Modification of Silk for Improvement of Weighting and Properties

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Abstract: Silk was modified by 2-hydroxy ethyl methacrylate (HEMA) and glycidyl methacrylate (GMA) and GMA/ derivatives to increase the weight, improve silk properties, antibacterial and fungicidal activities. Thus silk was grafted using a chemical method to different percentage add-on HEMA and GMA. Modified silk / GMA were further reacted with Diethylene triamine (DETA) at 85ºC for one hour to yield bactericidal and fungicidal silk fabrics. The weight of silk was increased and the properties were improved including moisture regain, crease recovery angles, abrasion resistance, whiteness and decrease of yellowness index. Characterization of modified fabric was done by FTIR, thermal gravimetric analysis (TGA) and SEM.

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Key words: modified silk, chemical redox method, HEMA, GMA/derivatives, weighting moisture regain, crease recovery angle, abrasion resistance, whiteness, yellowness index, bactericidal and fungicidal activities.

1. Introduction

Silk is one of the most expensive fabrics. It has excellent properties such as soft, smooth handle, pleasant luster and gives brilliant color shades on dyeing. Silk is used for the apparel women dressing and it is a traditional dress in some countries like India, Japan, and Sudan etc.

Nowadays, grafting modification of silk[1-7] is considered an alternative procedure for the old weighting technique using inorganic salts [8] which was used for a long time ago with the purpose to increase silk weight resulting from the demumming process. Graft copolymerization of active vinyl monomers onto silk by different techniques acquired a great interest on an industrial scale by researchers all over the world to increase silk weight and improve its properties.

In addition to the well known chemical redox method [9-13] and silk irradiation using electron beam or γ–rays[14] followed by grafting, other methods were investigated using micro-wave irradiation [15] or plasma grafting techniques [16].

Thus, silk grafting is not only an effective method to increase the silk weight but it is an excellent method for improving silk properties such crease recovery angle, abrasion resistance, photo yellowing, dimensional stability and inducing antimicrobial activity for biomedical applications.

In the present article, silk fabric was grafted by the chemical redox method with the aim of weighting, improving silk properties and inducing antimicrobial activity to the fabric. For this purpose ammonium persulfate (APS) was used as initiator followed by grafting GMA or HEMA. GMA was reacted with DETA to produce silk/GMA/DETA or silk/HEMA fabrics. Grafted silk fabrics were characterized by FTIR, TGA and SEM. The properties of silk /HEMA were evaluated including moisture regain, crease recovery angle (dry and wet). Abrasion resistance, whiteness and yellowness index, which were improved. In addition silk/ GMA/ DETA had imparted bactericidal and fungicidal activities to the fabric.

Experimental

2. Materials

Egyptian plain construction silk fabric (63 gm/m^2) was scoured by 2g/1 of monionic surfactant solution at 50ºC for one hour. The silk fabric was thoroughly washed with warm water, then with cold water and finally squeezed and air dried.

Reagents

2-hydroxy ethyl methacrylate (HEMA) and glycidyl methacrylate (GMA), were purchased from Aldrich Co. and were used without further purification. Potassium persulfate (PPS), ammonium persulfate (APS), copper sulfate (CuSo4, 5 H2O), Diethylene triarnine (DETA) and acetone were all analytical grade reagents.

Polymerization procedure

A graft coplymerization reaction was carried out by treating silk fabric with a solution (2% w/w) of PPS or APS for 20 minutes at room temperature. The fabric was removed, thoroughly washed with distilled water, squeezed and dried at room temperature.

Silk fabric pretreated with (PPS or APS) were introduced into a stoppered Erlenmeyer flask containing 100 ml of the solution. The solution consisted of water, monomer and copper sulfate. The stoppered flask was kept in a thermostated shaking water bath at the desired temperature during the polymerization reaction. After a desired time, the reaction mixture was then washed several times with warm water and then with acetone , dried in oven at 105ºC for one hr and cooled to room temperature in a desiccator until constant weight. The graft yield was calculated as follows.

$$\% \text{ Graft yield } (G^o) = \frac{W - W^o}{W^o} \times 100$$

Where W is the weight of grafted silk sample and Wº is the weight of original silk fabric.

