Continuous grafting of acrylic acid on mulberry silk for multifunctional effect

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Abstract - ***Grafting of acrylic acid onto silk fabric was successfully carried out using pad-cure technique in the presence of potassium persulphate (KPS). The various parameters of grafting were optimized to get highest graft add-on. Grafted silk was characterised by FTIR, SEM and TGA analysis. The modified silk showed enhanced cationic dyeability which may be attributed to newly introduced acrylic acid graft chains. The grafted samples showed increase in crease recovery angle (CRA) at optimized graft add-on (2.75%). The grafted samples also showed increase in moisture regains, although bending length and tensile strength showed adverse effects of grafting. Modified silk showed 100 times decrease in electrical resistivity when compared to that of ungrafted sample. Thus treated fabric showed enhancement in comfort. The success of this pad-cure technique of grafting has opened the possibility of continuous grafting.***

Key Words: *Silk, Continuous grafting, Acrylic acid, Dyeability, Crease recovery angle, Electrical resistivity.*

1. INTRODUCTION

Consumer demand of functional polymers is increasing day by day and industries want advanced functional polymer either in form of new fibres or by modification of existing ones. Grafting is a well-established technique used to cause more or less extensive modification of properties and textile performance of silk, as well as other natural and synthetic fibres [1, 2]. Over the centuries silk has been high valued fibre for its luxurious and asthetic looks, lusture, smoothness, comfort to handle, moisture regain and comfort to wear [3, 4, and 5]. With all these properties, it has some limitations towards photo yellowing, crease recovery, tensile strength, dimensional stability, etc [6, 7, and 8]. These limitations of silk fibres can be improved by modification through various processes like, surface modification, chemical modification, UV treatments, beam irradiation, plasma treatment, etc [4]. Chemical modification of natural fibres through graft copolymerization is an effective method to incorporate useful properties to the main polymer backbone [9]. Many researchers had worked on grafting of vinyl monomer onto silk with different redox initiators. These vinyl monomers are very useful to enhance its properties such as, crease recovery, water repellency, oil repellency, moisture regain, dyeability, tensile strength, etc [5, 10]. The grafting of acrylamide on muga silk was reported by many researchers where it showed increase in tensile strength after grafting [8]. Grafting of acrylic acid and acrylamide on bamboo rayon fibre improved its dyeability towards cationic and acid dye [11, 12]. Grafting of bifunctional vinyl monomer diethylene glycol dimethacrylate (EGDMA-2) onto silk backbone in the presence of potassium persulphate (KPS) initiator increased its crease recovery property [5]. The researchers have also worked on continuous grafting by using different techniques like photo initiation, electron beam irradiation, UV initiation, plasma, dip pad, etc [13, 14, 15, 16].Continuous grafting of polypropylene in inert atmosphere with 2-hydroxyethyl methacrylate (HEMA) with benzophenone as photoinitiator was also reported. A graft yield of 30% was observed with increase in initiator concentration [17]. Continuous grafting through plasma, on cotton fabric has been carried out successfully [15]. However, in case of silk, continuous grafting using chemical initiation technique has so far been not reported.

In current research work, grafting of acrylic acid is successfully carried out onto silk fabric by pad cure method in the presence of KPS initiator. This technique has scope to convert it into continuous. The characterisation of the various grafted silk has been done and its properties such as crease recovery angle, tensile strength, moisture regain, dyeability towards cationic dye and electrical resistivity of acrylic acid grafted silk have also been investigated.

2. Materials and methods

2.1 *Materials*

Bleached plain weave silk fabric (EPI-110, PPI-115, GSM-40) was supplied by Adive Pure Nature (Mumbai). Non-ionic detergent, Auxipon NP was supplied by Auxichem Ltd., Mumbai. Acrylic acid of laboratory grade was supplied by S D fine Chem Ltd., Mumbai. Potassium persulphate ($K_2S_2O_8$) initiator was supplied by Molychem pvt. Ltd., Mumbai. Acetic acid was supplied by Rankem pvt. Ltd. Coracryl Red C4G SUPRA provided by Colourtex Industries Ltd., Astrazon Blue F2RL 200% and Astrazon G. Yellow GL-E 200 cationic dyes were provided by Dystar Pvt. Ltd. All the chemicals used were of Laboratory grade.

