

Finishing of Silk by Acrylic Acid in the Presence of Sodium Citrate and Potassium Per Sulphate as Catalysts Under Thermal Treatment

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ABSTRACT: Silk fabric was finished using acrylic acid (AA) as the finishing agent in the presence of sodium citrate and potassium per oxodisulphate catalysts separately or in selected combinations employing a pad-dry-cure technique. Treatment with 6% AA at 30°C and at pH 7 produced optimum effects; a batching time of 45–60 min at 30°C, followed by drying of the batched fabric at 95°C for 5 min and curing of the dried fabric at 140°C for 5 min produced most balanced improvements in the properties such as wrinkle recovery, extensibility, and moisture regain with retention of

more than 80% of original strength. Sodium citrate catalyst allowed esterification of AA with proteinoous constituent of silk and potassium per sulfate catalyst allowed radical polymerization of free AA or silk bound AA moieties; the said process ultimately led to some degree of crosslinking of the chain polymers of silk. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 770–776, 2011

Key words: acrylic acid; finished silk; wrinkle recovery; crosslinking; esterification; radical polymerization

INTRODUCTION

Crease resistance finishing of silk textile using resins from amine formaldehyde condensates results in some odd disadvantages in respect of relatively poor tensile strength retention despite significant improvement in wrinkle recovery.^{1–4} Such amine formaldehyde condensate resin finishes are also associated with the disadvantage of formaldehyde splitting during processing and use, endangering the health of processors and users.^{5–9} Finishing of silk with polycarboxylic acid as formaldehyde free finishing agent appears to be much more prospective in this respect.^{10–13} Such compounds have evoked immense interest in the recent past in view of their environment friendly and nontoxic characters. However, sodium salts of phosphorous containing mineral acid used as esterification catalyst with such polycarboxylic acid are not environment friendly.^{14–16} Such catalysts containing sulfur influence reproduction of fish and favors growth of a kind of seaweed which consumes large amount of oxygen from water. Also, finishes based on such nonpolymeric polycarboxylic acid cannot retain

and/or improve strength and moisture-regain characters of silk. It is therefore, thought to be of interest to finish silk by a combination of (a) esterification, (b) chain polymerization, and (c) ultimate crosslinking, consequent to application of a monomeric readily polymerizable acid such as acrylic acid under the influence of phosphorous free esterification and free radical polymerization catalyst. This work is therefore, aimed at establishing optimum condition for application of acrylic acid and evaluating attainable changes or improvements in the fabric nature and properties including crease resistance, whiteness index, stiffness, strength, and moisture regain. Results of related studies are reported in the present article.

EXPERIMENTAL

Materials

Fabric

Raw silk fabric with 360 ends dm^{-1} and 320 picks dm^{-1} , 50 denier warp, and 50 denier weft; having average area density 38 g m^{-2} were used for the present study. Commercial grade acrylic acid (AA) obtained from M/s Macromols India was used without any treatment or purification. All other chemicals used were of laboratory reagent grade.

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Methods

Degumming of silk

To remove silk gum from the raw silk fabric, the later was degummed at 90°C for 1.5 h in an aqueous solution containing 6 g L⁻¹ olive oil soap and 2 g L⁻¹ sodium carbonate at fabric to liquor ratio 1 : 20. Degummed fabric was washed using water at 70°C for 10 min, cold washed, and finally dried in air.

Application of acrylic acid on silk

Presoaking of degummed silk fabric with potassium peroxydisulphate (K₂S₂O₈) solution of concentration 0.5% (w/v) and subsequent application of aqueous AA monomer formulation on the presoaked silk fabric were performed separately by padding technique in a laboratory two-bowl padding mangle.^{17,18}

After two successive fabric dippings in the methacrylic formulation, the pressure between the squeezing rollers was adjusted to enable an overall pick up of 100%. The pH of the monomer solution was adjusted at different specified levels with the use of required dose of soda ash and caustic soda. The aqueous monomer formulation usually contained a known dose of sodium citrate as the esterification catalyst. The padded squeezed fabrics were subjected to drying in an oven at 90°C for 5 min. The dried fabrics were then oven cured at 140°C for 5 min, soap washed following ISO-I,¹⁹ washed further with water, and dried in air. They were then analyzed for weight gain and some textile related properties.