Grafting silk with GMA derivatives

Silk was grafted with GMA using the previous conditions and gave a fabric of the following composition: silk/109.7 GMA. Then it is allowed to react with DETA solution at a liquor ratio 1:50 (the solution mixture is 30 ml distilled water and 20 ml DETA) in an alkaline medium (addition of 1gm pyrophosphate). The reaction temperature was adjusted at 85ºC for one hr. The dry weight increase of the fabric was determined and the fabric was of the following composition:
Silk/109.7% GMA/7.7% DETA

Measurements

FTIR Spectroscopy

The FTIR spectrums of the silk fabrics were recorded on a Pirken Elmer 781 Infrared Spectro-photometer, as KBr disks.

Thermogravimetric analysis

Thermogravimetric analysis TGA was carried out using Pirken Elemer 7 Series instrument. The samples were placed on an aluminium holder and covered with gold. The rate of heating was adjusted at 10ºC/min. The thermograms were recorded from 50ºC to 600ºC under normal atmosphere.

Crease recovery angle measurement

The crease recovery angle of silk was measured by an iron recovery apparatus (Type FF-07 Metrepex) for 10 min crease period. The sum of crease angles of the warp (W) and weft (F) directions were measured.

Abrasion resistance measurement

One hundred fifty cycles were used for each fabric sample using the Universal Textile Abrasion Tester (Custom type, ASTMD). The percentage weight loss was determined.

Yellowness and Whiteness Indexes

The yellowness and whiteness indexes of silk fabric were measured using Erichsen Model 299/300, Erichsen GMBH and Co, Germany.

Antimicrobial activity

Antimicrobial activity was done by the diffusion disc method. A sample of the fabric is placed in a Petri dish containing solid bacterial medium (nutrient agar broth) or fungal medium (Doxs medium) which has been heavily seeded with the spores suspension of the tested organism. After inoculation, the sample is incubated at 37ºC for 24 or 48 hrs. The diameter of the clear zone of inhibition surrounding the sample is taken as a measure of the fabric inhibition action against the particular test organism[18-21].

Scanning electron microscopy

SEM micrographs were done on JEOL Model JSM-T20 instrument operating at 19 KV Photos which were prepared at a magnification range 2500X. The samples were placed on aluminium holder and covered with gold.

3. Results and Discussions

Effect of cupric ions concentration

The effect of copper sulfate concentration on the percentage graft yield of HEMA onto silk fabric is shown in Figure1. It was observed that the presence of cupric ions played a significant role in increasing the grafting reaction. An increasing in the graft yield was achieved when Cu^{2+} ion concentration increased gradually and reached 100% at 0.1 m.mol/1. The presence of Cu^{2+} ion caused an accelerating effect on the decomposition of PPS and by further increasing of Cu^{2+} concentration, the graft yield became constant.

Effect of HEMA concentration on the graft yield

The effect of HEMA concentration on percentage HEMA graft yield onto silk fabric is shown in Figure 2. It was observed that the percentage graft yield increases by increasing the HEMA concentration to 1.2×10^{-4} mmol/1 and attains a corresponding graft yield of 78%.

FTIR Study

FTIR were done for the degummed silk Figure 3 (a) and for the modified silk ie silk/GMA (b), silk/GMA/DETA (c) silk/ HEMA (d).

In the spectrum (a) the ungrafted silk[17] shows the absorption bands at 1516 and 1647 cm^{-1} assigned for=C=O stretching of amide I and amide II respectively. The peaks at 2925 and 3301 cm^{-1} are attributed to the C-H stretching and N-H stretching deformation.

In case of spectrum (b) for grafted silk, it revealed new absorption bands of GMA-grafted silk at 1151 cm^{-1} which is attributed to C-O stretching and at 1734 cm-1 which is due to C=O stretching of ester groups and increase absorption bands of epoxide group at 1261 cm^{-1} and appearance of extra bands at 906 and 847 cm^{-1}. In case of spectrum (c) silk/GMA/TETA the appearance of the bands at 906 and 847 cm^{-1} which correspond to the unreacted epoxide group. For spectrum (d) silk/HEMA, it reveals the same previous ester bands and a sharp peak at 3296 cm^{-1} corresponding to the hydroxyl group of HEMA.

