

Improvement of Dyeing and Weighting Properties of Silk Via Grafting with Acrylic (AA) and Glycidyl Methacrylate (GMA)

S. H. Abdel Fattah*, A. M. Ramadan, S. M. Abo El-Ola, M. Abdelkreem

Textile Research Division, National Research Centre Dokki, Giza, Egypt

Email address:

dr.salehh@yahoo.com (S. H. A. Fattah)

To cite this article:

S. H. Abdel Fattah, A. M. Ramadan, S. M. Abo El-Ola, M. Abdelkreem. Improvement of Dyeing and Weighting Properties of Silk Via Grafting with Acrylic (AA) and Glycidyl Methacrylate (GMA). *Science Journal of Chemistry*. Vol. 3, No. 1, 2015, pp. 11-17.

doi: 10.11648/j.sjc.20150301.12

Abstract: Copolymerization of acrylic acid (AA) and /or glycidyl methacrylate (GMA) with silk was carried out using $\text{H}_2\text{O}_2/\text{Cu}^{2+}$ reduced system. The results revealed that increasing H_2O_2 concentrations enhance polymerization up to 0.078 meq/l and also decreased the (TC) and (GY). Presences of Cu^{+2} ions up to 5 mmol/l accelerate the polymerization of (GY), (GE) and (TC). Increasing GMA and AA concentrations within the range studied were accompanied by enhancing (GY) in contrast with the (HP), (GY), (TC), and (GE) while the (HP) decrease. Crease recovery angle increased from 233° to 324° in the dry state. Dyeability as well as weighting and moisture regain properties were also improved.

Keywords: Silk, Grafting, Crease Recovery, Dyeing, Moisture Regain

1. Introduction

Graft copolymerizations of synthetic as well as natural fibers with the aim of imparting specific, desirable properties are the main developments in macromolecular chemistry (1-3). The eliminations of some undesirable proprieties of silk such as photo – yellowing, crease recovery and weighting need to be improved by coating and / or grafting of vinyl monomers in order to compensate for the loss resulting from degumming (4-7).

In this article, we present the results of graft copolymerization of silk using both acrylic acid (AA) and / or glycidyl methacrylate (GMA) and their mixtures. Hydrogen peroxide /copper sulphate redox initiator is employed to induce polymerization. Factors affecting the polymerization process are studied and evaluated. Meanwhile Improving dyeing and weighting properties of silk are studied at the technological level.

2. Materials and Methods

2.1. Materials

Silk fabric was used after sericin was removed by conventional alkaline degumming, followed by washing with

distilled water and air drying. Glycidyl methacrylate (GMA), acrylic acid (AA), hydrogen peroxide, copper sulphate and methyl ethyl ketone were of laboratory grade chemicals. The dyes used were supranol Red G.W, supranol Blue BLW and Remazol Brilliant Blue.

2.2. Methods

2.2.1. Grafting Procedure

Graft copolymerization reaction was carried out on silk fabric in a medium containing the monomer, copper sulphate and hydrogen peroxide using fabric to liquor ratio 1:100. Erlenmeyer Stopper flask was used for this purpose. The flask containing all reaction media was placed in a thermostatic water bath at the desired reaction temperature ($30-80^\circ\text{C}$). The polymerization was allowed to proceed for different times ranging from 30 to 150 min. The reaction solution was shaken occasionally. The samples were then removed, washed well with warm water. Dilute solution of 2 gm/l of nonionic detergent was used to remove loosely adhered homopolymers, thoroughly washed and dried. The dried samples were washed repeatedly with methyl ethyl ketone till constant weight was obtained. Calculation of the percentage of homopolymer (HP), graft efficiency (GE %), graft yield (GY %) and the total conversion (T.C %) based on the dry weight were calculated as follows :

$$GY\% = [(W_g - W_o) \div W_o] \times 100$$

Where:

W_g : is the weight of grafted silk.