Determination of moisture regain and weight gain after treatment

Moisture regain of the initial and treated silk fabrics was determined following a standard procedure (Annual Book of ASTM Standards, 1974). For the determination of weight gain upon finishing treatments using AA, the finished fabric samples were first soap washed and then extracted under reflux in a water bath for 8–10 h successively using water to ensure removal of traces of unreacted AA monomer along with polymeric AA that remains unbound or ungrafted to the chain molecules of silk fabric samples. The extracted fabric samples were then oven dried to a constant weight (W_1) at 100°C. The weight gain (%) was then calculated on the basis of initial dry weight of degummed silk (W_2), using the following relationship: $\text{weight gain (\%)} = (W_1 - W_2) / W_2 \times 100$.

Tensile properties

Breaking strength of some selected fabric samples was measured in a Zwick 1445 CRT Universal Tensile Testing Machine, according to a method²⁰

(Hand Book of Textile Testing, 1981) prescribed by IS: 1969–1968. The results obtained were based on an average of 10 tests in the warp direction of each sample. The test strip specimens were raveled to a size of 50 mm × 20 mm between the jaws of the machine, and the tests were performed with a traverse speed of 100 mm min⁻¹ at a pretension of 0.5N.

Determination of wrinkle recovery angle

Dry wrinkle recovery angle (Warp + Weft) of selected fabric samples was determined according to a method prescribed by ASTM-D-1295-67 using a SASMIRA Wrinkle Recovery Tester with specimen size of 25 × 200 mm².

IR spectroscopy

IR spectra of unmodified and selectively modified silk samples were obtained following KBr pellet technique as detailed elsewhere.²¹ using Shimadzu IR 440 spectrophotometer. The dried fiber samples were crushed to a size finer than 20 mesh before palletizing with KBr. Four KBr pellet test specimens (each 0.3 g) were prepared separately for unmodified silk and silk modified with AA in presence of different catalytic systems as specified. Each of such test KBr pellets contained about 1% powdered fibers.

RESULTS AND DISCUSSION

It would be useful if we consider, at the outset, the mechanism of modification of silk (Fig. 1) with AA under the influence of (1) sodium citrate used as the esterification catalyst and (2) K₂S₂O₈ used as the catalyst to induce free radical polymerization and graft copolymerization of AA on silk. Serine and tyrosine are amino acids having primary hydroxyl and phenolic-OH groups respectively, in them, which are expected to bring about intended modifications of silk under the sequence of reactions shown in Figure 1, which would be expected to take place, ultimately leading to notable weight gain and changes in the chemical nature of silk during the overall process. Reaction 1(a) producing acrylic acid ester of silk would be the direct consequence of catalytic action of esterification catalyst. However, the AA ester of silk may then react with the monomeric acid as revealed by 1(b) (i) and subsequent crosslinking of silk as shown in eq. (1b) (ii) during the drying and curing steps. Direct consequence of esterification under the influence of esterification catalyst is therefore, unlikely to enhance -COOH group content of silk even though it would lead to enhancement in the ester group of the product. However, uncatalysed thermal graft polymerization of AA under the treatment condition ultimately leading to grafting of poly

