Studies on Silk Anticrease Improving by Use of Acrylic Monomer Polymerization Method

Byong Hee Choe and Yang Hoo Lee College of Agriculture, Seoul National University, Suwon 170, Korea

아크릴單量體重合에 의한 絹織物 防皺度 改善에 대한 研究

崔 炳 熙·李 良 厚 서울大學校 農科大學

摘 要

筆者의 絹織物防皺度改善研究에서 只今까지 報告된 것은 尿素포르마린合成樹脂 重合法에 의한 것이었다. 그러나 絹織物이 高級織物인 關係로 1970年代에 이르러 皮膚衛生上 포르마린을 加工作業에使用禁止하기에 이르러 本人도 포르마린 不使用原則을 세워 研究하여 오던증 아크린 單量體의 重合方法에 의한 加工方法開發에 成功하였으므로 이에 報告하며 얻어진 結果는 다음과 같다.

- (1) 防皺度가 不良한 絹織物은 本 加工으로 25% 以上 改善을 보였다.
- (2) 플리에스터처럼 防皺度가 좋은 絹織物—例로 crape de chin과 같은 薄地高燃絹織物은 數 % 改善하에 不過하였다.
- (3) 本加工處理로 織物硬軟度는 別 變化가 없었다.
- (4) 本加工處理物은 先後染을 莫論하고 染色直後에 實施함을 勸告한다.
- (5) 本加工織物은 dry cleanning 함을 原則으로 한다.

I Introduction

The author's former reports (Choe '78, '82) regard as anticrease improving studies on silk textiles were based upon urea formaldehyde resin polymerization method among fibrils in silk fiber. Because of silk textiles are high quality fabric, the use of formal-dehyde has been prohibited since last decade to prove skin hygiene.

From such a reason, the author has tried to use other chemicals than this for the purpose and he has happened to work out his desire by using acrylic amide polymerization method for the improve of silk anticrease.

General polyacrylic amide is known as water soluble polymer, but the water solubility is controlled in proper degree on this report.

II Materials and Methods

The silk textile samples used for this work are shown in next page.

Before prepare the specific acrylic amide polymerization, various basic investigations and polymerization methods were carried out to find a suitable processfor silk anticrease finishing.

For this purpose, two step system, that is, original mixture and dilution process of the mixture method are used for this report.

The composition of the mixture is as following.

Acrylic amide 100 parts
Water 150 parts
Solubility controller (20%) 100 parts
Ethylene glycol 20 parts

Then the mixture was diluted as much as 30 times.

Sample	Specification	Woven density
156. 1	Crepe de chine, TCL-100% silk, discharged and dyed	90cm- 80g/m
No. 2	28418, Honan, 100% Tussah silk, discharged and dyed	90cm-100g/m
No. 3	28375, Toile, 100% Spun silk, discharged and dyed	90cm- 90g/m
No. 4	24059, Shantung, Warp: Spun silk, yarn dyed	90cm-180g/m
	Weft: Dupion silk, yarn dyed	
No. 5	2761, Regatte, discharged and dyed, Warp: Spun silk/high twist raw silk	90cm-200g/m
	Weft: Spun silk	

45 and 60 times for the anticrease and stiffness tests with Sample No. 3 silk textile to find proper dilution rate. Such dilution degree is widely used for urea formaldehyde resin finishing method. Through this study, 50 times dilution method was used for the various silk textiles (Table 3) finishing test.

This paper has investigated the textile anticrease following after Monsanto Method and the fabric stiffness by Canti-Lever Method for each sample in order to compare the results between nonfinished fabric and finished one.

III. Results and Discussion

In the acrylic plastic industry, acrylic acid and methyl methacrylate (Bovey '55 and others) are the most famous and practical monomers for industry use. The former is mainly used for synthetic leather or coating and the latter is used for synthetic glass or sheet type plastics like as advertising sign boards etc.