2.2 Methods

2.2.1 *Preparation of fabric*

Although the fabric was supplied as bleached material it was treated with 2gpl Auxipon NP solution (non-ionic soap) at 80 $^{\circ}C$ for 15 minutes to make it free from any dirt, oil stains during handling. The fabric was then rinsed with cold water and was dried at room temperature.

2.1.3 Grafting

Silk fabric was padded with solution containing the required concentration of monomer (acrylic acid) and initiator (15 gpl KPS) with 75± 1% expression using two bowl vertical padding mangle and was then cured. The parameters were varied in order to study the optimization of the reaction parameters. After completion of padding and curing process, the treated fabric was washed with hot water at 95 $^{\circ}C$ in continuous washing range for 10 minutes to remove the homopolymers. The graft add-on was calculated using the following formula;

Graft add on (%) = $$\frac{W_2 - W_1}{W_1} X\ 100$$

Wherein, W_1 and W_2 were the weight of ungrafted and grafted fabric respectively.

3. Characterization of grafted product

Analysis of both ungrafted and grafted silk was done by the following methods.

3.1 FTIR analysis

The FTIR spectra of original and grafted silk samples were recorded using FTIR spectrophotometer (Shimadzu 8400s, Japan) using ATR sampling technique by recording 45 scan in %T mode in the range of 4000-600cm^{-1}.

3.2 Thermo gravimetric analysis (TGA)

The thermo grams of grafted and ungrafted silk fabric samples were recorded using aluminium pan between temperature range 27 to 500 $^{\circ}C$ and under inert atmosphere of N_2 at a flow rate of 50 ml/min Shimadzu 60H DTG machine.

3.3 Scanning electron microscopy (SEM)

Analysis of the morphology of dried silk and grafted silk were carried out using scanning electron microscope (JEOL, Japan), from Institute of Chemical Technology. The samples were sputter coated with gold layers and images were recorded using scanning electron microscope

3.4 Measurement of textile properties

3.4.1 Moisture regain

The moisture regain was determined by using vacuum desiccator method with sodium nitrite to give 65% RH at 21± 1^{o}C. The increase in weight of sample over control due to moisture was calculated using the formula

Moisture regain (%) = $$\frac{M_2 - M_1}{M_1} X\ 100$$

Where M_1 and M_2 were weight of oven dry sample and conditioned sample respectively.

3.4.2 Tensile strength

Tensile strength of finished fabric was evaluated using ASTM D-5035, raveled strip test method (ASTM standards manual). Specimen dimensions was kept as width 25 mm, length 150 mm, gauge length 75 mm, actual testing width 25 mm and Loading rate 300 mm/ mins.

3.4.3 Bending length

In order to estimate the stiffness of the fabric, its bending length was measured by ASTM D-1388 (ASTM standards manual) method using Shirley stiffness tester machine [Rossari Labtech, India].

3.4.4 Crease recovery angle (CRA)

The crease recovery angle was measured by ASTM D-1296 method (ASTM standards manual) using Shirley's crease recovery tester machine [Rossari Labtech, India].

3.4.5 Electrical resistivity

Volume and surface **e**lectric resistivity of grafted silk fabric was measured by ASTM D-257 using Keithley 8009, method for electrical resistivity measurement.

4. Results and Discussion

4.1. Mechanism of grafting

The tentative mechanism of the free radical graft copolymerization of acrylic acid (AA) as vinyl monomer, and polypeptide chain of silk fibre (Silk-OH), as a substrate in the presence of potassium persulfate ($K_2S_2O_8$) as initiator is given below.

The mechanisms of grafting reactions are as follow:
Decomposition of potassium persulphate ($K_2S_2O_8$)

$$S_2O_8^{2-} \xrightarrow{\Delta} 2\,SO_4^{*-}$$

$$2\,SO_4^{*-} + H_2O \xrightarrow{\Delta} HO^* + HSO_4^-$$

$$2\,HO^* \longrightarrow H_2O_2 + 1/2\,O_2$$

These free radical species (R*) are capable of initiating the following reactions