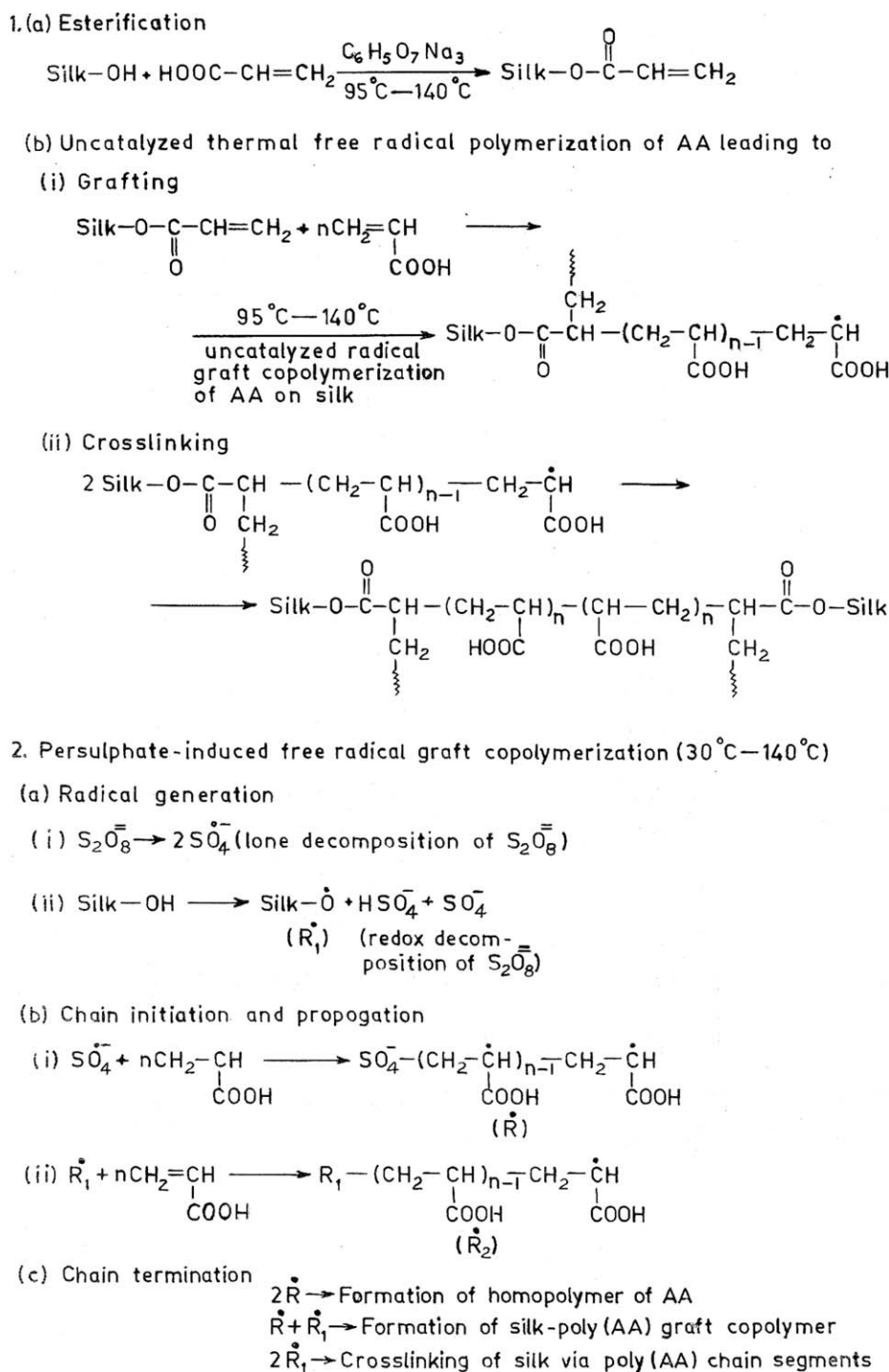


Figure 1 Reaction scheme showing modification of silk under the influence of sodium citrate as esterification catalyst and potassium persulphate as free-radical polymerization catalyst.

