

# Chemical Modification of Fibers by the Graft Copolymerization of Reactive Monomers. (I)

## Graft Copolymerization of Acrylamide and Glycidyl Methacrylate onto Cotton Fabric and Crosslinking of the Graft Copolymers\*

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Reactive monomers such as acrylamide and glycidyl methacrylate were graft copolymerized onto cotton fabric by  $\text{Co}^{60}$   $\gamma$ -ray irradiation method. Crosslinking was then introduced to these grafted cottons by use of the reactive side groups. The crease recovery and some tensile properties of the grafted and crosslinked cotton were examined. With appropriate crosslinking, dry and wet crease recoveries of the grafted cotton were improved in either case of acrylamide or glycidyl methacrylate. Though the tensile strength of the grafted cotton fabric was decreased by crosslinking, it was shown that the tensile damage of cotton resulted from crosslinking was remarkably decreased by the grafting.

### INTRODUCTION

Though the cotton fiber has various excellent properties, improvement of elasticity (crease recovery) and heat settability have been desired compared with many synthetic fibers. We have studied about this subject by graft copolymerization of styrene and butadiene.<sup>1,2)</sup>

Though the elasticity (crease recovery) of the cotton fabric is remarkably improved by crosslinking, large decrease of tensile strength accompanied with crosslinking is yet left as an unsolved problem. Many studies have been reported about influence of the length of crosslinking in cotton on the fabric properties. There observed some data<sup>3)</sup> which suggested long crosslinking caused some decreases of tensile damage. However, the length of crosslinking studied up to this time was less than about 20 carbon atoms, so further study must be necessary about longer crosslinking.<sup>4)</sup>

As the graft copolymerization of reactive monomers seemed to be one of the effective method to give longer crosslinking, acrylamide and glycidyl methacrylate were graft copolymerized onto cotton and the effect of chemical after-crosslinking using these reactive groups in the grafted side chains was studied.

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\* This work was reported in more detail in the *Annual Report of the Institute for Chemical Fiber, Kyoto Univ.*, 22, 11 (1965) and *J. Soc. Fiber Sci. and Technol. Japan*, 22, 504 (1966).

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## EXPERIMENTAL

### Materials

Cotton fabric: same as used in our previous work.<sup>1,2)</sup>

Acrylamide: recrystallized twice from benzene solution

Glycidyl methacrylate: shaken with 0.1 % NaOH aqueous solution, washed and dehydrated with Na<sub>2</sub>SO<sub>4</sub>.

Acrylic esters: distilled in vacuum.

Other reagents: reagent grade

### Graft copolymerization

1. Irradiation: Co<sup>60</sup>  $\gamma$ -ray was applied at room temperatures. Dose rate:  $3.54 \times 10^4$  r/hr.
2. Acrylamide (AM): Pre-irradiation method in air was used in many cases. After 1 hour irradiation in air (total dose =  $3.54 \times 10^4$  r), cotton fabric was immersed in 30 % AM aqueous solution and heat polymerized under vacuum of  $10^{-4}$  mmHg. In the case of simultaneous irradiation grafting in vacuum, 10 % AM aqueous solution was used. In both cases, the homopolymer was removed by hot water extraction, and the weight increase of the fabric was assumed to be caused by grafting.
3. Acrylamide-acrylic ester: Cotton fabric containing the same amount of water was immersed in AM/acrylic ester (50/50) mixed dioxane solution and irradiated under vacuum of  $10^{-4}$  mmHg. AM and acrylic ester homopolymers were removed with hot water and acetone extractions respectively. AM content in the grafted side chain was calculated from the nitrogen analysis of the grafted cotton.
4. Glycidyl methacrylate (GMA): Cotton fabric containing the same amount of water was immersed in dioxane solution containing GMA of weight 4 times to cotton fabric and irradiated at room temperature. GMA homopolymer was removed by hot dioxane extraction.

### Crease recovery

The test sample of cloth (1×4 cm: the larger dimension in warp direction) was folded at the center of its long direction and 500 g weight was put on it for 5 min., then the weight was removed and after 5 min. the crease angle was measured.

## RESULTS AND DISCUSSION

### 1. Acrylamide (AM)

#### 1.1 Graft copolymerization of AM

Examples of graft copolymerization of AM onto cotton fabric were shown in Table 1 (pre-irradiation in air) and Table 2 (simultaneous irradiation). In both cases, various % grafting up to 60 % were obtained at rather small dose of  $10^4 \sim 10^5$  r.