W_o : is the weight of ungrafted silk.

$$HP\% = (\text{dry weight of homopolymer} \div \text{weight of polymer}) \times 100$$

$$GE\% = [\text{weight of grafted polymer} / (\text{weight of grafted polymer} + \text{weight of homopolymer})] \times 100$$

$$TC\% = [(\text{weight of grafted polymer} + \text{weight of homopolymer}) / \text{weight of monomer}] \times 100.$$

2.2.2. Dyeing Techniques

(i) Acid Dyes

Dyeing was performed using an exhaustion method by immersing silk samples in a dye bath containing 2% (o.w.f) using fabric to liquor ratio of 1:100. The acidity of the bath was adjusted to pH 4 using acetic acid. The dyeing was started at 40 °C and the temperature was gradually increased up to 90 °C in one hour. The dyed samples were thoroughly rinsed with cold water, soaped at 50 °C for 30 minutes and finally dried at ambient conditions. Unfixed dye was extracted with 50 % dimethylformamide for 30 minutes at the boil.

(ii) Reactive Dye

Dyeing was carried out as mentioned before except that 10 % (o.w.f) Glauber salt was added and the pH was adjusted at 8.5.

2.2.3. Moisture Regain

The silk samples were conditioned at room temperature in desiccators containing a saturated solution of sodium nitrite for 4 days to acquire 63% relative humidity. The moisture regain (MR) was calculated as follows:

$$MR\% = [(W - W_o) \div W_o] \times 100$$

Where:

W is the weight of the conditioned silk.

W_o is the weight of the dry silk.

2.2.4. Crease Recovery

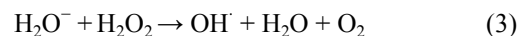
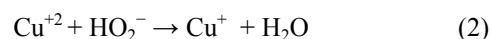
Crease recovery angles of silk were measured using the apparatus type FF (Metrimpex) for a creasing period of 10 minutes. Creasing angles were expressed as the sum of the crease recovery angle of warp (W) and weft (F).

3. Results and Discussion

3.1. Reactions Mechanisms

Previous reports (8-10) have disclosed that hydrogen peroxide together with metallic ions of Cu^{+2} forms a very effective system capable of initiating vinyl graft polymerization onto various macromolecules such as wool or cellulose. It appears of interest to establish the influence of such ions on grafting of silk fabrics with (GMA) and (AA) in

presence of hydrogen peroxide as initiator silk is presented by S-H and the monomer



The reaction mechanisms suggested by the above reaction scheme show that H_2O_2 is converted to OH^- and H_2O radicals in presence of Cu^+ when H_2O_2 is present in excess over Cu^+ ions (eq.1-3). The radicals attack silk macromolecules through abstracting hydrogen atom, thereby giving rise to silk macroradicals capable of initiating grafting of AA and /or GMA (eq.4). Also the grafting and homopolymer chains are propagated through addition of monomer molecules till termination step (eq.5-6). With the above mechanisms, it is obvious that silk, H_2O_2 , copper sulphate, monomer, water polymerization system will depend on various factors affecting the magnitude of graft yield, graft efficiency, homopolymer as shown from the following results and their discussions.

3.2. Initiator Concentration

3.2.1. Hydrogen Peroxide Concentration

Figure 1 (a & b) shows the influence of polymer yield % as a function of hydrogen peroxide concentration when (GMA) and (AA) were used. Obviously, the GY increases sharply initially to the maximum with increasing the concentration up to 0.078 meq/l and then decreases. It is a typical behavior observed in grafting processes occurring via chain transfer mechanism (11-12). This may be referred in grafting to the possibility of increasing silk macroradicals through the interaction of free radicals with the reactive groups of silk. However the higher concentrations of H_2O_2 will give more free radicals, as well as more homopolymer and the graft percentage will decrease as shown in reaction mechanism (Figure 1). The results of GE% display trends similar to those brought about the grafting formation which is observed to be the minimum at H_2O_2 concentration 0.078 meq /l then increases gradually.

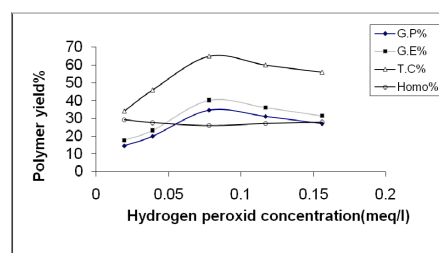


Fig. 1(a). Effect of hydrogen peroxide concentration on the polymer yield % of grafted silk using glycidyl methacrylate.