(acrylic acid) chains on the chain molecules of silk and ultimate crosslinking [eq. (1b)] potentially occurs (in addition to persulphate ($\text{S}_2\text{O}_8^{2-}$) induced free radical polymerization of AA [eq. (2a)–(2c)] if $\text{K}_2\text{S}_2\text{O}_8$ is also induced in the catalyst system.) Such uncatalysed graft copolymerization and crosslinking would cause enhancement of -COOH group content as well.

On the other hand, direct influence of free radical catalyst, $\text{K}_2\text{S}_2\text{O}_8$, over the batching time at room temperature and at higher temperatures during drying and curing would cause substantial enhancement of carboxylic acid group content in the modified silk. However, some purely thermal self catalyzed esterification involving -OH groups of serine and tyrosine present in the chain molecules of silk and

TABLE I
Acrylic Acid Finishing of Silk: Effect of Variation of Batching Time and pH^a

K ₂ S ₂ O ₈	Sodium citrate	Application pH	Weight gain (%)	Wrinkle recovery angle (W+F)		Tearing strength retention (%)	Breaking load (N cm ⁻¹)	Elongation at break (%)	Bending length (cm)
				Dry	Wet				
(A) Effect of variation of pH									
+	+	5	3.06	217	247	81%	43	18	1.4
+	+	6	3.82	228	260	83%	43	19	1.3
+	+	7	6.81	253	276	91%	44	20	1.3
+	+	8	6.37	257	278	71%	32	20	1.3
+	+	9	6.21	241	267	67%	30	19	1.3
+	-	7	4.65	224	231	74%	32	20	1.3
-	+	7	3.59	219	226	80%	41	17	1.3
(B) Effect of variation of batching time									
++	0	7	4.35	192	211	84	40	18	1.3
++	30	7	5.32	229	265	86	41	19	1.3
++	45	7	6.81	253	276	91	44	20	1.3
++	60	7	6.97	259	280	92	44	21	1.3
(C) Degummed silk									
-	-	-	-	175	188	100	44	17	1.4

^a Acrylic acid: 6%, Potassium peroxodisulphate (K₂S₂O₈): 0.5%, sodium Citrate: 6%, drying at 95°C, curing at 140°C.

finishing agent AA during drying and curing process (95–140°C) even in the total absence of esterification catalyst cannot be altogether precluded which may lead to enhancement of ester group content of silk.

Under the influence of two catalysts taken together for the curing of silk, all the reactions shown and discussed above are likely to take place simultaneously or successively leading to a weight gain for the fiber-fabric system. Moreover, additional reactions leading to further esterification and complex network formation (due to limited establishment of ester linkages between the carboxylic (–OH) groups of the same or other neighboring fibroin molecules) may also take place.

Effect of variation of batching time

Relevant results are shown in Table I. In each experiment, AA dose level was maintained at 6% (w/w) for batching at room temperature (30°C) for 0–60 min. under the dual catalyst system and subsequent drying by heating at 95°C for 5 min, followed by curing at 140°C for 5 min, there is a notable increase in the weight gain, wrinkle recovery angle, tear strength retention, breaking load retention, and elongation at break. Bending length, however, remained leveled for the entire period of batching time. The batching for an extended time distinctly favors a higher incorporation of AA moieties on silk by K₂S₂O₈ induced graft copolymerization. Initial S₂O₈²⁻ induced graft copolymerization or homo polymerization of AA, to increasing extents over increasing batching time periods, at ambient temperature (30°C), and further polymerization of free AA and silk-bound AA moieties during the subsequent drying period at 95°C cause an overall change in

environment and proximity of the hydroxyl groups of silk and carboxyl groups of the unbound or silk bound AA or poly (acrylic) acid moieties in a manner that finally causes an enhanced degree of sodium citrate-catalyzed esterification and further chain polymerization leading to substantial cross-linking during curing at 140°C as revealed by the relevant data for wrinkle recovery (Table I).

