JOURNAL OF APPLIED POLYMER SCIENCE VOL. 9, PP. 3721-3736 (1965)

Concerted Effects of Grafting and Crosslinking in Cotton Fabrics

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Synopsis

The formaldehyde crosslinking of the methyl, ethyl, or *n*-butyl acrylate-grafted cotton fabrics was performed in the dry or semi-dry systems. It was found that the reaction rates of crosslinking of the grafted cotton were not much retarded, the dry and wet crease recoveries of the grafted cotton, especially with *n*-butyl acrylate, were significantly improved with increasing bound formaldehyde, and the hydrophobicity of the butyl acrylate-grafted cotton had a tendency to be dissipated by a slight extent of crosslinking. Although the tensile and tear strength, breaking elongation, and thermosetting property of butyl acrylate-grafted cotton fabrics inevitably decreased with increasing bound formaldehyde, the loss was smaller than that of the ungrafted and formaldehyde-crosslinked cotton. Water imbibition, and moisture regain increased, and water repellency decreased with increasing bound formaldehyde. Crosslinking in the wet system, improved the wet crease recovery, as in the ungrafted cotton. Furthermore, in the butyl acrylate grafting after partial crosslinking with *N*-methylolacrylamide, the hydrophilic property of crosslinked cotton was almost retained unchanged and the thermosetting property recovered to that of the untreated cotton at about 35% graft-on.

INTRODUCTION

In a previous paper from our laboratory, it was reported that the cotton fabrics grafted with alkyl acrylates, such as propyl or butyl acrylate, having a homopolymer second-order transition temperature far below room temperature showed significant improvements of physical properties.[1] Especially the crease recovery in the wet state was remarkably improved without much loss in tear strength. Furthermore, the grafting imparted a thermosetting ability to some extent. However, because of their hydrophobic properties a longer time of immersion was required to obtain the equilibrium wet crease recovery, even in water containing a wetting agent. Also, results of measurements of the water imbibition in the presence of wetting agent suggested competition of the opening of fiber structure and the imparting of hydrophobic property in the grafting.

If an "open" structure facilitating the penetration of water molecules could be created in the grafted cotton, the hydrophobic property would be expected to be dissipated to a certain extent. A kind of chemical intermolecular crosslinking which is known to increase moisture regains or water imbibition[2,3] was therefore considered. The crosslinking was typically carried out on wet or swollen systems. In the grafted cotton, because an open structure was formed to some extent due to the presence of graft polymers, the above aim might be achieved appreciably even with crosslinking in the dry or unswollen systems. Furthermore, the effects of chemical crosslinking in concert with grafting are expected to bring about a further improvement of the crease recovery without much loss of tear strength and thermosetting properties.

For the above reasons cotton fabrics grafted with various acrylates were subjected to the formaldehyde crosslinking in the dry, semi-dry, or wet systems.

In addition, cotton fabrics crosslinked with *N*-methylolacrylamide in the semi-dry system were grafted with *n*-butyl acrylate in order to determine the effects of grafting and crosslinking together.

EXPERIMENTAL

Materials

The cotton fabrics used were two types of scoured and bleached broadcloth (40's, W55 × F29/cm.), designated A and B. The various acrylate monomers used for grafting were purified from the commercial materials by the usual method. Commercial formalin was used as the formaldehyde for crosslinking. *N*-Methylolacrylamide for crosslinking was synthesized from acrylamide and paraformaldehyde.[4]

Grafting Procedure

The grafting for cotton fabrics was carried out in an aqueous emulsion system by the same ceric ion method as in the previous report.[1] The cotton fabrics crosslinked with *N*-methylolacrylamide were grafted with *n*-butyl acrylate under the following conditions. The aqueous reaction liquor used for grafting contained 3% *n*-butyl acrylate, 0.005 mole/l. Ce^{+4}, 0.01 mole/l. HNO_3, and 0.5% cationic detergent (APC, alkylmethylpyridinium chloride). The reaction of grafting was performed at 30°C. for 30–180 min. and in air at atmospheric pressure, degassing being carried out before addition of the reaction liquor. After reaction, the cotton fabrics were washed with acetone, then water, and finally extracted with acetone for about 20 hr.

Crosslinking with Formaldehyde

Formaldehyde crosslinking of acrylate-grafted cotton fabrics was carried out by the dry (curing), semi-dry (Form-D), and wet (Form-W) methods.[2,3]

Dry crosslinking was performed by soaking the fabric in aqueous solutions containing 5 or 10% formaldehyde, 0.5% ammonium acetate as catalyst, and 0.2% nonionic wetting agent at 80 liquor ratio, room temperature, and for 120 min., pressing out to about 80% pickup of the solution, predrying for 7 min. at 60°C., curing for 10 min. at 110–130°C., and washing with water. The semi-dry crosslinking was carried out in aqueous solutions containing 3.6% formaldehyde, 78.4% acetic acid, 1.0% hydrochloric acid as catalyst, and 0.2% nonionic wetting agent for 30–120 min. at. 27.5°C. Wet crosslinking was performed in aqueous solutions containing 7.5% formaldehyde, 4.0% hydrochloric acid, and 0.2% nonionic wetting agent for 60–120 min. at 30°C. The cotton fabrics used for wet crosslinking were pretreated in boiling water containing 0.2% nonionic wetting agent for 2 hr., pressed out to about 100% pickup, and then subjected to the reaction. The content of bound formaldehyde was determined by the sodium bisulfite method and expressed on the basis of the cellulose component.[5]