Effect of grafted HEMA on crease recovery angle

The result of this study revealed that both dry wet crease recovery angles were improved due to grafting of silk fabric with HEMA, even at low graft yield which agree with our previous work [1]. Thus as shown in Table 1, dry crease recovery angles increased from 159º to 198º (29.3% HEMA) and then slightly decreased to 191º as the graft yield increases to 35.5% of HEMA, which may be attributed to steric hindrance.

The dry crease recovery angles of silk were improved due to grafting of silk by HEMA even at low HEMA graft yield, which is shown in Table 1.

The wet crease recovery angles (wetted in 1% nonionic detergent and then well squeezed) increased from 106ºC for the ungrafted silk to approximately mean constant value of 119ºC for all the HEMA graft yield (9.48 to 35.5% HEMA) i.e. increase grafting has the same effect on the wet crease recovery angles.

Table 1. Effect of grafted HEMA on the dry and wet crease recovery angles of silk.

HEMA Grafted Silk %	Dry Crease Recovery Angle (W+F)^o	Wet Crease Recovery Angle (W+F)^o
Zero	159	106
9.48	183	115
15	189	121
29.3	198	122
35.5	191	116

Effect of grafted HEMA on the abrasion resistance of silk fabric

Grating of silk by HEMA increases the abrasion resistances as shown in Table 2. It was observed that the percentage weight loss decreases from 11.59 for the control silk fabric (ungrafted) to 1.25% for 35.5% HEMA grafted silk fabric. As a result of grafting, the percentage weight gains by grafting compensate the percentage abrasion weight loss. As a conclusion grafting of silk fabric by HEMA leads to improvement of its abrasion resistance.

Table 2. Effect of grafted HEMA on the abrasion resistance of silk fabric.

HEMA Grafted Silk%	**Weight loss%**
Control sample	11.59
9.48	7.26
15	3.5
29.3	2.4
355	1.25

Yellowness and Whiteness Indexes

It is shown in Figure 4 that the photo yellowing index of modified silk fibers is decreased from 14 (ungrafted silk) to 9 for (20% grafted HEMA). The reverse is clear with the whiteness since the whiteness index increases from 12.5 (ungrafted silk) to 19 for (35.5% grafted HEMA). Therefore it can be deduced that grafting silk with HEMA reduced the native silk yellowing and thus protected silk against sunlight damage.

Moisture Regain

Table 3 shows that the percentage moisture regain increased by increasing HEMA yield induced by grafting silk, i.e. it increased from the 7.3% (blank silk) to 8.31% (for 15% grafted HEMA). This can be attributed to HEMA itself as it is contains hydroxyl groups grafted in its chemical structure, which are hydrophilic in nature and consequently increase moisture absorption of silk.

Table 3. Effect of percentage grafted HEMA on the moisture regain of silk.

Grafted HEMA %	Moisture regain%
Zero	7.3
9.48	7.52
15	8.31

Thermo gravimetric analysis TGA

TGA Study Table 4 and Fig.4 revealed that grafted silk fabric with (silk/108.6% GMA/7.7% DETA is slightly increased at 374ºC to 600º. On the other hand the grafted silk fabric of composition 29.3% HEMA, its thermal stability slightly decreased than that of silk at temperature beyond 250ºC to 600ºC.

SEM

SEM micrographs of ungrafted and grafted HEMA 35.5% silk fabrics are shown in Figure 6 (a,b). The ungrafted silk fabrics (a) has a smooth surface compared to that of silk/HEMA grafted fabrics (b) which shows a large amount of side chains, confirming the grafting of silk.