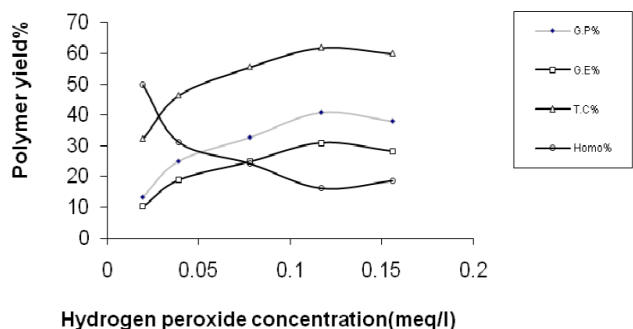


Fig. 1(b). Effect of hydrogen peroxide concentration on the polymer yield of grafted silk using acrylic acid as monomers

Conditions: 5% GMA (owf), reaction time 1 hr., temperature 80 °C, liquor ratio 1:100, copper sulphate 6 mmol/l.

Conditions: 5% AA (o. w. f), time 1 hr., temperature 80 °C, liquor ratio 1:100; copper sulphate 6 mmol/l.

3.2.2. Copper ion Concentration

Figure 2 (a & b) shows the dependence of the polymer yield as a function of increasing initiator concentration of Cu^{+2} ions in the free radical polymerization medium for grafting GMA and AA onto silk fibroin. It is obvious that the graft yield increases by increasing Cu^{+2} ion concentration up to 5 mmol/l. Thereafter the graft yield decreases as Cu^{+2} ion concentration increase. In case of GMA the increase in grafting could be associated with the increase decomposition of H_2O_2 to yield HO_2^- radicals which may be involved in the initiation of grafting (13) and to the increase in the number of free radicals formed on silk backbone. On the other hand, the decrease in graft yield by increasing Cu^{+2} ion concentration could be explained to the fast termination process. Figure 2 (a, b) revealed that the homopolymer exhibit an opposite trend to graft yield as well as the graft efficiency and total conversion are similar to that of grafting.

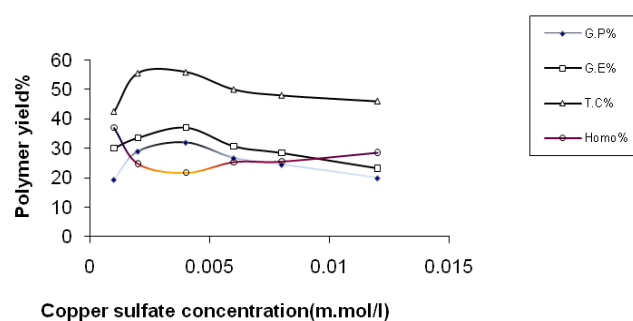


Fig. 2(a). Effect of copper sulphate concentration on the polymer yield of grafted silk using GMA monomer

Conditions: 5% GMA (o.w.f), 0.078meq / l of hydrogen peroxide, time 1 hr., temperature 80 °C, liquor ratio 1:100.

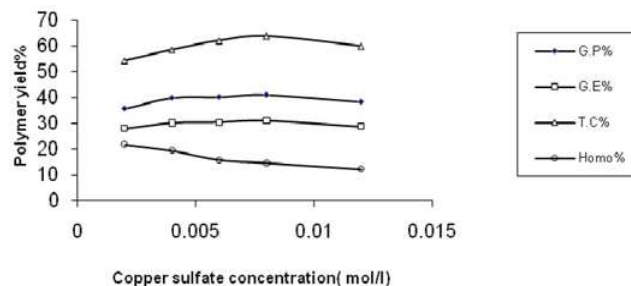


Fig. 2(b). Effect of copper sulphate concentration on the polymer yield of grafted silk using AA monomer.

Conditions: 5%AA (o.w.f), 0.078 meq/l of hydrogen peroxide, time 1 hr., temperature 80 °C, liquor ratio 1:100.