Crosslinking with *N*-Methyloacrylamide

The crosslinking of cotton fabrics with *N*-methylolacrylamide was carried out following Gardon's method.[6] However, ammonium chloride was used as the catalyst for acrylamidomethylation because of our preliminary experimental results that acid hydrolysis leads to a considerable loss of mechanical properties.[7] In the first step, the cotton fabrics were soaked in the aqueous solutions containing 5% *N*-methylolacrylamide and 2% ammonium chloride at about 50 liquor ratio, 5°C., and for 5 min., air-dried overnight without pressing out, cured for 15 min. at 100°C., and washed with water. The degree of etherification was determined to be 0.23 mmole/g. from the estimation of double bonds by the mercaptoethanol method. In the second step, the partially etherified cotton was treated with an aqueous 2% sodium hydroxide solution for 2 hr. at 60°C. In the second step, intermolecular crosslinking occurs between double bonds of substituted side chains and OH groups of cellulose chains by the Michael's reaction. From the determination of residual double bonds, the degree of crosslinking was found to be 0.18 mmole/g. and the conversion of double bonds 78.0%. The crosslinked cotton fabrics were subjected to graft copolymerization with *n*-butyl acrylate.

Physical Testing

The dry and wet crease recoveries, tensile strength, breaking elongation, and tear strength were measured as in the previous paper.[1] The wet crease recovery measured after being immersed in water containing 0.5 nonionic wetting agent for 2 hr. at 40°C. was taken as the equilibrated value, and compared with that by the usual method by immersion for 15 min. at 40°C. in water containing 0.2% nonionic wetting agent and 0.2% sodium carbonate. The crease recoveries were all measured only for the warp direction, as a previous study showed values for warp and filling of untreated cotton fabrics to be very close.[1]

Measurements of moisture regain, water imbibition, water repellency, and thermosetting properties were carried out as in the previous report.[1]

RESULTS AND DISCUSSION

Semi-Dry Formaldehyde Crosslinking

The rates of reaction of formaldehyde with the semi-dry crosslinking were investigated for the cotton fabrics grafted with methyl, ethyl, and *n*-butyl acrylates. The effects of reaction time on the content of bound

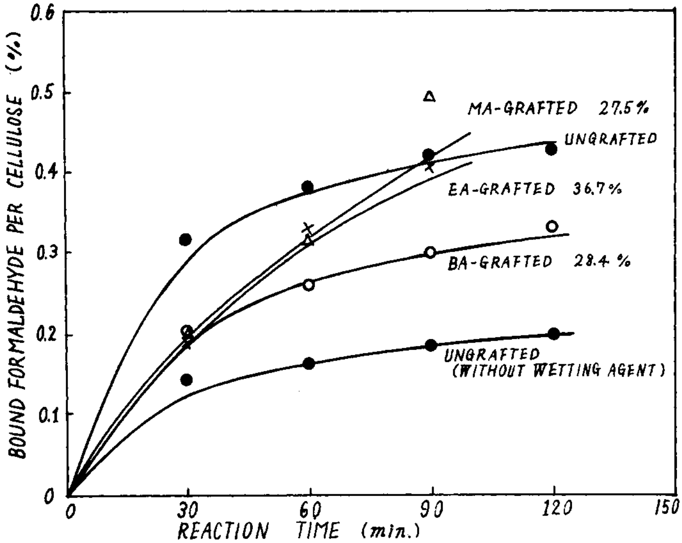

Fig. 1. Effects of reaction time on the content of bound formaldehyde expressed on the basis of the cellulose component for the ungrafted fabrics and cotton fabrics grafted with methyl, ethyl, or *n*-butyl acrylate.

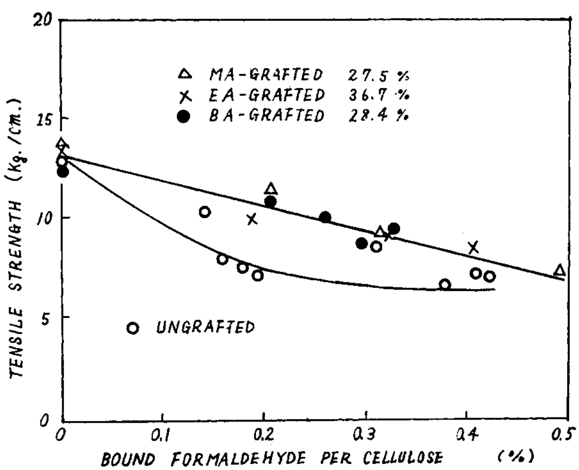

Fig. 2. Effects of the content of bound formaldehyde on tensile strength for the ungrafted fabrics and cotton fabrics grafted to about 30% graft-on with methyl, ethyl, or *n*-butyl acrylate.