The esterification reaction that assumes more prominence at the high processing temperature (140°C) in the final stage appears to be somewhat dependent on the initial batching time. Increase in batching time favors improved transformation of the grafted AA/poly (acrylic) acid units to ester moieties at the high curing temperature (140°C) under the influence of the esterification catalyst in the final stage of processing. Optimum batching time (45–60 min) also allows improved diffusion/penetration of the finishing agent AA within the chain molecules of silk.

Effect of variation of pH

Table I also shows the effect of variation of pH of the AA finishing formulation on the properties of the finished fabrics.

Relevant data clearly indicate that under neutral condition (pH 7), optimum grafting and esterification leading to much improved wrinkle recovery angle and substantial weight gain are achieved with no loss of breaking strength and with more than 90% retention of tear strength of the initial fabric. Under moderately acidic condition, (pH 5.6), moderate improvement in extensibility with more than 80% retention of the tear strength of the initial fabric was achieved.

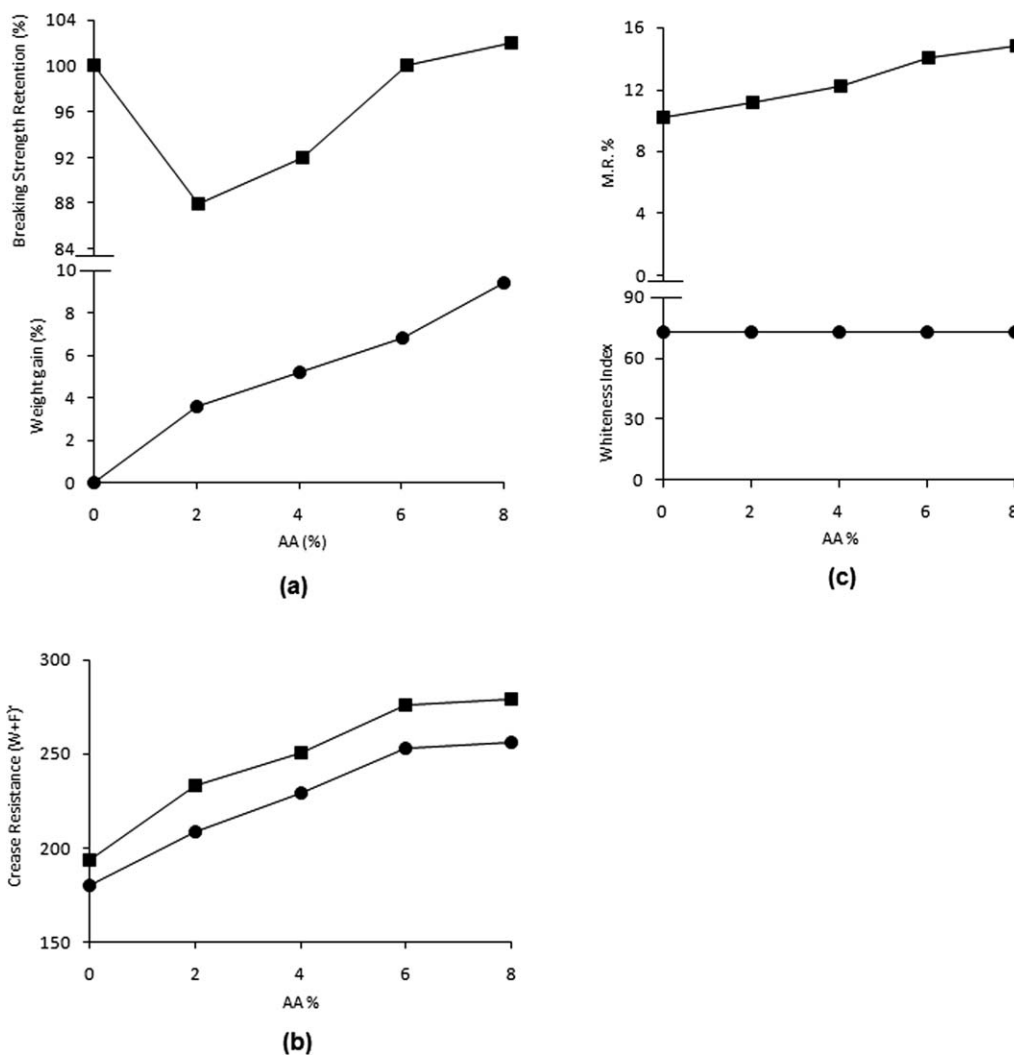


Figure 2 Effect of variation of acrylic acid (AA) dose level on (a) (i) Weight gain (●) (ii) Retention of breaking strength (■); (b) (i) Dry wrinkle recovery angle (DRCA) (●) (ii) Wet wrinkle recovery angle (WRCA) (■); (c) (i) Whiteness index (●) (ii) Moisture regain (■).

Moderate alkaline conditions, (pH 8.9) result in poor retention of breaking strength (<75%) and tear strength (<75%) despite substantial weight gain much as a consequence of weakening of the silk fiber in the fabric by alkali attack. Under slightly acidic condition, (pH 5.6), improvement in wrinkle recovery angle is comparatively poor even though tear strength and breaking strength retention are good, pH 7, therefore, apparently provides the most optimum condition of the finishing process.

Optimum application level of AA

Figure 2 shows plots of weight gain, retention of breaking strength, crease resistance, whiteness index, and moisture regain for application of different quantities of AA under dual catalyst system at pH 7. Figure 2 clearly indicates that optimum weight gain and balance of textile-related properties for the finished fabrics are obtained for application of 6%