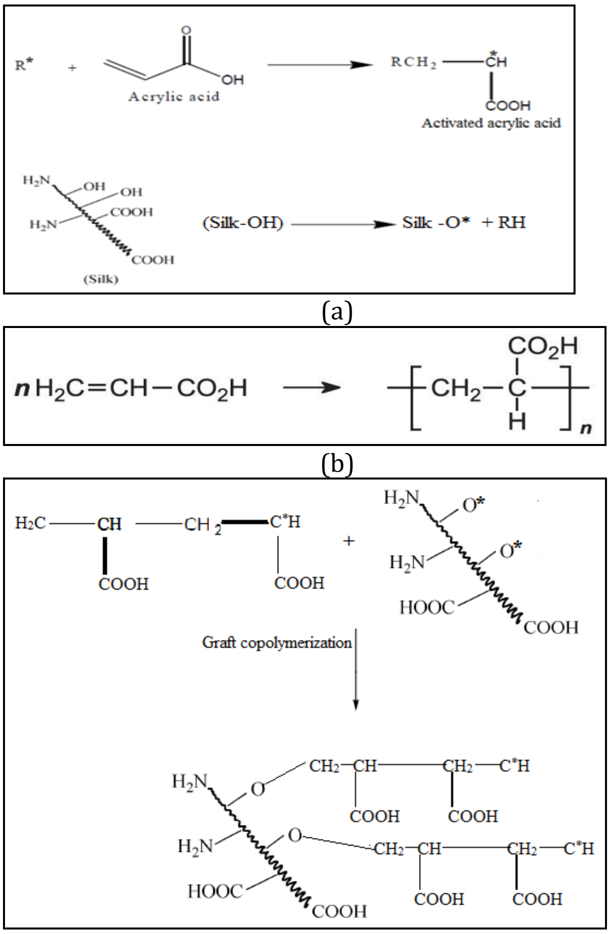


Figure 1: (a) Initiation reactions of acrylic acid and silk fibre chain, (b) Homo polymerization reaction and (C) Acrylic acid grafted silk

Optimisation of grafting of AA onto silk was carried out for temperature, time and concentration of monomer.

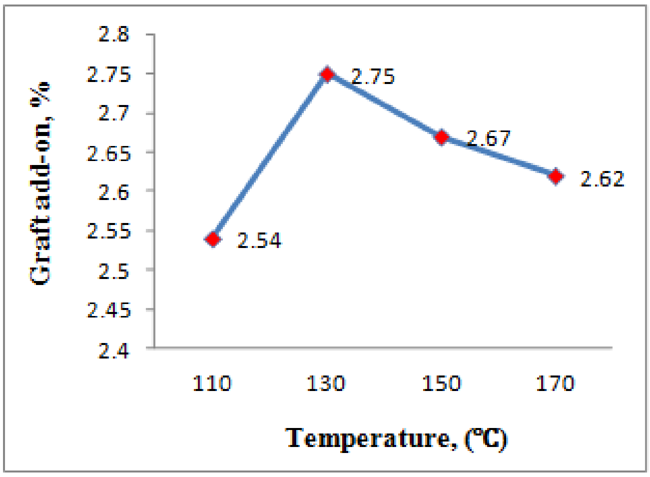


Figure 2 Effect of temperature on grafting at 100 gpl monomer and 5 minutes of curing

Effect of temperature

Results from Figure 2 indicate that with increase in curing temperature up to 130°C the graft add-on also increased. This is due to the increase in rate of dissociation of initiator and formation of active free radicals which enable more amount of AA getting grafted on silk fibre. However, beyond 130°C, the temperature adversely affected the grafting causing more homopolymer formation. At higher temperature growing homopolymer chain radicals rather than reacting with free radical sites on silk polymer backbone combine together forming bigger molecules of homopolymer, leading to lowering in graft yield.

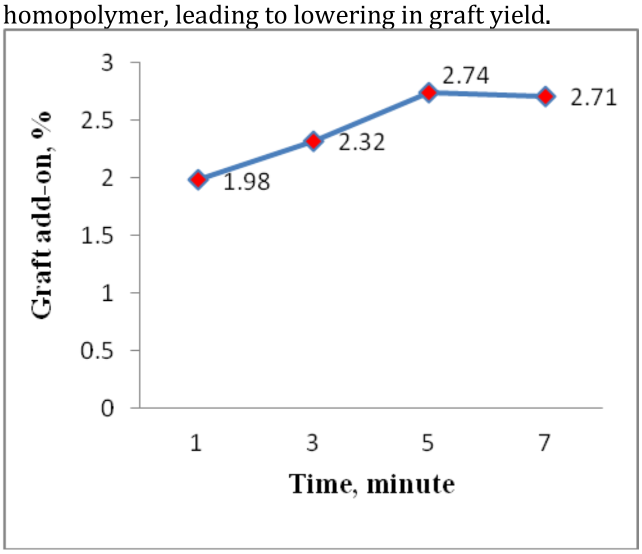


Figure 3 Effect of time on graft add-on %, at 130 °C temperature and 100 gpl Monomer (AA)