Table 1. Examples of % grafting of acrylamide using pre-irradiation method in presence of air.

Polymerization temperature (°C)		100	70
Polymerization time (hr)	1/2	22.8%	20.5%
	1	22.9	48.5
	3	36.1	—
	5	61.7	—

Total dose  $3.54 \times 10^4$  r.; 30 % acrylamide aqueous solution was used.

Table 2. Examples of grafting of acrylamide using simultaneous irradiation method in vacuum.

Time (hr)	Irradiation		% Grafting
	Total dose (r)		
1	$3.54 \times 10^4$		2.9
2	$7.08 \times 10^4$		14.1
3	$1.06 \times 10^5$		23.4
4	$1.42 \times 10^5$		30.8
5	$2.12 \times 10^5$		*

10 % acrylamide aqueous solution was used.

\* Insoluble homopolymer in hot water.

## 1. 2. Crosslinking of AM grafted cotton

### 1. 2. 1. Crosslinking with formaldehyde in aqueous solution

About 20 % AM grafted cotton fabrics were treated with formaldehyde aqueous solution (crosslinked with formaldehyde in fiber swelling state). The results were shown in Table 3. With AM grafting alone, though the decrease of tensile strength of the warp of the cotton fabric was small, crease recovery was improved a little only in wet state. When the grafted cotton was treated with 36 % formalin at 100°C, high value of about 95 % wet crease recovery was obtained while

Table 3. Crosslinking of acrylamide grafted cotton with formalin.

Reaction condition			% Grafting	Crease recovery (w) %		Tensile strength of warp (g)	
HCHO % <sup>a)</sup>	Temperature (°C)	Time (hr)		Dry	Wet	Dry	Knot
—	—	—	0 <sup>c)</sup>	40.2	46.6	319	341
—	—	—	22.8	33.6	55.8	318	267
7.5 <sup>b)</sup>	30	48	0	34.7	69.7	—	—
"	"	"	22.9	46.7	70.8	44	53
36	100	1/2	0	44.7	70.3	—	—
"	"	"	29.0	45.0	94.5	135	119
"	80	"	17.6	27.8	76.1	241	—
"	60	"	"	36.1	50.6	241	—

a) Catalyst, H<sub>2</sub>SO<sub>4</sub> 0.04 N

b) Catalyst, HCl 17.2 %

c) Original cotton, 0.1 % NaOH aqueous solution, 1 hr boil.

the tensile decrease of the warp was very large. Relative high wet crease recovery with small tensile damage of the warp was obtained at treating temperature of 80°C. Improved dry crease recovery was scarcely obtained by such a wet treatment as the case of ungrafted cotton.<sup>5)</sup>

### 1. 2. 2. Crosslinking with formaldehyde in the mixture of H<sub>2</sub>O/CH<sub>3</sub>COOH

Following the work of Reeves *et al.*,<sup>6)</sup> AM grafted cottons were treated with formaldehyde in CH<sub>3</sub>COOH aqueous solution, the water content of which was varied by adding various amounts of acetic acid. The result was shown in Table 4.

Table 4. Formaldehyde treatment of acrylamide grafted cotton in H<sub>2</sub>O/CH<sub>3</sub>COOH mixture of various water contents.

H <sub>2</sub> O/CH <sub>3</sub> COOH	% Grafting	Crease recovery (W) (%)		Warp yarn	
		Dry	Wet	Tensile Strength (g)	Elongation (%)
70/30	20.9	31.7	67.2	—	—
50/50	0	40.0	48.3	—	—
„	27.5	31.7	69.5	—	—
20/80	0	65.6	61.1	163	9.2
„	27.5	82.8	97.2	96	15.0

HCHO, 7.4 % ; H<sub>2</sub>SO<sub>4</sub>, 0.04 N ; 70°C, 1 hr.

Similar to the result obtained by Reeves,<sup>6)</sup> higher values of dry and wet crease recoveries were obtained, especially in AM grafted cotton, at the ratio of H<sub>2</sub>O/CH<sub>3</sub>COOH=20/80, though large tensile damage was caused.

### 1. 2. 3. Crosslinking of N-methylolated acrylamide grafted cotton with formaldehyde

When AM grafted cotton was reacted with formaldehyde as described above, it was supposed that formaldehyde reacted not only with amide groups in the grafted chains but also with hydroxyl groups of cellulose resulting short crosslink-

Table 5. Curing of N-methylolated acrylamide grafted cotton.