The purpose of this study was to find an anticrease silk finishing method other than urea formaldehyde polymerization method. In spite of the author has succeeded to finish silk with urea formaldehyde resin

satisfactorily before, he needed no more use of formaldehyde. For this purpose, acrylic amide was adopted in replace of urea formaldehyde polymerization method.

The poly acrylic amide is known as water soluble polymer and the key point is how to control the solubility after textile finishing. This is one thing different from urea formaldehyde method, which is necessary to use dry cleanning system after finish. Before carry out anticrease finish, the author had changed the dilution rate in three different ways from the condensed monomer solution as shown at Table 1.

This dilution rate was used in his former report on urea formaldehyde polymerization method, and could have chance to compare the finished results each other by using the same rate of dilution. Such finish was carried out with boil up heating diluted bath system at least for ten minutes, then waited the temperature drop down by and by.

Through this work, fifty times dilution method was adopted for various silk textiles finish as shown at Table 3 and 4. Stiffness tests were also carried out if there is any touch feeling change by the finishing.

These ploymers are not soluble in water or hygro-

Table 1. Silk Anticrease Variation by the Change of Acrylic Polymer Bath Dilution.

Item	Repeat or Result	1	2	3	4	5	Average	Increase
Control	Warp	80.3%	77.5%	78.5%	80.5%	79.5%	79.1%	
	Fill	82.0	80.2	80.4	81.0	80.5	80.8	
imes 30 diluted	Warp	84.4	87.2	87.7	87.2	83.3	86.0	+6.9%
	Fill	82.7	84.4	84.4	82.2	81.6	83.0	+2.2
imes 45 diluted	Warp	88.3	87.7	87.7	85.5	88.3	87.5	+8.4
	Fill	81.6	82.7	81.6	82.6	82.2	82.1	+1.3
$\times 60$ diluted	Warp	82.2	85.5	82.7	82.2	82.7	83.1	+4.0
	Fill	79. 4	81.6	81.1	78.8	79.4	80.1	-0.7

Table 2. Silk Stiffness Variation by the Change of Acrylic Polymer Bath Dilution.

Item	Repeat or Result	1	2	3	4	5	Average	Increase
Control	Warp	2.5	cm 2.8	cm 2. 4	2. 6	cm 2. 6	cm 2. 7	
	Fill	3.4	3.6	3.6	3. 4	3.4	3.4	
$\times 30$ diluted	Warp	2.9	2.8	2.5	2.4	2.4	2.6	-0.1cm
	Fill	3.7	3.8	3.3	3.4	3.8	3.6	+0.2
×45 diluted	Warp	2.6	2.5	2.7	2.4	2.8	2.6	-0.1
	Fill	3.7	3.8	3.5	3. 7	3.8	3.7	+0.3
$\times 60$ diluted	Warp	2.5	2.6	2.7	2.7	2.5	2.6	-0.1
	Fill	3.7	3.6	3.6	3.8	3.7	3.7	+0.3

Table 3. Various Silk Textiles Anticrease Increase after finished with Acrylic Polymerization Method.