Effect of time on grafting

Results in Figure 2, indicate that with increase in time of curing from 1 to 5mins, the graft add-on also increased which was obvious as more amount of AA could react with polymer backbone. Grafting reaction seemed to have reached a plateau after 5mins and hence no further increase in graft add-on was observed even at curing time 7min. This reaction time of 5min was found to be appropriate and optimum.

Effect of concentration of acrylic acid

In order to avoid wastage of monomer (AA), it is necessary to optimize monomer feed for cost effective grafting. **Figure 3** shows that graft add-on significantly increased initially with increase monomer concentration from 50 gpl to 100 gpl. However increase in graft add-on due to increase in monomer concentration was not very significant. This may be attributed to the fact that at higher concentration of monomer, greater number of monomer molecules becomes available for combination with the free radical on the backbone of the polymer chain and thus formation of homopolymers of AA. Hence 100gpl concentration of AA was found to be optimum for continuous grafting of acrylic acid onto silk.

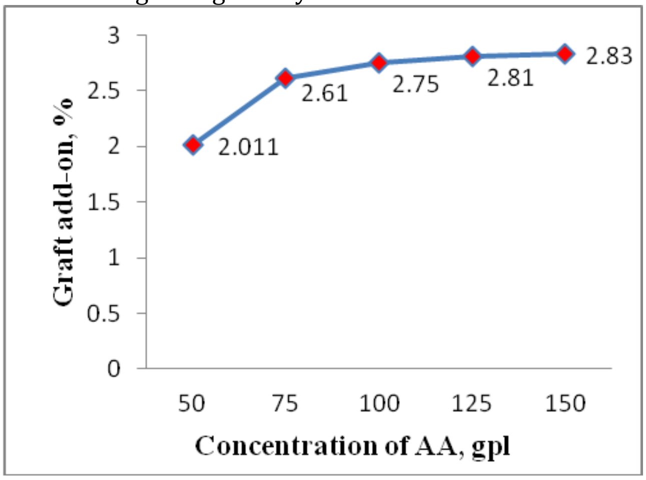


Figure 4 Effect of concentration of monomer (AA) on grafting at 130 °C temperature and 5 minutes of curing

FTIR analysis

The silk fabric grafted with acrylic acid (AA-g-Silk) was characterized in order to confirm grafting of AA onto silk polymer. In **Figure 5** the FTIR spectrum (A) of ungrafted silk shows the absorption bands at 1512 and 1620 cm^{-1} confirming C=O stretching of amide I and amide II respectively. The peaks at 2931 and 3292 cm^{-1} are attributed to the C-H stretching and N-H stretching deformation respectively.

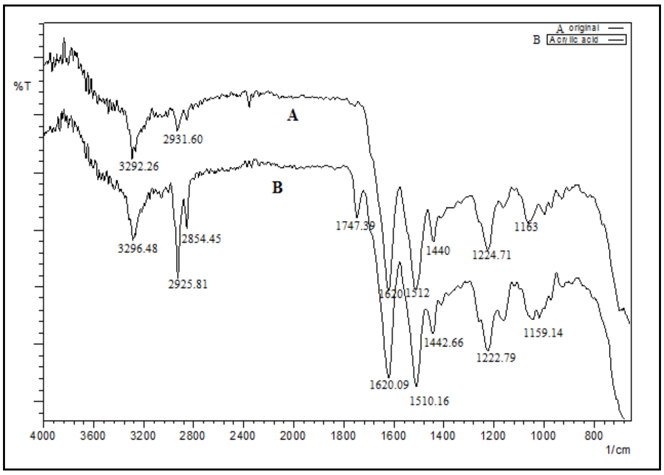
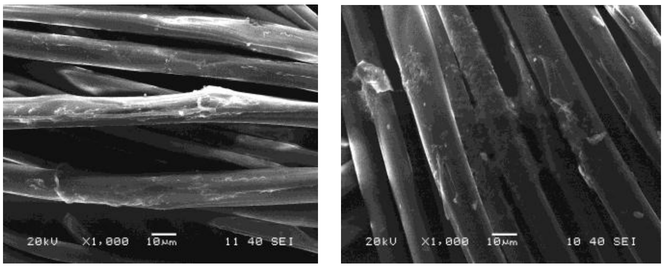


Figure 5 FTIR spectra of Original silk and Acrylic acid grafted silk

In case of spectrum (b) for grafted silk, it revealed new absorption band of AA-grafted silk at 1747 cm^{-1} caused by C=O stretching of carboxylates ($-COO^{-}$) functional group, confirming introduction of polyacrylic acid on to silk backbone.