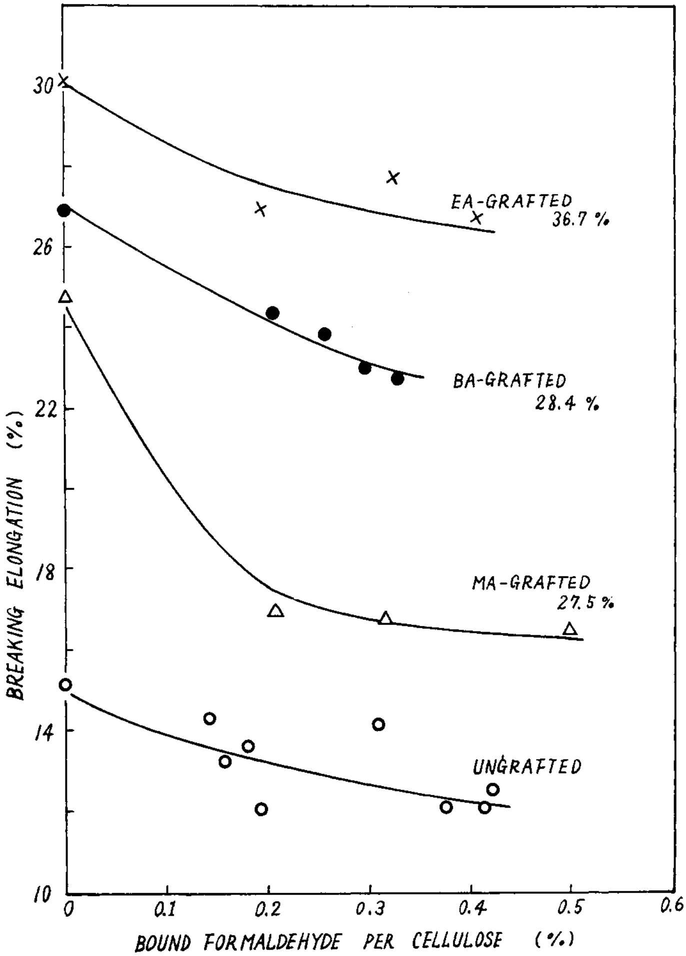

Fig. 3. Effects of the content of bound formaldehyde on breaking elongation for the ungrafted fabrics and cotton fabrics grafted to about 30% graft-on with methyl, ethyl, or *n*-butyl acrylate.

formaldehyde expressed on the basis of the cellulose component for the grafted cotton of about 30% graft-on, are shown in Figure 1. It is noteworthy that in the presence of wetting agent, the reaction rates of grafted cotton fabrics are considerable though somewhat smaller than those of the ungrafted cotton. This may be attributable to opening of the structure by grafting. The reaction rate of the butyl acrylate-grafted cotton is is somewhat less than that of the other grafted cottons, owing perhaps to its hydrophobicity.

The effects of the content of bound formaldehyde on tensile strength, breaking elongation, and tear strength for the grafted cotton fabrics of about 30% graft-on are shown in Figures 2, 3, and 4, respectively. Although the tensile and tear strength of any grafted cotton fabrics still

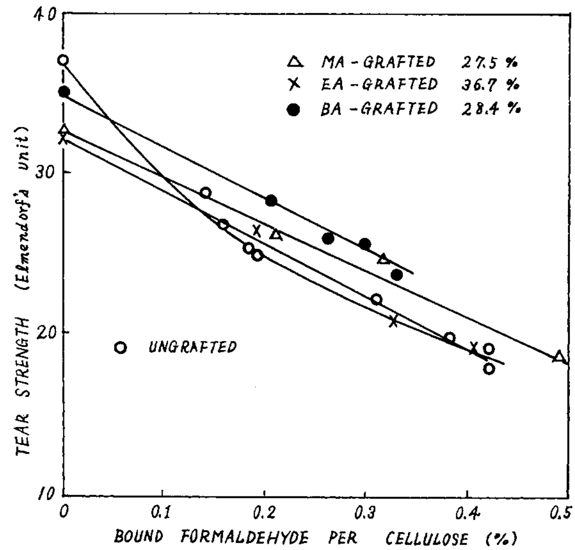

Fig. 4. Effects of the content of bound formaldehyde on tear strength for the ungrafted fabrics and cotton fabrics grafted to about 30% graft-on with methyl, ethyl, or *n*-butyl acrylate.

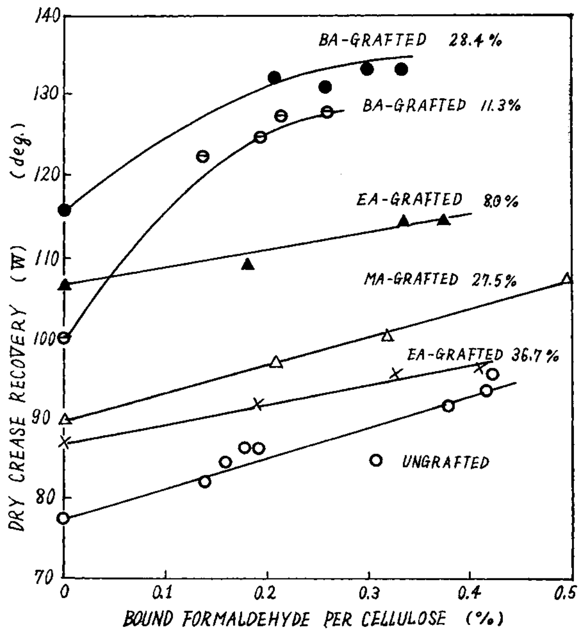

Fig. 5. Effects of the content of bound formaldehyde on dry crease recovery for the ungrafted fabrics and cotton fabrics grafted with methyl, ethyl, or *n*-butyl acrylate.

decrease with increasing bound formaldehyde, the decrease seems to be somewhat less marked than that of the ungrafted cotton fabrics. It is noted that the breaking elongation is retained much better than that of ungrafted cotton fabrics, even at a higher content of bound formaldehyde.