Item	Repeat or	Result	1	2	3	4	5	Average	Increase
Sample No. 1	Control	Warp	84.3%	84.5%	85.0%	83.0%	83.5%	84.3%	
		Fill	81.0	82.5	82.8	83.0	82.6	82.3	
	Treated	Warp	87.2	85.9	86.5	87.0	86.7	86.6	+2.3%
		Fill	84.0	83.7	83.9	83.2	83.2	83.8	+1.5
Sample No. 2	Control	Warp	64.5	64.0	64.3	64.2	63.8	64.1	
		Fill	61.4	61.5	61.8	61.9	62.0	61.7	
	Treated	Warp	67.1	68.7	68.7	67.5	68.0	68.0	+3.9
		Fill	66.9	71.7	69.3	71.0	69.5	65.3	+3.6
Sample No. 3	Control	Warp	80.3	77.5	78.9	80.5	79.5	79.1	
		Fill	82.0	80.2	80.4	81.0	80.5	80.8	
	Treated	Warp	88.3	87.7	87.7	85.5	88.3	87.5	+8.4
		Fill	82.7	84.4	84.4	82.2	81.6	83.0	+2.2
Sample No. 4	Control	Warp	65.4	62.1	63.7	64.0	63.8	63.8	
		Fill	53.9	56.7	55.7	55.0	56.0	55.4	
	Treated	Warp	79. 2	77.9	79.6	78.5	78.8	78.8	+15.0
		Fill	83.4	81.3	82.3	82.5	83.0	82.5	+25.1
Sample No. 5	Control	Warp	84.0	85.9	85.0	84.5	85.5	84.9	
		Fill	86.2	86.3	85.7	86.0	85.8	86.0	
	Treated	Warp	86.2	84.9	85.7	86.5	85.5	85.5	+0.5
		Fill	85.2	86.3	86.1	86.5	86.0	86.1	+0.1

Table 4. Various Silk Textiles Stiffness after finished with Acrylic Polymerization Method.

Item	Repeat or	Result	1	2	3	4	5	Average	Increase
Sample No. 1	Control	Warp	3. 1	2. 8	2. 6	cm 2. 4	cm 2.8	2. 7	
		Fill	3.4	3.3	3.0	3.0	3.3	3. 2	
	Treated	Warp	2.8	2.4	2.8	2.7	2.7	2.7	0 cm
		Fill	3.1	2.7	3.0	3.0	3.2	3.0	-0.2
Sample No. 2	Control	Warp	2.3	2.2	2.2	2.3	2.4	2.8	
	1	Fill	2.4	2.3	2.4	2.6	2.5	2.4	
	Treated	Warp	2.4	2.3	2.3	2.6	2.1	2.3	0
		Fill	2.5	2.4	2.1	2.0	2.1	2.2	-0.2
Sample No. 3	Control	Warp	3.4	3.6	3.6	3.4	3.4	3.4	

		Fill	3.6	3.7	3.7	3.5	3.6	3.6	
	Treated	Warp	3.7	3.8	3.3	3.4	3.6	3.6	0. 2°
		Fill	3.7	3.8	3.5	3.7	3.7	3.7	0.1
Sample No. 4	Control	Warp	5.8	5.3	5.5	5.4	5.8	5.6	
		Fill	5.2	5.6	5.5	5.7	6.0	5.6	
	Treated	Warp	4.9	4.9	4.7	4.8	4.6	4.8	-0.8
		Fill	4.5	5.0	4.7	4.4	4.6	4.6	-1.0
Sample No. 5	Control	Warp	4.5	4.0	4.0	3.9	4.1	4.1	
		Fill	3.8	4.1	4.0	4.2	3.9	4.0	
	Treated	Warp	4.3	4.2	4.2	4.3	4.3	4.3	+0.2
		Fill	3.7	3.8	3.9	3.7	3.8	3.8	-0.2

phobic form and need rather complicated polymerization process for use of textile finishing.

On the other hand, acrylic amide is not used for plastic industry because the polymer is soluble in water, but there is much chance to use it for textile finishing. The chemical monomer and polymer structures of these are known as (Rlory '53 and others);

(1) Acrylic acid:

Its polymer:

(2) Methyl methacrylate:

Its polymer:

(3) Acrylic amide

Its polymer:

There are three different plastics on acrylic polymers like as hard shape, semi hard shape and soft shaped one, which the former two polymers are used as hard or semi hard type and the latter is used for soft type to be useful for textile finishing.

The industrial compositions for acrylic polymer are as followings.