(A) (B)

Figure 6 Scanning electron micrographs of ungrafted silk (A) and AA-grafted-silk (B)

SEM analysis

From Figure 6, it is clear that the presence of AA graft polymer deposits on silk is apparent in case of AA grafted silk.

TGA analysis

In **Figure 7**, the thermogram of ungrafted and grafted silk samples is shown. 10% weight loss was seen at 272 °C for ungrafted silk and 262 °C for grafted silk respectively.

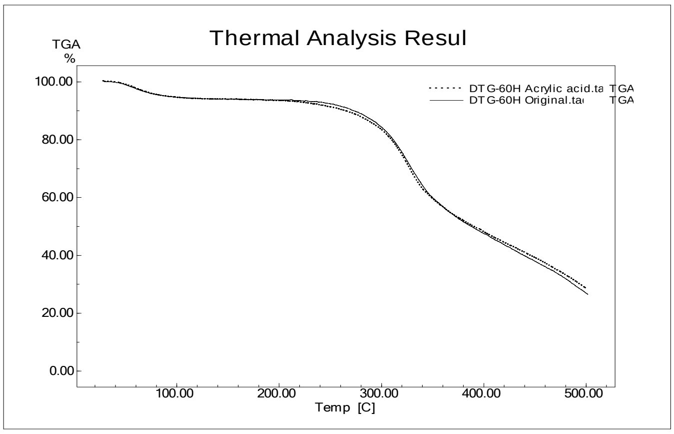


Figure 7 Thermogram analysis of Original (control) silk and AA-grafted-silk

In the range of 200°C to 388°C thermal stability of grafted silk slightly decreased as compared to the ungrafted one. Drastic decomposition of the samples resulted into the significant weight loss which was 73.08% for ungrafted and 71.47% for grafted silk fabric between 260- 500°C Ingenral there has not been any significant effect on thermal decomposition properties on the grafted silk fabric.

Effect of grafting on textile properties of silk

Mechanical properties of grafted silk may get affected considerably by the parameters used during grafting like high temperature, prolonged time of curing and higher concentration of monomer (AA). The mechanical properties of grafted silk are summarized in Table 1. It was found that with increase in graft add-on, 22.17% increase in moisture regain occurred for optimum level grafted sample. Moisture regain is an important physical parameter and can significantly influence the functional behaviour of silk (i.e., comfort, crease recovery, etc.). This improvement in moisture regain was due to incorporation of acrylic acid in molecular structure of silk substrate during grafting as Polyacrylic acid is hydrophilic in nature [18].

Table 1: Effect of graft add-on on textile physical properties

Sr. No.	Graf add on %	Moisture regain (%)	Tensile strength (kgf)	CRA (⁰)	Bending length (cm)
*UG	0.00	9.29	16.68	214	1.75
1	1.98	9.91	15.80	265	1.78
2	2.011	10.28	15.80	266	1.85
3	2.32	10.69	15.78	269	1.82
4	2.54	10.76	15.02	271	1.88
5	2.61	10.85	15.34	273	1.87
6	2.67	11.01	14.19	275.5	1.90
7	2.75	11.35 **(+22.17)	15.29 (-8.33)	282 (+31.77)	1.92 (+9.71)
8	2.83	11.44 (+23.14)	13.75 (-17.5)	284.5 (+32.9)	1.95 (+11.42)

*UG- Ungrafted silk fabric and ** (change %)

The tensile properties were found to be negatively influenced by extent of grafting. Tensile strength thus decreased with increased in graft add-on which might have been resulted due to increase in acrylic acid. The increase in interlocking of graft chains creating cross linked like of structure was responsible. At optimized parameters of temperature, time and concentration for graft add-on level of 2.75% and tensile strength loss was 8.33% which was well within acceptable limit (refer table 1). Intrinsic tensile properties of silk have been reported to be influenced by grafting as a result of various physicochemical and morphological changes. Selective anchoring and cross linking of grafted AA, poly AA chains created weak spots while fabric was tested for tensile strength. As grafting took place in the amorphous region, it restricted chain mobility, thus causing decline in the load at break and elongation at break. Possibility of some cleavage of covalent bonds at such high temperature curing may not also be ruled out [18].