Treating	% Grafting	Crease recovery (W) (%)		Warp yarn	
		Dry	Wet	Tensile Strength (g)	Elongation (%)
N-Methylolation	0	52.8	56.8	312	9.4
	5.0	44.5	61.1	312	8.7
	15.1	38.3	54.5	268	8.4
	20.9	42.8	66.7	266	9.7
	36.1	25.0	56.1	208	13.1
N-Methylolation followed by curing	0	58.3	65.6	155	6.6
	5.6	69.5	72.2	178	7.8
	15.1	38.3	65.6	235	9.8
	20.9	40.6	59.5	218	11.7
	32.6	38.9	83.9	222	11.8

ing and no effect of grafting was appeared. Therefore, according to Kamogawa *et al.*,<sup>7)</sup> amide groups in the grafted side chains were first N-methylolated with formalin and then cured. It was supposed that possibility of forming of short crosslinking in the cotton cellulose was much prevented by this procedure even though there might be some short crosslinkings formed by free formaldehyde. After N-methylolated AM grafted cotton was padded with 0.1N NH<sub>4</sub>Cl aqueous solution to about 100% wet pick up and dried at 80°C for 10 min., then it was cured at 130°C for 10 min. As shown in Table 5, crease recovery was not enhanced by N-methylation alone, but after curing, much improved crease recoveries in both dry and wet state were obtained for 5.6% grafted cotton with rather small tensile damages.

Next, the samples of AM grafted cottons with and without N-methylation were padded with 5% formalin and 0.1% NH<sub>4</sub>Cl aqueous solution and followed by curing as described above. Remarkable improvement was observed in crease recoveries in both wet and dry as shown in Table 6, but large tensile damage was occurred.

Table 6. Formalin curing of N-methylolated acrylamide grafted cotton.

Treating	% Grafting	Crease recovery (W) (%)		Warp yarn	
		Dry	Wet	Tensile Strength (g)	Elongation (%)
N-Methylation followed by curing with formalin	0	92.2	86.1	84	5.3
	5.0	100.0	92.2	70	6.2
	15.1	76.7	76.7	136	9.7
	20.9	90.0	89.5	27	10.0
	36.1	95.6	91.7	27	25.8
Curing with formalin without N-Methylation	0	84.5	84.5	71	5.5
	5.0	76.1	77.2	95	6.3
	15.1	40.0	75.6	151	13.6

## 2. Cograft polymerization of AM and acrylic ester onto cotton.

In order to study dilution effect of reactive groups in the grafted side chains and influence of soft polymer such as butyl acrylate, cografted cottons of AM and some acrylic esters were examined.

### 2. 1. Cograft polymerization of AM and acrylic ester

Methyl acrylate (MA), ethyl acrylate (EA) and butyl acrylate (BA) were used as a comonomer in the cograft polymerization. The results were shown in Table 7. Rather high AM contents were obtained in the grafted side chains as the copolymerization rate of AM was higher than that of acrylic esters. With increase of % grafting, relative contents of AM in the grafted side chains showed a tendency to decrease.

### 2. 2. Acid curing of N-methylolated AM-acrylic ester grafted cotton

As it was found no remarkable improvement in both dry and wet crease recoveries was obtained for the samples cografted with AM-acrylic ester, then it

Table 7. Examples of graft copolymerization of acrylamide-acrylic ester<sup>a)</sup> (simultaneous irradiation in vacuum).

Comonomer	Total monomer concentration (%)	Total dose (r)	% Grafting	AM contents in the grafted chain (%)
MA	20	$6.02 \times 10^5$	11.5	103.0
	30	„	15.8	93.7
	40	$1.77 \times 10^5$	20.1	59.9
	„	$6.02 \times 10^5$	37.1	—
	50	„	52.1	77.0
	„	$8.50 \times 10^5$	36.0	86.5
EA	20	$1.77 \times 10^5$	11.4	—
	50	„	21.5	—
BA	20	$1.77 \times 10^5$	18.3	83.6
	„	$6.02 \times 10^5$	28.0	58.3
	30	„	28.4	—
	40	$1.77 \times 10^5$	50.5	64.6
	„	$6.02 \times 10^5$	54.5	—
BA alone	20	$1.77 \times 10^5$	4.9	0
	30	„	7.3	0
	40	$6.02 \times 10^5$	12.7	0

<sup>a)</sup> Monomer ratio 50:50

Table 8. Acid curing of N-methylolated acrylamide-acrylic ester cografed cotton.

