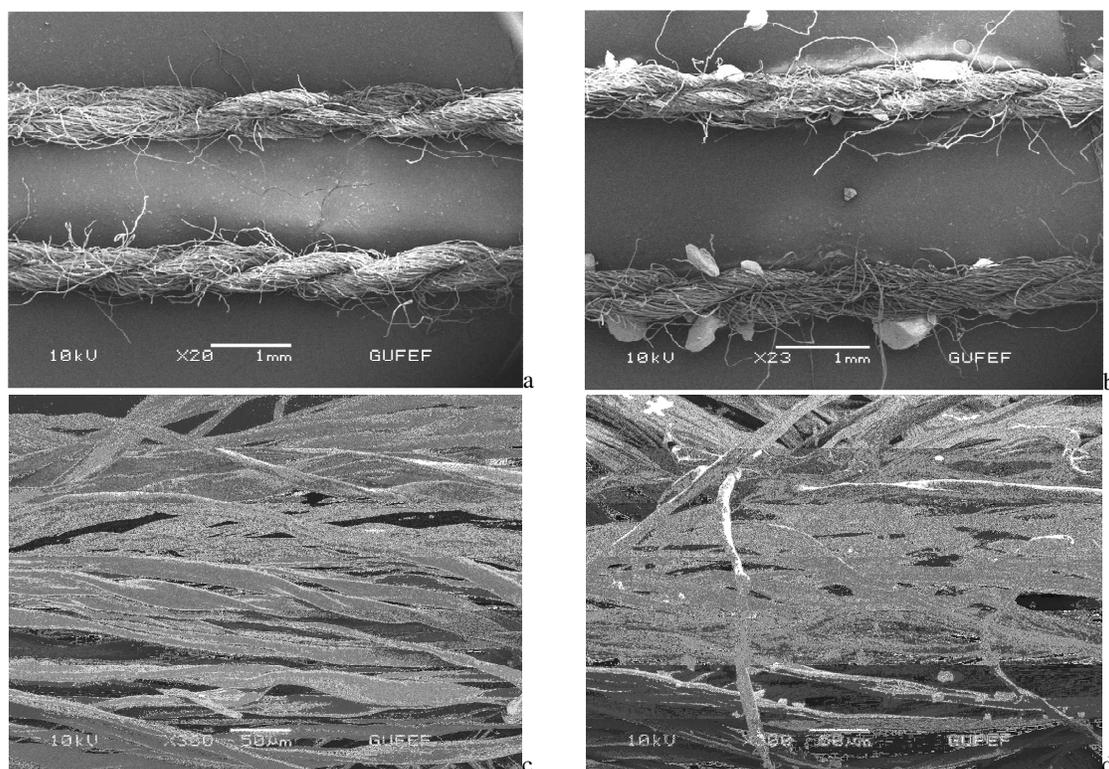


Figure 5: SEM micrographs of ungrafted cotton fibers at (a) 20X and (c) 300X ; HEMA grafted fibers at (b) 23X and (d) 300 X

Table 3
Comparative fastness rates of grafted and ungrafted cotton fibers

Sample	Weather fastness	Washing fastness	Wet rubbing fastness	Dry rubbing fastness
Ungrafted cotton fibers	5	4	3	5
HEMA grafted cotton fibers	5	5	5	5

CONCLUSION

Graft copolymerization of HEMA monomers onto cotton fibers was performed, by using BPO, which is an original initiator for the HEMA/cotton system. The polymerization conditions were investigated and the optimum grafting conditions were found as 0.25 M of HEMA concentration, 50 °C, 2 hours of grafting time and 0.08 M of BPO concentration. The maximum GY and GE values were obtained as 47.6% and 51.2%, respectively. The existence of graft copolymerization was proved via SEM analysis. Swelling percentage values show that the swelling capacities of grafted fibers are nearly 3 times higher than the capacity of ungrafted cotton fiber. Fastness tests were performed and satisfactory results were obtained, in comparison with those reported in the literature. Although the grafted and ungrafted cotton fibers present similar weather and dry

rubbing fastness ratings, the grafted cotton fibers had higher ratings of wet rubbing and washing fastness than the ungrafted cotton fibers.

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