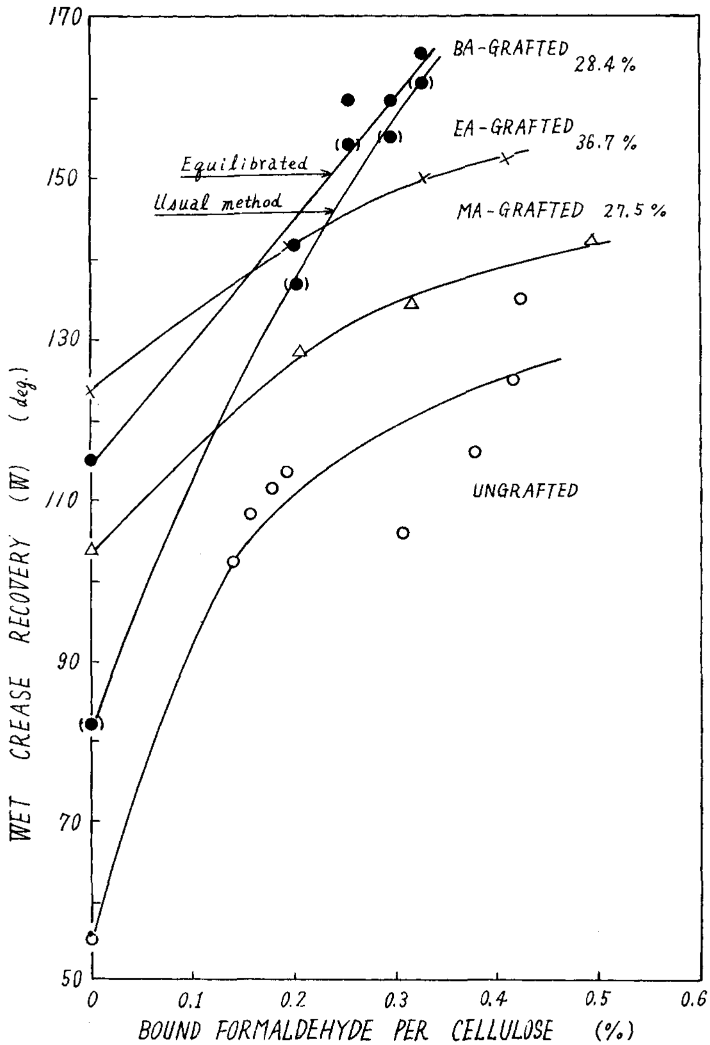

Fig. 6. Effects of the content of bound formaldehyde on wet crease recovery for the ungrafted fabrics and cotton fabrics grafted with methyl, ethyl, or *n*-butyl acrylate.

The dry crease recovery of grafted cotton fabrics is improved with increasing bound formaldehyde, as shown in Figure 5. It should be noted that the improvement in the butyl acrylate-grafted cotton fabrics is characteristic and distinctly higher than that of all other grafted fabrics at the slight extent of bound formaldehyde. The improvement in behavior for

TABLE I
Effects of Bound Formaldehyde by Semi-Dry Method on Water Imbibition, Moisture Regain, Water Repellency, and Thermosetting Property of Acrylate-Grafted Cotton Fabrics

Sample	Extent of grafting, %	Content of bound formaldehyde/cellulose, %	Water imbibition/cellulose, %		Moisture regain, %[a]	Water repellency at time of sinking, sec.[b]	Thermosetting property as angle of opening[c]
			Water	0.5% Nonionic wetting agent			
Ungrafted cotton (A)	0	0	36.0	38.0	8.1	0.90	37°
		0.143	41.6	40.5	7.7	0.88	~180°
		0.160	—	—	8.3	—	—
		0.182	40.0	40.1	8.6	0.72	—
		0.195	—	—	8.4	—	~180°
		0.312	40.8	41.0	—	0.54	—
		0.380	—	—	—	0.44	—
		0.418	—	—	—	0.52	—
		0.422	—	—	—	0.42	—
Grafted cotton (A)							
Methyl acrylate	27.5	0	—	—	—	—	27°
		0.209	—	—	—	—	39°
		0.317	—	—	—	—	58°
		0.494	—	—	—	—	100°
Ethyl acrylate	36.7	0	—	—	4.2	—	26°
		0.192	—	—	4.9	—	36°
		0.324	—	—	4.8	—	58°
		0.408	—	—	5.2	—	81°
n-Butyl acrylate	11.3	0	22.4	40.7	5.5	68.7	29°
		0.137	32.3	44.9	6.5	53.9	58°
		0.192	—	—	6.9	34.2	68°
		0.214	36.8	40.8	7.2	29.3	—
		0.258	43.3	40.8	7.1	21.3	83°
n-Butyl acrylate	28.4	0	19.6	50.3	4.9	101.3	22°
		0.205	24.4	46.2	5.5	58.8	49°
		0.259	30.6	41.5	5.6	39.5	57°
		0.298	40.5	47.5	5.5	32.1	58°
		0.330	41.1	44.4	5.6	35.6	67°

[a] At 65% R.H. and 20° C.
[b] Using specimens 1 cm.^{2} and water containing 0.2% nonionic wetting agent at 20°C.
[c] Iron-pleated for 90 sec. at 165–175°C., allowed to open for 10 min. in the water containing 0.2% nonionic wetting agent at 40°C., and air-dried at 65% R.H. and 20°C.

the methyl or ethyl acrylate-grafted cotton fabrics appears to be almost the same as for the ungrafted cotton fabrics.