Comonomer	Grafting %	AM contents in the grafted chain (%)	Crease recovery (W) (%)		Warp yarn	
			Dry	Wet	Tensile Strength (g)	Elongation (%)
	0	—	45.6	47.8		
MA	11.5	103.0	45.0	69.5		
	23.1	—	38.3	80.6	252	13.9
	36.0	86.5	27.2	88.9		
	52.0	77.0	20.6	75.6		
EA	11.4	—	48.3	58.9	269	9.8
	21.5	—	47.2	90.0	237	10.5
BA	18.3	83.6	58.3	73.9		
	28.0	58.8	73.9	92.2	192	8.3
	50.5	64.6	44.5	83.3	168	16.2
BA alone	4.9	0	57.3	46.7	265	11.1
	7.3	0	60.6	53.4	243	10.9
	12.7	0	85.0	85.6	209	12.5

was subjected to N-methylolation and acid curing.

Compared with the cotton which was grafted with AM alone and subjected to N-methylolation followed by acid curing (Table 5), generally higher wet crease recovery was obtained in bicomponent cografed cotton, and especially in the case of BA, good dry crease recovery was obtained as shown in Table 8.

### 3. Glycidyl methacrylate (GMA)

As GMA molecule has a vinyl double bond and a reactive epoxy ring, graft copolymerization onto cotton using this double bond and then various chemical reactions including crosslinking by used of this epoxy ring may be performed. Iwakura *et al.*<sup>8)</sup> and Nakahara<sup>9)</sup> reported the graft copolymerization of this monomer onto cellulosic fiber by ceric salt method and discussed the reaction of epoxy ring in the grafted side chain. Improvement of dyeability was obtained, but no information had been given about crease recovery of the GMA grafted cotton fabric.

#### 3. 1. Graft copolymerization of GMA onto cotton fabric

As we used simultaneous irradiation method at room temperatures, the % grafting was varied by the irradiation temperature. But no significant deviation was observed if graft copolymerization was carried out at the same temperature, and % grafting was generally controlled by the total doses. As seen from Table 9, % grafting below 70~80 % was obtained with  $\gamma$ -ray irradiation of up to  $2 \times 10^5$  r, but insoluble GMA homopolymer was produced above this dose. About 20 % GMA grafted cotton was insoluble in cupraammonium hydroxide and it was confirmed by the HCl-dioxane titration method<sup>10)</sup> that the epoxy rings in the grafted side chains did not opened. Recently Manaka and Tomioka<sup>11)</sup> also observed in their experiment of the irradiation grafting of GMA onto polyethylene that the epoxy rings of GMA did not effected by  $\gamma$ -ray irradiation below  $1 \times 10^7$  r.

Table 9. Examples of graft copolymerization of glycidyl methacrylate onto cotton by simultaneous irradiation in the presence of air.

Irradiation		% Grafting (%) <sup>*</sup>	
Time (hr)	Total dose (r)	I	II
1.0	$3.54 \times 10^4$	4.9	10.2
2.0	$7.08 \times 10^4$	17.0	25.9
2 <sup>1/2</sup>	$8.85 \times 10^4$	25.1	—
3.0	$1.06 \times 10^5$	—	60.1
4.0	$1.42 \times 10^5$	45.9	—
5 <sup>1/6</sup>	$1.83 \times 10^5$	60.1	—
5 <sup>1/2</sup>	$1.95 \times 10^5$	80.1	—
6.0	$2.12 \times 10^5$	—	**

\* I. Room temperatures about 0~10°C

II. Room temperatures about 20~30°C

\*\* Insoluble homopolymer in hot dioxane.

#### 3. 2. Crosslinking of GMA grafted cotton

##### 3. 2. 1. Crosslinking by ethylene diamine or phosphoric acid-methylethyl ketone aftertreatment

No improvement was observed in both dry and wet crease recoveries of GMA grafted cotton fabric before or after the treatment with ethylene diamine.

It was accepted that the epoxy ring of GMA reacted with ketone in the presence of  $H_3PO_4$  and produced ketal which was crosslinked by heating.<sup>12)</sup> Table 10

Table 10. Curing of glycidyl methacrylate grafted cotton aftertreated with  $H_2PO_4$ -methyleneethyl ketone.