Example 1. (Acronal II D)

1, 320kg	Ethylacrylate
9.5kg	Acrylic acid
3.0kg	Amphoseife 18
0.5%	Hydrogen peroxide
1,800kg	Water

Example 2. (Acronal 500 D) (Schildknecht, '52)

1, 375kg	Butylacrylate
1,375kg	Vinylacetate
50kg	Acrylic acid
25kg	Amphoseife 18
25 kg	Emniphor 0
0.05%	Potassium persulfate
2,500kg	Water

Like ordinary polystyrene, acrylic polymers are amorphous under all conditions, due to dl-isomerism or the bulky sidegroups. Isotactic polymers have not been prepared. One outstanding property of acrylic polymers are their optical clarity and lack of color, specially acrylic amide does not have any smell under solution which may bring no processing smell pollution during its polymerization work.

In normal polymerization, chain transfer agents and buffers to control pH may be used for initiating purposes. Specially, urea-formaldehyde polymerization takes place many changes by use of such initiating method. The acrylic polymer is, however, not sensible as much as other polymers.

The discussions of polymerization kinetics far have dealt with polymerization of pure monomer of homogeneous solutions of monomero in a solvent. Certain other types of polymerizing systems are of great interest because they offer practical advantages in textile finish applications. Among these are polymerizations in which the monomer is carried in an emulsion or in solution in an aqueous phase.

The general features of emulsion and liquid polymerization (Harkins '52 and others) are similar by vigorous stirring or col loiding, an aqueous dispersion is obtained of very small droplets of monomer. The polymerization may be carried out at temperatures between 0 and 100°C, depending on the initiator used. At the end of the reaction, the polymer is

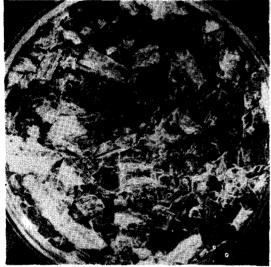
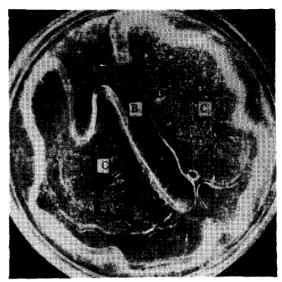


Fig. 1. Monomer recrystallization



C: Crystal part
B: Polymer part

Fig. 2. Incomplete polymerization (1)



C: Crystal part, B: polymer part

Fig. 3. Incomplete polymerization (2)

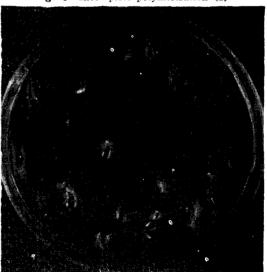


Fig. 4. Complete polymerization

obtained in the form of glutinized form from liquid ploymerization. Such liquid polymerization is essentially a bulk polymerizing system as shown at Fig. 4. The initiator is confined almost entirely to the the monomer phase.

Normal type for an liquid polymerization might consist of 100 parts (by weight) monomer, 180 parts of water, and 0.1 to 0.5 part of initiator. The author, however, used 20 parts of initiator for this work which the initiator seemed work not only as an

initiator but also a partnership of copolymerization to decrease solubility and the mechanism of such formation is not known yet. In case short of the initiator, the polymerization was not completed as shown at Fig. 2 and 3, when processing them with room temperature. When no initiater or solubility controller used, the condensed acrylic amide solution crystallized again like as Fig. 1 or when the addition of the initiater was not enough, partial polymerization and denatured crystallization was observed as shown at Fig. 2, 3 (C: crystal form, B: bulk polymer form). Such phenomena had no relation with polymerizing time. In case enough initiator was used, complete polymer was obtained as shown at Fig. 4.

Swelling occurs for the same reason that an analogous linear polymer dissolves. The swollen gel is in fact an elastic rather than a viscous solution. The addition of solvent affords an increase in entropy. The tendency to swell is opposed by an elastic retractive force arising as the chains between network junctions are forced to assume elongated configurations. Ultimately, an equilibrium between the two forces is reached. The equilibrium is closely analogous to an osmotic equilibrium with the network structure acting as solute, osmotic membrane, and pressure generating device. A gel previously swollen with pure solvent will "deswell" to a smaller equilibrium volume when it placed in contact with a polymer solution. The swollen degree of general polyacrylic amide is as much as eight times of the dryed weight but the degree was droped down in half by using solubility controller. The physical and chemical natures are similar with gelation or sericin in many cases (Mark, H. '50).