3.3. Monomer Concentration

Figure 3 (a, b) shows the polymer yield percentage versus the monomer concentration when GMA and AA were used as monomers. With both monomers the results, show that increasing the monomer concentration is accompanied by a substantial increase of grafting where the graft yield decreases as monomer concentration increases. This can be referred to the depletion in monomer and initiator concentrations as well as reduction in the available sites for grafting on silk backbone as the reaction proceeds. The figure shows also that the homopolymer decreases with increasing both monomer GMA and AA.

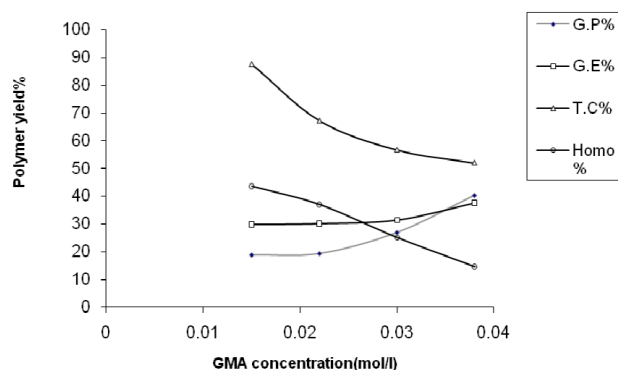


Fig. 3(a). Effect of GMA concentration on the polymer yield % of grafted silk.

Conditions: Hydrogen peroxide 0.078 meq / l, copper sulphate 5 mmol/l, time 1 hr., temperature 80 °C, liquor ratio 1:100.

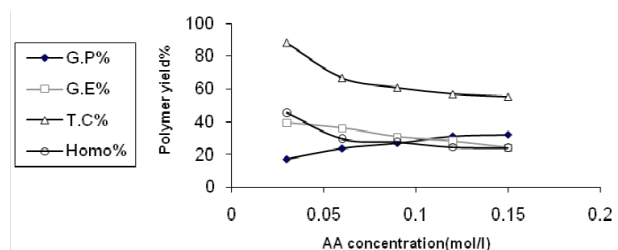


Fig. 3(b). Effect of acrylic acid concentration on the polymer yield % of grafted silk.

Conditions: Hydrogen peroxide 0.078 meq /l, copper sulphate 5 mmol/l, time 1 hr., temperature 80 °C, liquor ratio 1:100.

3.4. Polymerization Temperature

The grafting of GMA and AA into silk was performed at various temperatures (30 - 80 °C) and the results obtained are presented in Figure 4 (a, b). It is obvious that the graft yield increases by raising the polymerization temperature from 30 °C to 70 °C for GMA and from 30 °C to 60 °C for AA. Further increase in the reaction temperatures lead to decrease in the graft yield. The increase in grafting by raising the temperature could be associated with the increase in the number of free radicals formed in the silk backbone and increase in propagation of grafting. Also, there is an increase in the mobility of monomer molecules and there collision with silk macroradicals (14).

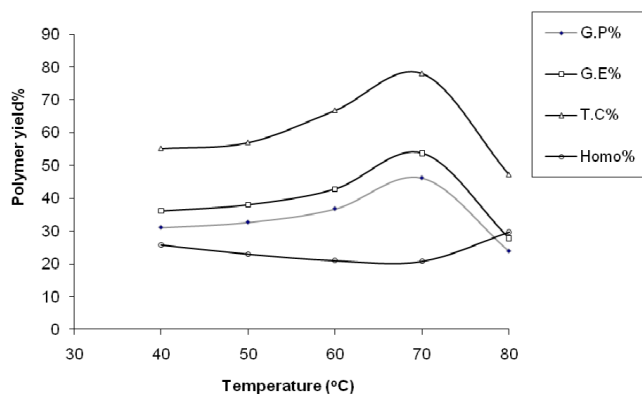


Fig. 4(a). Effect of temperature on the percentage polymer yield of grafted silk using GMA monomer.

Conditions: 5% GMA; hydrogen peroxide 0.078 meq/l; copper sulphate 5 mmol/l; time 1 hr. and liquor ratio 1:100.