% Grafting	Crease recovery (W) (%)		Warp yarn	
	Dry	Wet	Tensile strength (g)	Elongation (%)
3.6	53.9	57.8	162.2	5.8
16.8	52.2	60.0	207.8	5.8
21.3	55.6	56.7	242.1	8.8
37.5	79.4	48.3	240.6	7.9
43.2	66.1	51.6	262.8	7.2

All samples were padded to 100% wet pick up with  $H_2PO_4$ -MEK (1%) dioxane solution and cured at 120°C for 30 min.

shows the result of this crosslinking method.

Though the dry crease recovery increased to about 80% in some cases, no improvement was observed in wet crease recovery. Tensile damage of the warp of the cotton fabric thus treated was lowered as the % grafting was increased.

### 3. 2. 2. Crosslinking by oxalic acid-morpholine aftertreatment

In this case, no improvement of crease recovery was observed in wet state, though dry crease recovery was enhanced in accordance with increase of % grafting (Table 11). The tensile damage decreased to some degree by the GMA grafting.

Table 11. Curing of glycidyl methacrylate grafted cotton aftertreated with oxalic acid-morpholine.

% Grafting	$(COOH)_2$ (%)	Morpholine (%)	Crease recovery (W) (%)		Warp yarn	
			Dry	Wet	Tensile strength (%)	Elongation (%)
3.9	5	0.3	57.8	56.2	97.2	5.9
16.8	„	„	60.5	55.6	162.4	6.8
21.3	„	„	67.2	57.3	150.1	7.9
36.4	„	„	74.5	48.9	174.5	7.2
43.2	„	„	71.2	57.8	179.2	6.8
16.8	„	—	63.3	57.8	105.0	5.3
16.8	—	0.3	50.0	47.8	—	—

All samples were padded to 100% wet pick up with  $(COOH)_2$ -morpholine aqueous solution and cured at 120°C for 30 min.

### 3. 2. 3. Curing with $Zn(BF_4)_2$

$Zn(BF_4)_2$  is acidic and acts as a catalyst of ring opening reaction of epoxy ring. Table 12 was the result of curing at different temperatures with  $Zn(BF_4)_2$  of some different concentrations.

By this process, crease recoveries were remarkably improved and the cotton fabric with both dry and wet crease recoveries of about 70% were obtained. As to wet crease recovery, generally better results were obtained with larger  $Zn(BF_4)_2$  concentration, though larger tensile damages occurred.



Table 12. Curing of glycidyl methacrylate grafted cotton padded with  $Zn(BF_4)_2$  methanol solution.

% Grafting	Curing		Crease recovery (W) (%)		Warp yarn	
	Zn ( $BF_4$ ) <sub>2</sub> (%)	Temperature (°C) (5 min.)	Dry	Wet	Tensile strength (%)	Elongation (%)
0	5.0	150	38.9	48.9	33.8	4.1
22.7	1.5	125	76.7	62.8	150.9	4.2
22.7	5.0	125	79.4	72.2	—	—
22.7	1.5	150	76.7	67.8	159.9	8.4
22.2	5.0	150	77.8	76.7	77.2	5.1

All samples were padded to 100 % wet pick up with  $Zn(BF_4)_2$  methanol solution and cured.

Table 13. Curing of glycidyl methacrylate grafted cotton padded with 1.5 %  $Zn(BF_4)_2$  aqueous solution.

% Grafting	Crease recovery (W) (%)		Warp yarn	
	Dry	Wet	Tensile strength (g)	Elongation (%)
0	47.2	50.0	99.7	7.4
4.9	69.5	60.6	207.0	8.6
9.8	60.6	48.3	267.5	11.2
16.5	63.9	46.7	267.9	9.0
22.7	76.7	62.8	148.8	7.8
43.0	72.8	60.0	201.3	9.8
61.0	76.1	61.7	159.2	9.9
80.1	60.0	48.9	229.4	9.5

All samples were padded to 100 % wet pick up with 1.5 %  $Zn(BF_4)_2$  aqueous solution and cured at 125°C for 5 min.

Table 13 was the result of curing of the GMA grafted cotton of various % grafting at low  $Zn(BF_4)_2$  concentration (1.5 %). Considerable improvement was observed in dry crease recovery by the grafting of GMA and wet crease recovery of above 60 % was obtained in some cases, though the values were generally less than that of shown in Table 12. Though the tensile damage of warp of the grafted cotton fabric was caused by crosslinking, it was remarkably prevented by the GMA grafting.

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