Antimicrobial activity

The modified silk fabric of composition silk/109.6% GMA/7.7 DETA showed antimicrobial activity against *Escherichia* Coli (G$^-$) and Staphylococcus *Aureus* (G$^+$). Table 4 shows that the inhibition zones were 25 mm and 28 mm/cm fabric respectively for 24 hrs incubation. Also the same fabric gave fungicidal activity against *Candida Albicans and Saccharomyces Cereviseaes* and the inhibition zones were 24 and 26 mm/cm fabric respectively for 24 hrs incubation. Ungrafted Silk fabric was inactive against the above microorganism. These findings support the mechanism of the antimicrobial action whereby a hydrophobic polycationic chain penetrate bacterial cell membranes/ walls and fatally damage them [22-23]. The bactericidal modified silk prepared are active not only to pathogenic bacteria but to fungi as well.

Table 4. Effect of percentage grafted silk on the inhibition growth of bacteria

Samples	Inhibition Zones Diameter (mm/cm sample)							
	E. coli (G-)		S. aureus(G+)		C. albicans (Fungus)		S. cereviseae (Fungus)	
	24 h	48 h	24 h	48 h	24 h	48 h	24 h	48 h
Grafted silk	25	25	28	28	24	24	26	26
Blank	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Grafted silk: 109.6% GMA/7.7% DETA; G: Gram reaction.

Table 5. Thermal Gravimetric Analysis (TGA) for grafted & native silk.

Temperature ºC	Silk control	Silk/29.3% HEMA (2)	Silk/109.6% GMA/7.7% TETA (3)
	Residual weight %		
200	94.917	95.325	93.386
250	93.568	93.904	91.227
300	85.432	83.414	79.225
350	61.923	52.680	58.543
400	45.168	37.535	46.922
450	33.544	2.816	37.922
500	21.839	18.414	26.922
550	4.962	6.285	13.22
600	-	-	3.269

References

1. Ramadan, A.M.; Mosleh, S.; Gawish, S.M.; J Appl Polym Sci; **93**, 1743 (2004) 2004.
2. Watt, I.C.; J Macromol Sin Rev, Macromol Chem; C5, 176, (1970).
3. Arai K. In Block and Graft Copolymerization; Wiley: London, **1**, 193, (1973)
4. Nayak, P.L.; J Macromol Sin Rev, Macromol Chem. **C14**, 192, (1976).
5. Lenka, S.; J Macromol Sin Rev, Macromol Chem Phys. **C22**, 303, (1982).
6. Freddi, G.; Tsukada, M.; Polym Mater Encycl. **10,** 7734, (1996)..
7. Czerny, A.R.; Vbler, A.M.; Schindler, W.; Melliand Textil Brichte **71**, 211, (1990).
8. Peng, W.; Chen, D.; Zhou, Z.; Zhong, A.; Du, Z.; J Appl Polym Sci. **69**, 247 (1998).
9. Nayak, P.L.; Lenka, S.; Pati, N.C. J Appl Polym Sci. **23**, 1345 (1979).
10. Nayak, P.L.; Lenka, S.; Mishra, M.K. J Appl Polym Chem Ed. **18**, 2247 (1980).
11. Pati, N.C.; Lenka, S.; Nayak, P.L.; J Macromol Sci Chem. **A16**, 487 (1981).
12. Maji, T.K.; Banerjee, A.N.; J Appl Polym Sci. **62**, 595 (1996).
13. Schindler, W.; Dietel, A,Melliand Textilberchte, **74**, 81, (1996).
14. [Tsukada, M; Islam, S; Arai, T; Boschi, A.; Freddi G; Autex Research Journal, **5 (1)**, 40 (2005).
15. Zhu, Y.Q.; Kang, E.T.; Neoh, K.G.; Osipowicz, T.; Chan,, I.; J of the Electrochemical Soxiety, **152 (9)**, F 107-F114 (2005).
16. Prochayawarakorn, J.; Klairatsamee, W.; Songklanakarin, T.; J Sci Technol; **27(6)**, 1233 (2005)
17. Grayer, R.J.; Harbone J.B.; Phytochemistry; **37**, 19 (1994)
18. [18] Irob, O.N.; Moo-Young, M.; Anderson, W.A.; Int J Pharmacog, **34**, 87 (1996)/
19. Jawetz, E.; Melnick, J.L.; Adelberg, E.A. Review of Medical <icrobiology 13^{th} Edition, Lange Medical Publisher: Los AltoCA, 1974.
20. Muanza, D. N.; Kim, B.W.; Euler, K.L.; Williams, L.; Int. J. Pharmacog. 32, 337 (1994).