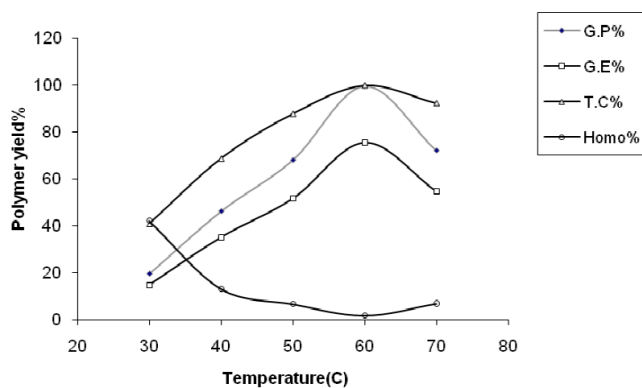


Fig. 4(b). Effect of temperature on the percentage polymer yield of grafted silk using AA monomers.

Conditions: 5% AA ; hydrogen peroxide 0.078 meq/l, copper sulphate 5 mmol/l, time 1 hr. and liquor ratio 1:100.

3.5. Polymerization Time

Figures 5 (a, b) show the percentage polymer yield as a function of duration of polymerization. It is seen that the

percentage polymer yield increases in case of GMA by prolonging the duration of polymerization within the range studied. It is expected that the homopolymer tends to decrease after about 45 min. This indicates that the polymerization time exert a favorable effect on grafting and consequently on the grafting efficiency. In case of AA there is a tendency for the graft to decrease by increasing the time of contacts and namely the monomer to the silk. As a result the polymer yields decrease. This includes the trend observed with grafting.

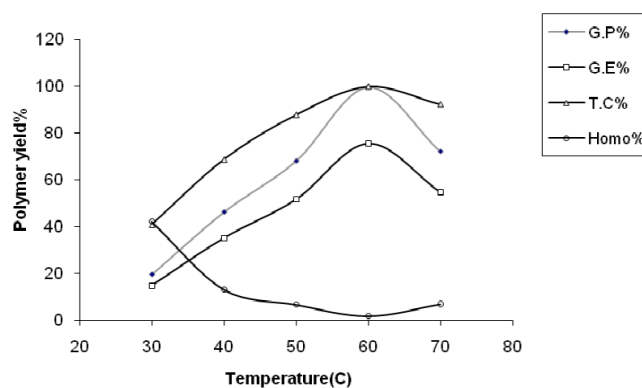


Fig. 5(a). Effect of duration on the polymer yield of grafted silk using GMA monomer.

Conditions: 5% GMA; hydrogen peroxide 0.078 meq/l ; copper sulphate 5 mmol/l and liquor ratio 1:100.

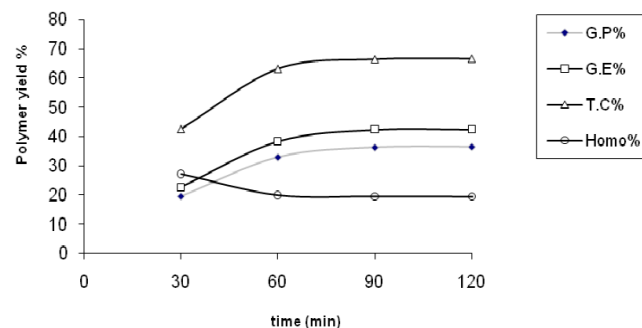


Fig. 5(b). Effect of time on the percentage polymer yield of grafted silk using AA monomer.

Conditions: 5% GMA; hydrogen peroxide 0.078 meq/l; copper sulphate 5 mmol/l and liquor ratio 1:100.

3.6. Effect of GMA/AA Mixture on the Percentage Grafted Yield

Based on the investigation observed, it may be concluded that the most appropriate conditions for GMA graft copolymerization onto the silk fabrics comprise H_2O_2 0.078 meq /l, copper sulphate 5 mmole/L, GMA 0.03 mol/l at 60 °C for 60 min. and the material to liquor ratio 1:100 which are employed. The application of GMA /AA mixture of monomers onto silk fabric was used to obtain silk with different graft yields. Table 1 show that the extent of increased grafting depends on the ratio of AA in monomer ratio with GMA. This may be assumed to presence of

epoxide ring in acidic medium and its change to hydroxyl group leading to increase graft yield.