The crease recovery behaviour is one of the weak points of silk fabrics which should be improved. From Table 1 it can be seen that the crease recovery angles increased with increasing graft add-on. Grafting reaction results in deposition of side chain on the silk backbone consuming the hydroxyl groups and thereby reducing the formation of H-bond between them to form crease and hence increase the ability of fabric to recover from the crease. Generally, the crosslinking between fibre molecules can reduce or prevent fibres from slippage and achieve an improved crease resistance. The interlocking graft chains and creating crosslinked kind of structure which also decreased tensile strength, was obviously responsible for increase in CRA. At optimized graft add-on (2.75%), CRA increased by 31.77%. The bending length also increased by 9.71% with increase in graft add-on (2.75%) which obvious due to slight addition in the stiffness after grafting of AA on silk fabric.

Effect of Grafting on Cationic Dyeing of modified silk fabric

The ungrafted and grafted silk fabrics were dyed with cationic dyes namely Coracrylic Red C4G SUPRA (C.I. Basic red 14), Astrazon Blue F2RL 200% (C.I. Basic blue 14) and Astrazon G. Yellow GL-E 200% (C.I. Basic yellow 28) in rota dyeing machine.

The acrylic acid grafted silk was studied for its dyeability towards cationic dyes. Results are summarized in Table 2, indicate that colour strength (K/S) increased with increase in graft add-on. This was due to grafting of acrylic acid on silk which increased the number of COOH groups available on silk for cationic dye adsorption. The optimised grafted sample (with graft add-on 2.75%) showed the increase in colour strength, compared to ungrafted silk by 259.09% for Coracrylic Red C4G SUPRA dye.

Table 2: Effect of grafting on dyeing properties with cationic dyes

Graft add-on (%)	K/S	L*	a*	b*	Washing fastness		Rubbing fastness		Light fastness
					C	S	Dry	Wet	
Cationic dye used- Coracrylic Red C4G SUPRA (λ_{max}- 530 nm)									
0.00	4.09 (0.00)	62.00	66.40	2.05	4	4	4-5	4	4
1.98	11.49 (+180)	60.34	66.55	-1.77	4-5	4-5	4-5	4	4-5
2.01	11.64 (+184)	60.12	66.82	-2.54	4-5	4-5	5	4-5	4-5
2.32	12.95 (+216.6)	60.79	66.98	-2.07	4-5	4-5	5	4-5	5
2.54	14.38 (+245.6)	60.13	66.54	-1.92	4-5	4-5	5	4-5	5-6
2.61	14.38 (+251.6)	61.90	65.23	-2.74	4-5	4-5	5	4-5	5-6
2.71	14.53 (+255.2)	58.00	65.45	-2.05	4-5	4-5	5	4-5	6
2.75	14.69 (+259.2)	57.09	65.67	-2.14	4-5	4-5	5	4-5	6

* (change in K/S, %)

The effect of other cationic dyes and their shades (0.5, 1 and 2%) on dyeability of modified silk was also studied and results are summarized in **Table 3**. In general increase in K/S as a result of AA grafting varied from 27% to 289%.

The extent of increase in the depth of dyeing (K/S) was maximum at lower shades (%) dyed and vice versa. This may be because initially at 0.5% shade of dye, availability of COOH groups was more and hence maximum dye interaction between positively charged dye cations with negatively charged COO^- anions on silk back bone was possible. As concentration of dye cations increased, the availability of COO^- anions relatively get decreased, and the extent of dye uptake also got relatively slowed down. This phenomenon was common for all the three dyes.