AA. Whiteness index of the bleached silk fabric practically remains undiminished on finishing with AA as evident from curve shown in Figure 2. A comparison between AA finished and DMDHEU finished silk fabric against unfinished silk fabric with respect to their property parameters are shown in Table II. Table II clearly indicates that AA produces much desired improvement in the fabric quality; AA specifically imparts a lower order of stiffness (bending length) a higher retention of strength and higher moisture regain for a comparable improvement in wrinkle recovery angle.

Effect of variation of cure time

Data in Figure 3 indicate that with rise of cure time (0–7 min) for a fixed curing temperature of 140°C, the breaking load suffers a monotonous fall while the dry, and wet recovery angle attained maximum for a cure time of 5 min. The degradative process of

TABLE II
Comparison of Properties of AA and DMDHEU Finished Silk Fabrics

Type of the reagent	Wrinkle resistance (W+F)		Tearing strength retention (%)	M.R.(%)	Bending length (cm)	Tensile strength retention (%)	Elongation at break
	Dry	Wet					
None	175	188	100	10.1	1.4	100	16%
6% AA	253	276	97	14.01	1.3	100	20%
6% DMDHEU	260	281	61	8.21	1.5	59	9.2%

polypeptide chain for curing for an extended time period in presence of AA and catalyst becomes severe while going from cure time of 5–7 min, as indicated by fall in breaking load (Fig. 3) of the cured fabric. For AA application on silk, pad-dry-curing at 140°C from 5 min produces the most balanced effects.

Effect of progressive wash

AA finished silk fabric was washed in launder-*o*-meter following ISO-I washing method and effect of such wash on wrinkle recovery and breaking strength retention of finished silk is given in Figure 4. Figure 4 shows that with increase in wash cycle, wrinkle recovery of silk suffer a monotonous fall and the trend of lowering is more in wet than in dry silk. However, the difference in wrinkle recovery of wet silk sample for 0 and 10 numbers of wash cycles is not more than 24° against a value of only 14 for dry silk. Breaking strength shows a falling trend with increase in wash

cycle with a final strength retention value of 96% of the finished fabric for 20 cycles of wash. Such trends of changes of wrinkle recovery and strength indicate that AA finish renders the silk much improved for practical use in a durable manner.