Table 1. Effect of GMA /AA mixture on the percentage graft yield on Silk fabrics

GMA/AA ratio (mol/l)		GP %	GE %
GMA	AA		
0.03	-----	19.44	22.7
0.03	0.03	24.9	14.5
0.03	0.06	28.9	13.5
0.03	0.09	46.9	11.1

3.7. Dyeing Properties

3.7.1. Effect of Percentage (GMA) Grafted onto Silk Dyeability with Remazol Dye by Alkaline Method

Table 2 and Figure 6 show the epoxy content the exhaustion and the fixation percentage of Remazol dye in alkaline medium onto silk sample grafted with GMA. It is evident that the grafted samples are much accessible to dyeing than untreated samples. This can be attributed to the lower stability and ring opening with alkaline media occur or via addition of H₂O molecules to the free epoxy ring according to the typical S_N² mechanism (15).

Table 2. Effect of grafted polymerization of GMA with silk on fixation of Remazol Brill Blue 3R dye

Polymer addition based on increase in weight %	Calculated epoxy content based on increase in weight mol epoxy /100g	Fixation of Remazol Brill Blue 3R in alkaline medium
-	-	71.6
14.5	0.131	73.2
23.88	0.168	74.8
32.44	0.172	81.2
54.08	0.247	89.1
72.1	0.275	94.3

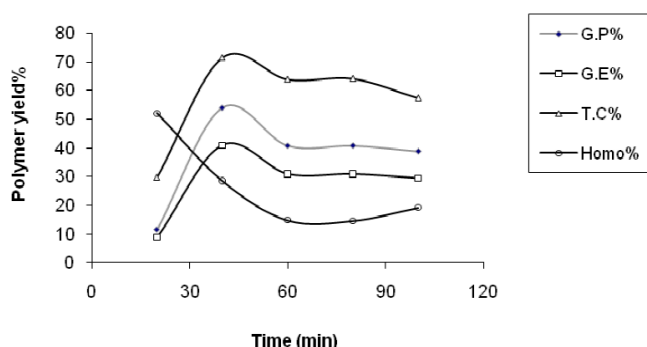
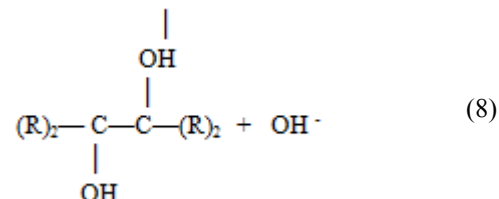
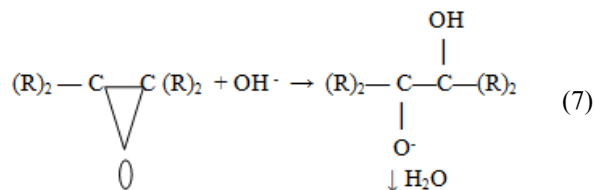


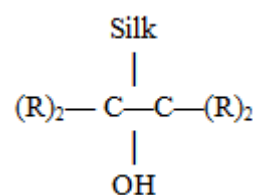
Fig. 6. Effect of grafted silk using GMA on dyeability with Remazol Brill Blue 3R dye

3.7.2. Acid Dyes

Table 3 and Figures 7, 8 show epoxy content, percentage exhaustion and fixation of acid dyes obtained on grafted silk



Equation 8 is the fast, so it is reasonable that silk ion is substituted for OH ion and the reaction represent as follows



with poly GMA and the control, when they are dyed with acid dyes. In dyeing silk with acid dye, the dye molecule attached to silk by ionic bonds, but it observed from the study with both acid dyes that the exhaustion increases by increasing the time. In case of polyGMA grafted silk the same trend is also observed compared to control, but the latter shows a much slower rate of dyeing. This is due to the introduction of epoxide group into silk fibroin molecules in acidic medium of pH 3 and the change of epoxide group to hydroxyl group causing an increase to positive silk surface potential. As a result the capability of grafted silk to absorb dye is increased. This reflects the effect of the nature of the dye and its affinity for silk fibroin. It appears that higher grafting polymer chains open up the silk structure. The rate of dyeing is also depending on the nature of dye, higher rate was found with both Supranol Blue B.L.W and Supranol Red G.W.