Table 3: Effect of different shades of cationic dyes on K/S values of dyed AA-g- silk fabric

Silk samples	Cationic Dyes	K/S		
		0.5 %	1.0%	2.0%
Ungrafted	Coracryl Red C4G SUPRA	1.81	4.09	8.12
AA-Grafted		7.08 (+289.4)	14.69 (+259.0)	17.67 (+117.5)
Ungrafted	Astrazon G.Yellow G-LE 200%	1.49	2.98	7.19
AA-Grafted		3.62 (+141.4)	6.43 (+115.4)	12.02 (+67.1)
Ungrafted	Atrazon Blue 2FRL 200%	4.16	8.88	14.95
AA-Grafted		5.93 (+27.1)	11.93 (+34.3)	17.07 (+14.1)

*(Change in K/S, %)

The various fastness properties of the dyed samples got improved for all three dyes after grafting (**Table 4**). Improvements in light fastness (by ½ or 1 grade) in grafted samples were due to increase in absorption of cationic dye molecules and salt linkage being with the grafted fibre. Overall fastness properties of dyed grafted samples were found to be improved.

Table 4: Colour fastness properties of ungrafted and AA-grafted Cationic dyed fabrics

Samples	Dyes	Wash fastness			Light fastness			Rubbing fastness					
	Shade %	0.5 %	1%	2%	0.5 %	1%	2%	0.5%		1%		2%	
								Dry	Wet	Dry	Wet	Dry	Wet
Ungrafted	Red	4	4-5	4-5	3	4	5-6	4-5	4	4-5	4-5	4-5	4-5
Grafted		4-5	4-5	5	4	4-5	6	5	4-5	5	4-5	5	4-5
Ungrafted	Yellow	4	4	4	6-7	6-7	6-7	4-5	4	4-5	4-5	4-5	4
Grafted		4-5	4-5	4-5	6-7	6-7	7	5	4-5	5	4-5	5	4-5
Ungrafted	Blue	4	4	4	5	5-6	5-6	4-5	4	4-5	4-5	4-5	4-5
Grafted		4-5	4-5	4-5	5-6	6	6	5	4-5	5	4-5	5	4-5

Table 5: Electrical resistivity of Grafted silk fabrics

Sr. No.	Samples/Graft add-on %	Surface Resistivity (Ω / cm^2)	Volume Resistivity (Ω / cm^2)
1	Ungrafted silk	9.0639×10^{14}	1.5851×10^{11}
2	1.98	7.9726×10^{13}	1.0056×10^{10}
3	2.011	3.7864×10^{13}	1.0176×10^{10}
4	2.32	6.9045×10^{12}	8.9092×10^{9}
5	2.54	6.3109×10^{12}	8.1679×10^{9}
6	2.61	5.8895×10^{12}	7.9675×10^{9}
7	2.67	5.6390×10^{12}	7.7150×10^{9}
8	2.75	4.5647×10^{12}	7.1793×10^{9}
9	2.83	4.0755×10^{12}	7.044×10^{9}

Silk fabrics possess a fair amount of moisture regain whereas AA grafted silk fabric showed increase in moisture regain compared to that of ungrafted silk (shown in **Table 1**). After AA- grafting of silk, electrical resistivity of silk fabrics was found to be decreased as compared to that of the ungrafted silk fabric as showed in Table 5. With increase in AA-graft add-on, causing increase in moisture content, conductivity was expected to be increased as the static charge dissipation will be faster. AA-graft causing increase in number of –COOH polar groups would enhance such conductivity. The scale of electrical conduction covers a broad range from the surface resistivity R of native textiles at more than 10^{14} Ohms down to antistatically finished textiles (R $<$ 10^{10} Ohms). As the resistivity of the grafted silk fabric tested here decreased by the order of "2", it can be said that there was increase in electrical conductivity almost 100 times as a result of AA-grafting which would help in improving comfort properties.

5. Conclusion

Pad-cure technique having potential to make the operation continuous for acrylic acid grafting on to silk fabric. The various parameters of grafting were optimized. Optimum curing temperature was 130 °C, curing time, 5 min and acrylic acid concentration was 100 gpl. The crease recovery angles improved by 31.77% and moisture regain increased by 22.17% as a result of grafting. However, tensile strength decreased to some extent (8.33%) and there was slight increase in stiffness due to grafting. The grafted fabric showed tremendous enhancement in cationic dyeability with distinct improvement in fastness properties. The grafted fabric also has shown uniform dyeing indicating the uniformity of grafting. The continuous grafting using such a pad-cure technique hence can be claimed to be efficient, uniform and operation friendly technique for silk fabrics.

6. Acknowledgement

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