The wet crease recovery is improved much more markedly than dry crease recovery with increasing bound formaldehyde, especially in the butyl acrylate-grafted cotton fabrics, as shown in Figure 6. As expected, the wet crease recovery of butyl acrylate-grafted cotton fabrics measured by the usual method tends to approach the equilibrium value at small bound formaldehyde levels. This may perhaps be attributed to the effects of intermolecular methylene crosslinks; these crosslinks may open the structure to some extent, facilitating the penetration of water and development of swelling-elastomeric behaviors.[8]

Water imbibition in water alone per cellulose component of butyl acrylate-grafted cotton fabrics tends to approach the level attained in the presence of wetting agent with relatively light formaldehyde crosslinking, as shown in Table I. The moisture regain increases and water repellency decreases with increasing bound formaldehyde. These results show a qualitative correspondence with the improvement of wet crease recovery.

The thermosetting property of acrylate-grafted cotton fabrics inevitably decreases with increasing bound formaldehyde, as shown in Table I. Although it may be the effect of crosslinking, it is interesting that the thermosetting property of acrylate-grafted cotton of about 30% graft-on and 0.2% bound formaldehyde is retained near that of untreated cotton fabric. On the contrary, the thermosetting property of ungrafted cotton fabrics is all but lost by slight crosslinking. More graft-on will be required to improve the thermosetting property of grafted and crosslinked cotton fabrics. The results obtained above should seem to be important in evaluating the concerted effects of grafting and crosslinking.

Dry Formaldehyde Crosslinking

Since an opened structure is formed by grafting, the crease recovery especially in the wet state of grafted cotton fabrics, is expected to be improved even by the formaldehyde crosslinking in the dry state.

First, the reaction rates of butyl acrylate-grafted cotton of about 20% graft-on with formaldehyde in the curing method were compared with those of ungrafted cotton. The results are shown in Table II. The reaction rates for grafted cotton are almost the same as those for ungrafted cotton. Various mechanical properties measured are shown in Table III. These data show that the decreases of tensile strength, breaking elongation, and tear strength of butyl acrylate-grafted cotton fabrics on formaldehyde

TABLE II
Effects of Curing Condition on Extent of Bound Formaldehyde for Ungrafted and *n*-Butyl Acrylate-Grafted Cotton Fabrics

Sample	Extent of grafting, %	Curing conditions: CH_2O, %	Temperature, °C.	Time, min.	Content of bound formaldehyde/cellulose, %
Cotton fabrics (B)	0	5	110	10	0.078
	"	5	130	10	0.119
	"	10	130	10	0.155
Cotton fabrics (A)	23.7	5	110	10	0.085
	"	5	120	10	0.125
	"	10	120	10	0.187

curing are less than those of ungrafted cotton to almost the same extent as when the semi-dry method is used. As expected, the crease recovery, especially in the wet state, is improved significantly by formaldehyde curing, and the wet crease recovery measured by the usual method tends to come near the equilibrium value with increasing bound formaldehyde (see Table III). These results appear to be interesting in practice.

TABLE III
Effects of Bound Formaldehyde by Curing Method on Tensile Strength, Breaking Elongation, Tear Strength, and Crease Recovery for Ungrafted and *n*-Butyl Acrylate-Grafted Cotton Fabrics

Sample	Content of bound formaldehyde/cellulose, %	Tensile strength, kg./cm.	Breaking elongation, %	Tear strength, Elmendorf units	Crease recovery W, deg.		
					Dry	Wet	Equilibrium (wet)
Ungrafted cotton (A)	0	12.5	15.0	38.2	78°	56°	60°
Ungrafted cotton (B)	0	12.6	15.1	36.0	91°	79°	—
	0.078[a]	12.0	15.1	34.3	—	—	—
	0.119[a]	12.2	13.9	38.3	94°	94°	—
	0.155[a]	12.2	14.6	33.3	—	—	—
	0.181[b]	9.8	12.5	32.3	100°	117°	—
	0.315[b]	8.1	7.8	27.0	113°	128°	—
	0.439[b]	—	—	—	118°	117°	—
n-Butyl acrylate-grafted cotton (A), 23.7% graft-on	0	12.0	25.0	33.3	110°	79°	110°
	0.085[a]	10.7	24.0	30.0	114°	100°	120°
	0.125[a]	10.5	23.1	29.0	119°	119°	129°
	0.187[a]	9.5	23.3	27.6	124°	127°	137°

[a] Cured by the conditions shown in Table II with ammonium acetate as catalyst.
[b] Cured for 5 min. at 110–130°C. using the solution containing 0.5% $Zn(NO_3)_2 \cdot 6H_2O$, 5% CH_2O, and 0.2% nonionic wetting agent.

Wet Formaldehyde Crosslinking

From Table IV, the reaction rates of formaldehyde with the aqueous swollen cotton seem to be almost unaffected or even increased somewhat by butyl acrylate grafting; this is attributed to formation of an open structure by grafting.