Table 3. Effect of GMA graft polymerization with silk for fixation of acid dyes.

Polymer addition based on increase in weight %	Calculated epoxy content based in weight mol epoxy /100g	Fixation of acid dyes	
		Supranol Red G.W	Supranol Blue B.L.W
-	-	64.4	70.2
19.5	0.121	70.1	76.1
23.88	0.134	72.2	77.8
32.44	0.172	76.2	78.2
54.08	0.247	81.3	82.8
72.1	0.275	89.8	92.1

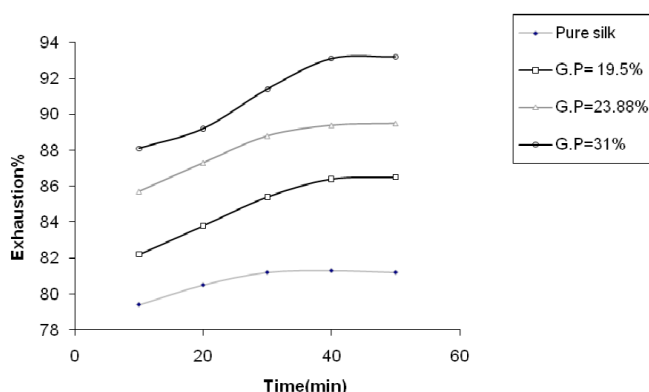


Fig. 7. Effect of grafted silk using GMA on dyeability with Supranol Red G.W

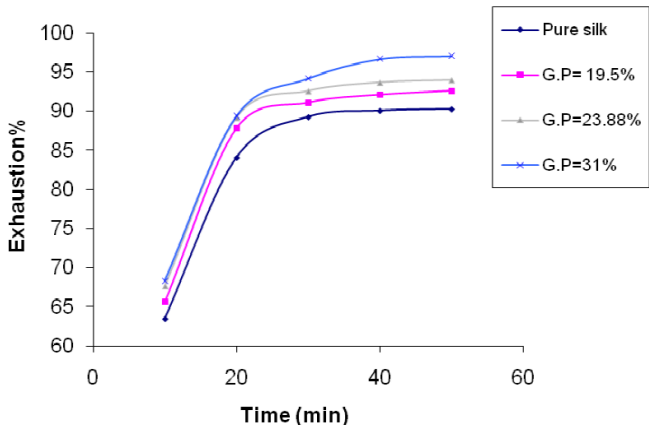


Fig. 8. Effect of GMA grafted silk on dyeability with Supranol BlueB. L. W

3.8. Crease Recovery Angle

The samples that were used in the study are given in Table 4, from these results it is clear that grafted samples exhibit higher dry crease recovery than untreated samples. Differences in the application conditions seem to be responsible for the presence of poly (GMA) and poly (AA) graft copolymers which induce stabilization of the fabric in the dry state by virtue of involvement in reaction of silk and provide the fabric with the observed extra dry crease recovery.

Table 4. Effect of application of poly (AA) and poly (GMA) and their mixture grafting copolymers on the crease recovery angle (CRA) and the moisture regain properties of silk fabric.

Sample	(F°)	(W°)	C.R.A (F°+ W°)	Moisture regain %
Blank (untreated silk)	106	127	233	10.6
GMA/Silk (19.5%)	129	135	264	9.6
GMA/Silk (23.88%)	136	140	276	8.8
GMA/Silk (31%)	157	162	319	7.3
AA/Silk (19.4%)	130	141	271	11.6
AA/Silk (25%)	144	156	300	14.1
AA/Silk (28.9)	158	160	318	15.7
GMA/AA/Silk (1:1)	127	139	266	10.9
GMA/AA/Silk (1:2)	155	160	315	11.3
GMA/AA/Silk (1:3)	159	165	324	12.1

3.9. Moisture Regains

Water content is an important physical parameter together with other factors, which can significantly influence the behavior of silk (i.e. comfort, crease recovery, etc.). Changes in percentage moisture regain induced on silk via grafting with GMA, AA and their mixture were studied as a function of weight gain. The relative humidity of silk is 11% but it is observed from Table 4 that grafting of GMA onto silk decreases the moisture regain to 7.3% or 31% GP. This may be attributed to addition of more hydrophobic poly (GMA) chains on fiber surface which limit the chemical and physical interactions with silk fibroin chains at the boundary contacts. Poly (AA) is hydrophilic in nature and enhances moisture absorption demonstrated by positive slope of the curve, whereas the intermediate properties of poly GMA/AA mixture do not significantly influence the balance of absorbed moisture.