21. Trommsdorff, H.; GmbH & Co.; K.G. Arzneimittel Fabrik Fr. Pat. 2209582 (1974).
22. Tiller, J.C.; Liano C.J.; Lewis K.; Klibanov A.M.; Proc Natl Acad. Sci USA, 98, 5981 (2001).
23. Lin J.; Qiu S.; Lewis K.; Klibanov A.M.; Biotechnology and bioengineering, 83(2), July 20 (2003).

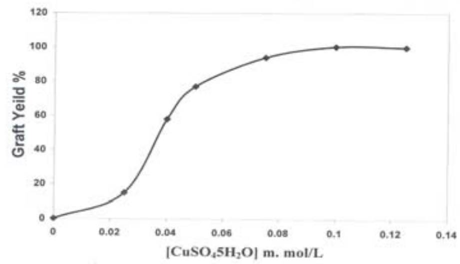

Figure 1: Effect of cupper sulfate concentration on percentage of HEMA graft yield

Grafting Condition: HEMA concentration 165 mol/l, $K_2S_2O_8$ 0 .74 x 10^{-4} mol/L, grafting temperature 80 °C, Liquor ratio 1:100 , reaction time 60 min.

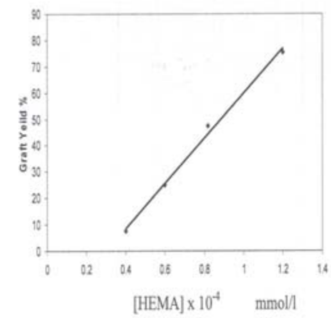

Figure 2: Effect of HEMA concentration on its graft yield %
Grafting Conditions: [$K_2S_2O_8$] 0.74x 10^{-4} mol/l, Cu SO_4 0.1 mole/l, grafting temperature 80 ^{0}C, reaction time 60 min, liquor ratio 1:100

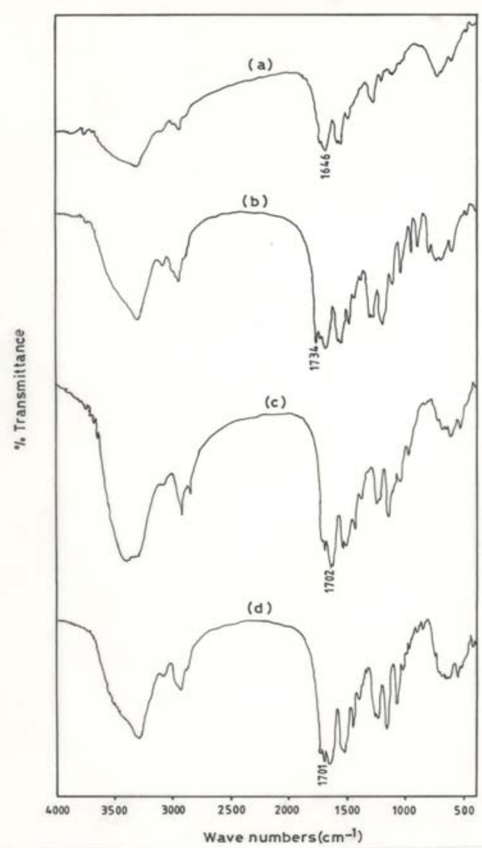

Fig.3 FTIR , ungrafted silk (a),silk/57.5 % GMA (b),Silk/109.8 % GMA/7.7DETA (c) , silk /35.5% HEMA