As shown in Table V, the decreases of tensile strength, breaking elongation, and tear strength with increasing bound formaldehyde are very slight and to the same degree as the ungrafted cotton. The dry crease recovery of grafted cotton fabrics is only slightly improved and the wet crease recovery significantly improved by formaldehyde crosslinking in the swollen state. This is quite the same behavior as in the ungrafted cotton and it may be due to the existense of crosslinking mainly in the amorphous region of the relatively high lateral order in both cases. Also, in this case it is found that the wet crease recovery of grafted cotton fabrics measured by the usual method comes near the equilibrium value in the same way as fab-

TABLE IV
Reaction Rates between Formaldehyde and Ungrafted or *n*-Butyl Acrylate-Grafted Cotton Fabrics in Swollen State

Sample	Reaction conditions		Content of bound formaldehyde/cellulose, %
	Temperature, °C.	Time, min.	
Ungrafted cotton (B)	30	60	0.242
	"	90	0.322
	"	120	0.345
n-Butyl acrylate grafted cotton (B), 31.9% graft-on	30	60	0.226
	"	90	0.321
	"	120	0.450

ric subjected to dry or semi-dry crosslinking. In good correspondence with the above behavior, moisture regain and water imbibition of butyl acrylate-grafted cotton fabrics increase significantly on formaldehyde crosslinking in the swollen state, as shown in Table VI. It is important that even at 50% graft-on, a considerable extent of moisture regain and water imbibition have been imparted by the formaldehyde treatment in the swollen state. It is also noteworthy that the thermosetting property of ungrafted and grafted cotton fabrics is almost unaffected by the formaldehyde crosslinking in the swollen state, the property remaining almost the same as that of untreated cotton fabrics (Table VI).

TABLE V
Effects of Bound Formaldehyde in Swollen State on Tensile Strength, Breaking Elongation, Tear Strength, and Crease Recovery for Ungrafted or *n*-Butyl Acrylate-Grafted Cotton Fabrics

Sample	Content of bound formaldehyde/cellulose, %	Tensile strength, kg./cm.	Breaking elongation, %	Tear strength, Elmendorf units	Crease recovery *W*		
					Dry	Wet	Equilibrium (wet)
Ungrafted cotton (B)	0	12.6	15.1	36.0	91°	79°	—
	0.164	—	—	—	91°	103°	—
	0.242	12.0	15.3	31.0	—	—	—
	0.264	—	—	—	89°	112°	—
	0.322	11.7	15.1	30.0	—	—	—
	0.333	—	—	—	83°	108°	—
	0.345	11.4	14.7	31.5	—	—	—
	0.479	—	—	—	88°	120°	—
	0.529	—	—	—	91°	130°	—
n-Butyl acrylate-grafted cotton (B)	0	9.1	19.0	33.7	114°	123°	146°
	0.226	8.6	17.8	31.5	109°	138°	149°
	0.321	8.1	17.8	32.5	113°	155°	157°
	0.450	8.6	17.1	32.5	116°	158°	159°

TABLE VI

Effects of Formaldehyde Crosslinking in Swollen State on Moisture Regain, Water Imbibition, and Thermosetting Property of *n*-Butyl Acrylate-Grafted Cotton Fabrics

Sample	Extent of grafting, %	Content of bound formaldehyde %	Moisture regain, %	Water imbibition/cellulose, %		Thermosetting property as angle of opening
				Water	0.5% Nonionic wetting agent	
Ungrafted cotton (B)	0	0	7.8	37.0	36.0	47°
		0.333	—	—	—	46°
n-Butyl acrylate grafted cotton (B)	29.6	0	5.1	17.0	39.8	39°
	"	0.327	5.2	36.5	40.8	43°
	41.7	0	3.0	12.3	40.9	39°
	"	0.319	4.2	27.6	38.5	43°
	50.1	0	2.7	7.0	16.0	37°
	"	0.334	4.0	22.7	28.9	45°

Although grafting after semi-dry or dry crosslinking has been found to be quite difficult, grafting of the cotton fabrics crosslinked in the swollen state does not seem to be as difficult, as indicated by experiments now in progress.

Grafting for Cotton Crosslinked with *N*-Methylolacrylamide

For partially acrylamidomethylated (0.23 mmole/g.) and its crosslinked (0.18 mmole/g.) cotton fabrics the rates of grafting with *n*-butyl acrylate were measured as compared with that for untreated cotton fabrics. The results obtained are shown in Figure 7.

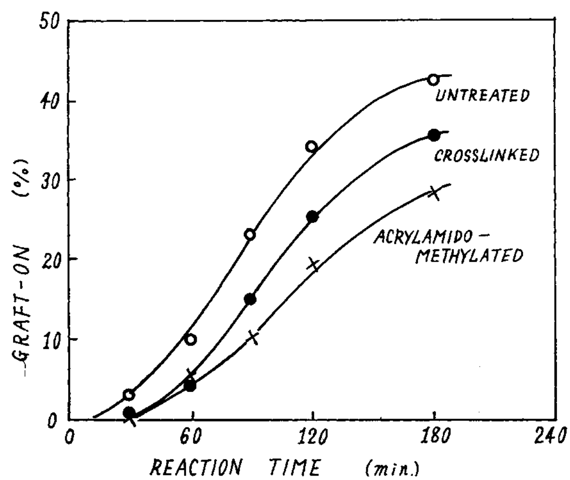

Fig. 7. Effects of reaction time on the graft-on of *n*-butyl acrylate for the untreated. partially acrylamidomethylated, and crosslinked cotton fabrics.