IR analysis

Infra red spectra of unmodified silk fiber (Spectrum a) and of the silk fiber differently modified with AA treatment using only $K_2S_2O_8$ as the free radical polymerization catalyst (Spectrum b), using only sodium citrate as the esterification catalyst (Spectrum c) and using both $K_2S_2O_8$ and sodium citrate catalysts together (Spectrum d) are shown in Figure 5. A broad absorption band over $3400\text{--}3000\text{ cm}^{-1}$ characteristic of hydrogen bonded $N\text{--}H$ stretching vibration and an absorption band at 1652 cm^{-1} characteristic of amide stretching vibration are common to all the four spectra. One notable absorption band at 1555 cm^{-1} existing in the spectrum of unmodified silk is characteristic of carboxylate anion appear at the end of polypeptide chain. In the spectrum of unmodified silk absorption bands at 1735 and 997 cm^{-1} are practically not

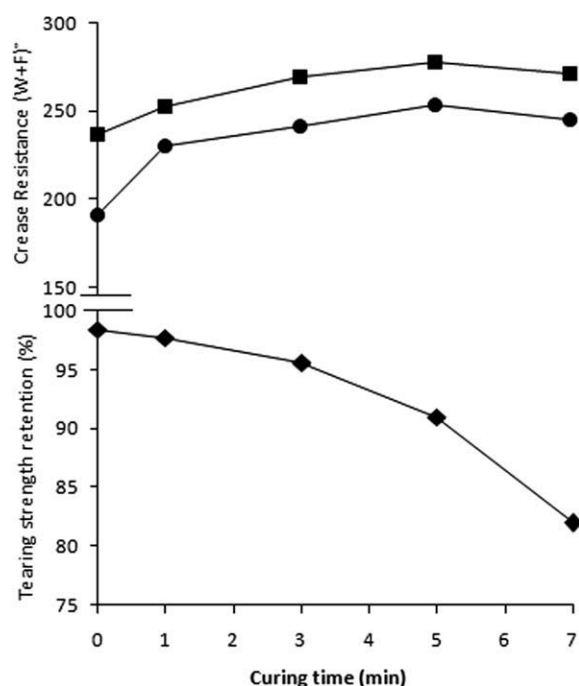


Figure 3 Effect of variation of curing time on (i) Tearing strength retention (◆) of the finished silk fabric (ii) Dry wrinkle recovery angle (DCRA) (●) and (iii) Wet wrinkle recovery angle (WCRA) (■).

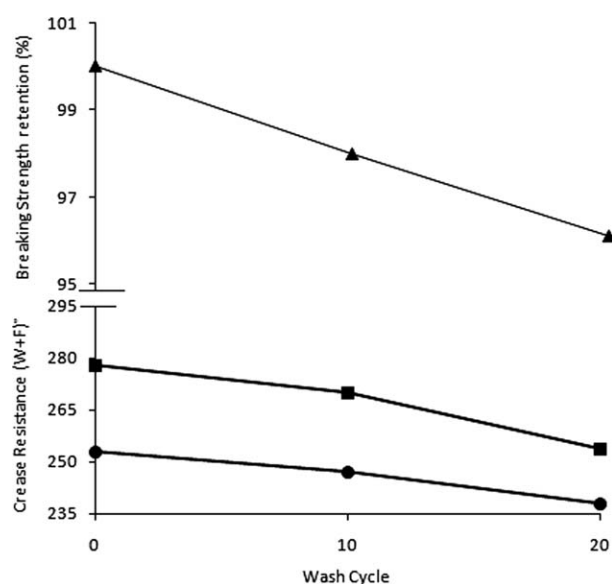


Figure 4 Effect of variation of wash (laundering) cycle on (i) Dry wrinkle recovery angle (DRCA) (●) (ii) Wet wrinkle recovery angle (WCRA) (■) (iii) Retention of breaking strength (▲).