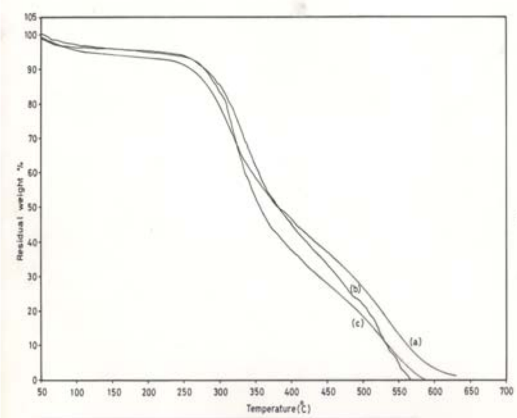

Fig4TGA of Silk control (b) ,Silk/29.3 % HEMA (c) ,Silk/109.6%GMA/7.7% TETA (a)

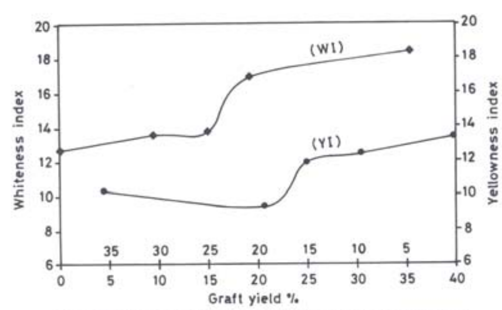

Fig. 5 Effect of SilK/HEMA modification on the whiteness & yellowness indexes

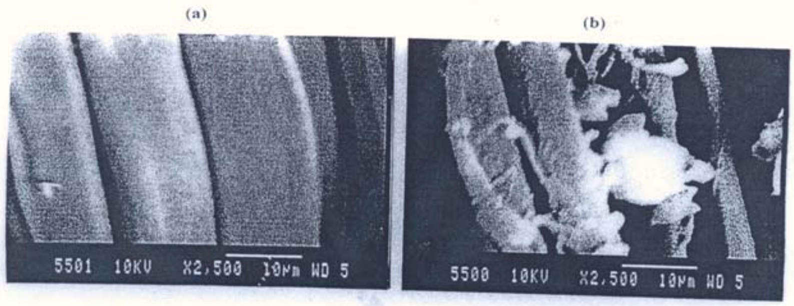

Fig. 5 SEM micrographs of ungrafted silk (a) and HEMA 3505% grafted silk (b)

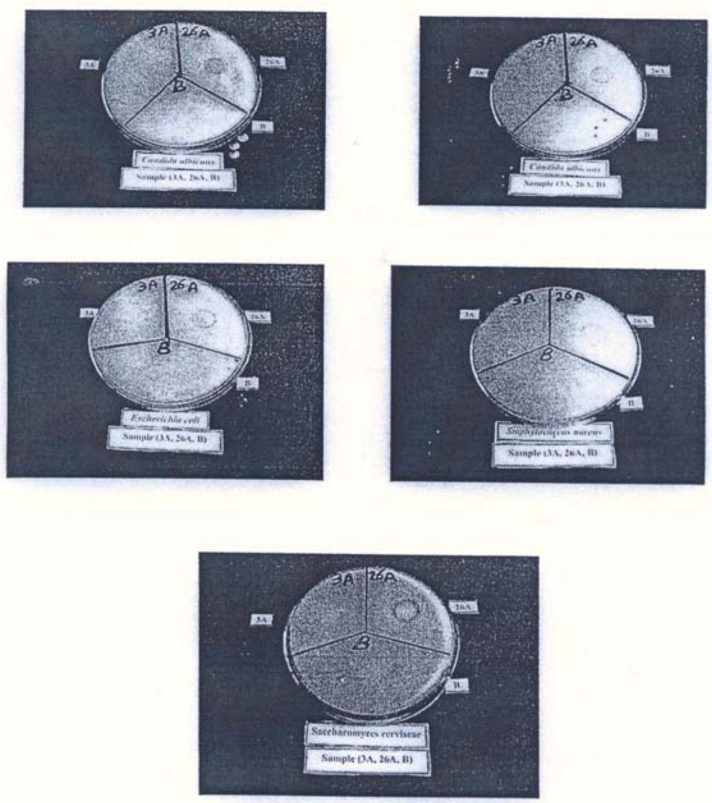

Fig.. 6 Effect of grafted silk on the inhibition bacteria growth zones.
Blank silk (B), silk / 109.6% GMA / 7.7% TATA (26A)

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