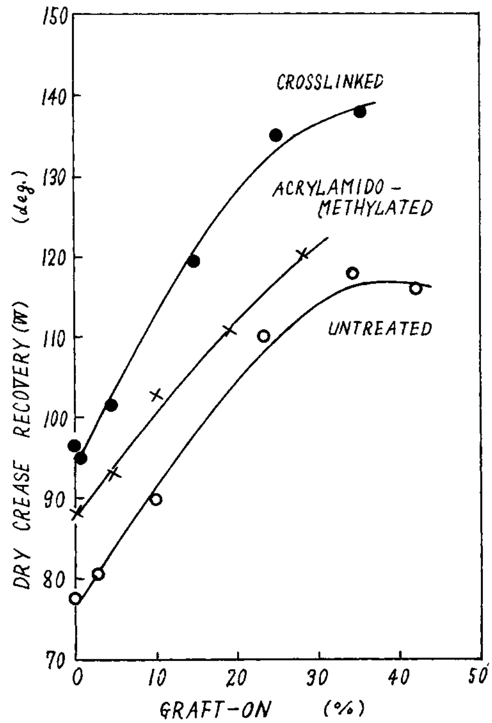

Fig. 8. Effects of *n*-butyl acrylate grafting on dry crease recovery of the untreated, partially acrylamidomethylated, and crosslinked cotton fabrics.

TABLE VII
Effects of *n*-Butyl Acrylate Grafting on Tensile Strength, Breaking Elongation, and Tear Strength of Untreated, Partially Acrylamidomethylated, and Acrylamidomethylated and Crosslinked Cotton Fabrics

Sample	Extent of grafting, %	Tensile strength, kg./cm.	Breaking elongation, %	Tear strength, Elmendorf units
Untreated cotton (A)	0	13.0	15.2	38.3
	3.0	12.8	18.0	38.2
	10.0	11.5	22.4	37.4
	23.2	11.2	26.0	35.8
	34.0	11.0	27.2	33.8
	42.4	9.2	27.8	34.2
Partially acrylamidomethylated (0.23 mmole/g.)	0	12.2	14.0	37.3
	4.7	12.0	16.3	36.8
	10.0	11.0	19.5	35.6
	19.0	10.0	21.0	35.2
	28.0	9.5	23.7	33.8
Acrylamidomethylated and crosslinked (0.18 mmole/g.)	0	9.4	12.4	33.7
	0.5	9.3	12.5	33.7
	4.5	9.8	13.5	33.4
	15.0	8.0	16.0	31.7
	25.3	8.7	17.7	31.7
	35.4	7.9	19.2	29.8

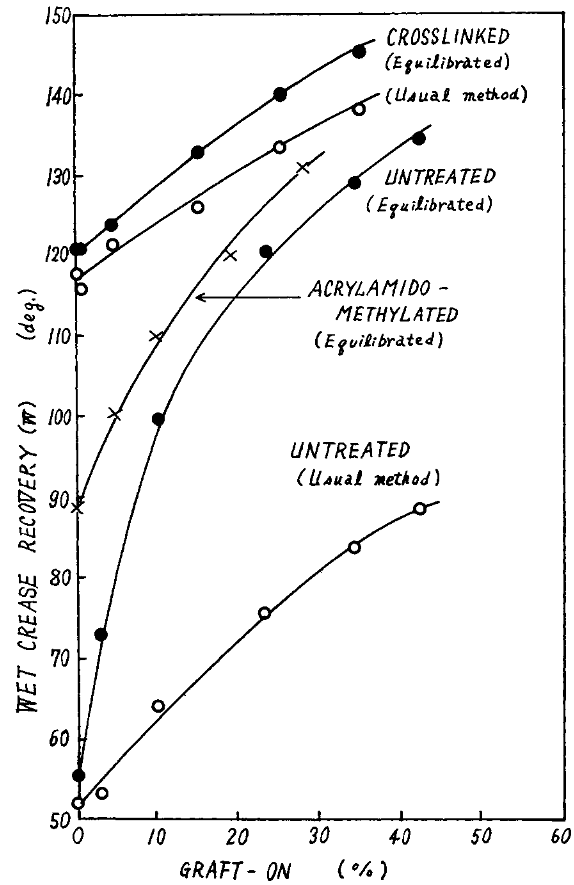

Fig. 9. Effects of *n*-butyl acrylate grafting on wet crease recovery of the untreated, partially acrylamidomethylated, and crosslinked cotton fabrics.

The rate of grafting is decreased by acrylamidomethylation but increased by the subsequent crosslinking, although somewhat less than untreated cotton. This may perhaps be attributed to opening of the structure of cotton fibers by the semi-dry crosslinking.[6]

Table VII shows that on partial acrylamidomethylation and subsequent crosslinking, the tensile strength, breaking elongation, and tear strength of cotton fabrics decrease to a certain extent. However, these decreases seem to be much less as reported by Gardon.[6] On grafting the crosslinked cotton fabrics with *n*-butyl acrylate, tensile strength and tear strength decrease furthermore somewhat, but the breaking elongation increases significantly with increasing graft-on. It is noteworthy that these general trends are the same as in the grafting of untreated or acrylamidomethylated cotton fabrics.