According to Table 3, the finishing shows very intersting results. Some of silk fabrics, specially spun silk fabric, increased anticrease as much as more than 25% against original one. Mean while, light density with high twisted textiles showed a few per cent increase. In case the original fabric is woven to be good anticrease, like as crepe de chine, the increase of anticrease by the finishing stayed only a few per cent improve. Such result was obtained from polyester fabric also.

In case we work out the anticrease improvement,

the process is apt to increase the silk textile stiffness to be harsh, but the result of this paper did not show any significant increase of stiffness by such finishing method according to Table 4.

The results of this work were evaluated as satisfactory and he believes that the work will be able to extend the silk demand through out the world. One thing it should be beared in mind is that this processing is not for apparent or visual improvement but it is improved for practical use of them.

IV. Summary

This studies have been carried out to find anticrease finishing method other than urea formaldehyde polymerization method which the author had done it with his former report. Acrylic amide polymerization method with water solubility controlling device was developed in this paper and the obtained results are as followings.

- 1. Poor anticrease silk textile could improve as much as 25% than original fabric.
- 2. Light density with high twisted silk textiles may improve a few per cent increase of anticrease, because they held good anticrease nature as well as polyester fabric.
- 3. There was no significant stiffness change after such finish.
- 4. This finish is recommended to carry after dyeing process either yarn dye or cloth dyeing.
- 5. The finished textile with this method is recommended to wash with dry cleanning method.

V. References

Choe, B.H. and Lee, Y.H. (1982) Studies on Wash and Wear Silk Finishing Collaborating Anticrease, Seri, J. Korea Vol. 24. No. 1. p. 39.

Choe, B.H. and Lee, Y.H. (1978) Urea Resin Treat on Silk Textile, Seri, J. Korea. Vol. 20. No. 1. p. 15.

Bovey, F.A., I.M. Kolthoff, A.I. Medalia, and E.J. Meehan, (1955) Emulsion Polymerization, Interscience Publishers, Inc., New York, N.Y., and London.

- Burnett, G.M., (1954) Mechanism of Polymer Reactions, Interscience Publishers, Inc., New York, M.Y., and London, Chap. IX.
- Rlory, P.J., (1953) Principles of Polymer Chemistry, Cornell University Press, Ithaca, N.Y., Chap. V-3.
- Fryling, C.F., Chap. 7 in G.S. Whitby, C.C. Davis, and R.F. Dunbrook, eds., (1954) Synthetic Rubber, John Wiley and Sons, Inc. New York, N.Y.
- Harkins, W.D., (1952) The Physical Chemistry of Surface Films, Reinhold Publishing Co., Inc., New York, N.Y., Chapter on Emulsion Polymerization. See also W.D. Harkins, J. Am. Chem. Soc. 69 1428 (1947).
- Mark, H., and A.V. Tobolsky, (1950) Physical

- Chemistry of High Polymeric Systems, 2nd ed., Interscience Publishers, Inc., New York, N.Y., and London, Chap. XII-G.K.
- Williams, H.L., Chap. IV in C.E. Schildknecht, ed., (1956) Polymer Processes, Interscience Publishers, Inc., New York, N.Y., and London.
- Schildknecht, C.E., (1952) Vinyl and Related Polymers, John Wiley & Sons, Inc., New York. N.Y., Chaps IV and V.
- Greenberg, S.A., and T. Alfrey. (1954) J. Am. Chem. Soc. 76, 6280.
- Rehberg, C.E., and C.H. Fisher, Ind. Eng. Chem 40 1429 (1948)