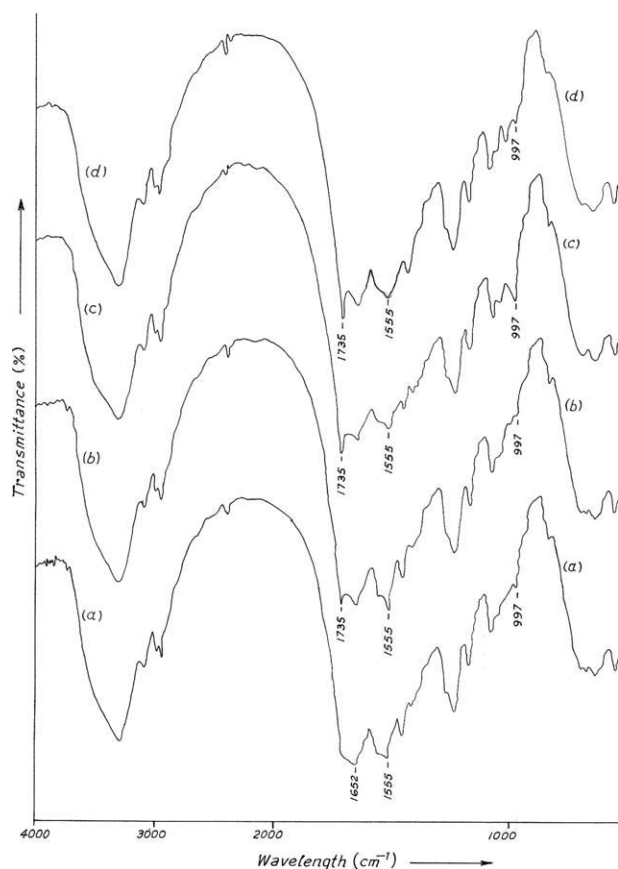


Figure 5 IR spectra of (a) unmodified (degummed) silk, and of the degummed silk modified with AA in the presence of (b) potassium peroxosulphate, (c) sodium citrate and (d) mixture of potassium peroxosulphate and sodium citrate as catalysts.

existent. AA finish of silk in the presence of $K_2S_2O_8$ catalyst only (Spectrum b in Fig. 5) results in intensification of absorption band at 1555 cm^{-1} for carboxylate anion and appearance of new weak absorption band at 1735 cm^{-1} characteristic of ester stretching vibration. AA finish of silk in the presence of esterification catalyst sodium citrate only (Spectrum c in Fig. 5) however results in intensification of absorption band at 1735 cm^{-1} characteristic of vinyl ester stretching, substantial weakening of absorption band at 1555 cm^{-1} characteristic of carboxylate (anion) stretching and appearance of a strong absorption band at 997 cm^{-1} characteristic of unsaturation present in the vinyl group as expected. However, AA finish on silk under the influence of dual catalyst system (Spectrum d in Fig. 5) results in weakening of the band at 997 cm^{-1} due to significant disappearance of the vinyl group unsaturation during final stage polymerization

induced by heat and catalytic action of $K_2S_2O_8$, along with sharp intensification of the band at 1735 cm^{-1} due to ester stretching with retention of band corresponding to 1555 cm^{-1} for carboxylate (anion) stretching. The results of the IR analysis are in tune with the mechanism proposed.

CONCLUSIONS

The appropriate AA finish on silk under neutral condition (pH 7) establishes a formaldehyde free route for achieving simultaneous core and surface modification of silk with high scope for incorporation of much improved physical and mechanical properties for the fabric.

The major property advantages that can be derived from AA finishes by following a pad-dry-cure technique under the dual catalytic influence of sodium citrate and $K_2S_2O_8$ are substantial improvements in (1) wrinkle recovery, (2) extensibility, and (3) moisture regain with associated retention of high order of tensile and tear strength.

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