4. Conclusion

The results reported in this work indicated that acrylic acid and glycidyl methacrylate or their mixture could be successfully grafted onto silk using $\text{Cu}^{+2}/\text{H}_2\text{O}_2$ redox system. The grafting degree can be turned by altering monomer, initiator concentration and reaction time.

The physical properties of silk were improved by grafting including crease recovery angle, moisture regain and dyeability as compared to the untreated one.

References

- [1] Hu C., Yejuan T. & kai S. Easy-care finishing of silk fabrics with a novel multifunctional epoxide. Part 2. *J. Soc. Dye. & col.* 116 (2000) 204-207.
- [2] Zaisheng C. , Guochuan J. & Shaojun Y. Chemical finishing of silk fabric. *Caloration Technology*.117 (2001) 161-165.
- [3] Tsukada M., Arai T., Freddi G, Imai T. & kasai N. Grafting Vinyl Monomers Onto Silk Using Different Initiators: Properties of Grafted Silk *J.Appl.Polym.Sci.* 81 (2001) 1401-1409.
- [4] Kawahara Y., Shioya M. & Takaku A. Effects of non-formaldehyde finishing process on dyeing and mechanical properties of cotton fabrics. *Am. Dyest. Rep.* 85 (1996) 88.
- [5] Das A., Saikia C.N. & Hussaain S. Grafting of methyl methacrylate (MMA) onto *Antheraea assama* silk fiber. *J Appl. polym. Sci.* 81 (2001) 2633-2641.
- [6] Tsukada M., Imai T., Freddi G, Lenka S. & Kasai N. Grafting of vinyl Monomer onto Silk Using Redox System. Yellowing of Silk. *J.Appl.Polym.Sci.* 69 (1998), 239-246.
- [7] Bendak A., Abdel-Fattah S.H. & Hebeish A. Graft Copolymerization of Vinyl Monomer Onto Wool Fibers. *Die AngewMakro.* 43 (1975) 11-25.
- [8] Steitn H. H. & Guarnaccio J. Infrared Study of Oxidized Keratin *Text. Res. J.* 29 (1959) 492-496.
- [9] Hebeish A. & Bendak A. Redox-initiated vinyl graft polymerization onto wool with thiourea as the reductant. I. Grafting of methyl methacrylate with the hydrogen peroxide–thiourea catalyst system. *J. Appl. Polym. Sci.* 18 (1974) 1305-1317.
- [10] EL-Rafie M.H., Khalil M.I. & Hebeish A. Graft Copolymerization of vinyl Monomers on Modified Cotton, *Die Angew.Makromol Chem* 37(1974) 149-160.
- [11] Patel A. C., Brahmabhatt R. B., Jain R.C. & Devi S. Grafting of 2-HEMA on IPP and *in situ* chlorinated PP through solution polymerization *J. Appl.Polym.Sci.* 69 (1998) 2107-2113.
- [12] Hebeish A. & Bendak A. Redox-initiated vinyl graft polymerization onto wool with thiourea as the reductant. I. Grafting of methyl methacrylate with the hydrogen peroxide–thiourea catalyst system. *J. Appl. Polym.Sci.* 18 (1974) 1305-1317.
- [13] Tsukada M. & Freddi G. Absorption of metal cations by modified mori silk and preparation of Fabrics with Antimicrobial Activity. *Polym.Material Encyclopedia* 10 (1996) 7728.
- [14] Harris J.A. & Arthur J.C. Single Dye bath Application of Direct, Acid, and Basic Dyes to Cotton-Poly (Glycidyl Methacrylate) Fabrics. *Text. Res. J.* 46 (1976) 219-223.
- [15] Hamerton. I. Recent Developments in Epoxy Resins. Smithers Rapra Publishing (1996)176 pp.