The dry and wet crease recoveries of the cotton fabrics are improved by acrylamidomethylation to some extent, and further significantly improved

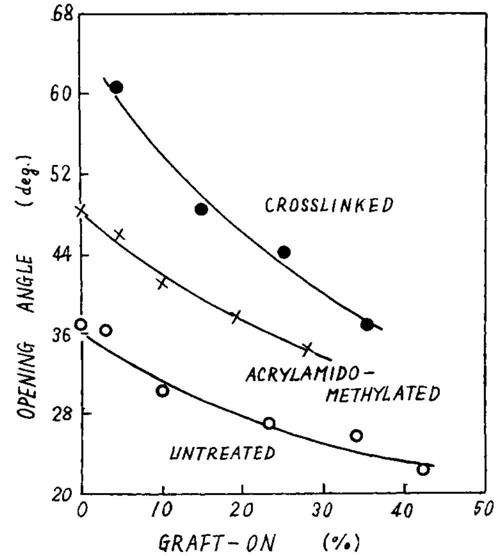

Fig. 10. Effects on *n*-butyl acrylate grafting on thermosetting property of the untreated, partially acrylamidomethylated, and crosslinked cotton fabrics.

by subsequent grafting of *n*-butyl acrylate with increasing graft-on as shown in Figures 8 and 9. More importantly, these data show that the equilibrated value of wet crease recovery for grafted cotton fabrics tends to diverge rather far from the value obtained by the usual method with increasing graft-on, however, it is still much nearer the value by the usual method, even at about 35% graft-on. (Fig. 9). Although crosslinking with *N*-methylolacrylamide after grafting has been not yet performed, the effect of crosslinking in concert with grafting on the wet crease recovery seems to be substantially the same as that of formaldehyde crosslinking after grafting described above.

The thermosetting property is lost with crosslinking and recovered to a level equal to that of untreated cotton fabrics at about 35% graft-on of *n*-butyl acrylate (Fig. 10). This might also be one of the concerted effects of crosslinking and grafting.

The financial assistance of the Japan Cotton Technical Institute, Osaka, was given in this work, and sincere thanks are extended to this organization. We are grateful to Nitto Spinning Co., Ltd. for offering the cotton fabrics for research.

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Résumé

La réticulation par le formaldéhyde du coton greffé à l'acrylate de méthyle, d'éthyle, ou de *n*-butyle a été effectuée dans un système sec ou semi-sec. On a trouvé que les vitesses des réactions de pontage du coton greffé ne sont pas retardées aussi fortement, que le défroissage à l'état sec et humide du coton greffé, spécialement avec l'acrylate de *n*-butyle, est fortement amélioré avec une augmentation du formaldéhyde lié, et que l'hydrophobie du coton greffé à l'acrylate de butyle a une tendance à diminuer par une légère augmentation du pontage. Bien que la force de tension et de déchirement, l'élongation à la rupture, et les propriétés thermodurcissables des cotons greffés à l'acrylate de butyle diminuent inévitablement avec une augmentation du formaldéhyde lié, la perte est plus petite que celle observée pour le coton non greffé et ponté par le formaldéhyde. L'absorption d'eau et la récupération l'humidité augmentent, et la répulsion d'eau diminue avec une augmentation du formaldéhyde lié. Par pontage, dans le système humide, le défroissage à l'état humide est amélioré ainsi qu'on peut le voir dans le coton non greffé. De plus, on a effectué le greffage à l'acrylate de butyle après pontage partiel au moyen de *N*-méthylolacrylamide, avec comme résultat que les propriétés hydrophiles du coton ponté ont été presque conservées et ses propriétés thermodurcissables retrouvées d'une façon semblable à celle du coton non traité possédant 35% de greffage. On a trouvé que les caractéristiques du polymère greffé et le pontage chimique pouvaient être développés suivant les désirs de la pratique.

Zusammenfassung

Die Formaldehydvernetzung von Baumwollgeweben mit aufgepfropften Methyl-, Äthyl-, oder *n*-Butylacrylat wurde in einem trockenen oder halbtrockenen System durchgeführt. Es wurde gefunden, dass die Geschwindigkeit der Vernetzungsreaktion der aufgepfropften Baumwolle nicht stark verzögert, die Trocken- und Nassknitterfestigkeit der aufgepfropften Baumwolle, besonders mit *n*-Butylacrylat bei steigendem Gehalt an gebundenem Formaldehyd merklich verbessert wurde und der hydrophobe Charakter der mit Butylacrylat gepfropften Baumwolle eine Dissipationstendenz durch schwache Vernetzung zeigte. Obgleich die Zug- und Rissfestigkeit, die Bruchdehnung und die Wärmehärtungsfähigkeit von Baumwollgeweben mit aufgepfropftem Butylacrylat mit steigender Menge an gebundenem Formaldehyd unvermeidlich abnehmen, war dieser Verlust doch kleiner als bei ungepfropfter und formaldehydvertnetzter Baumwolle. Die Wasserimbibierung und die Feuchtigkeitsaufnahme stiegen mit zunehmender Menge an gebundenem Formaldehyd, während die Wasserabstossung absank. Durch Vernetzung im feuchten System wurde die Nassknitterfestigkeit verbessert, wie es auch bei ungepfropfter Baumwolle der Fall ist. Weiters führte eine teilweise Vernetzung der Butylacrylataufpfropfung mit *N*-Methylolacrylamid zu einer Beibehaltung der hydrophilen Eigenschaften von vernetzter Baumwolle und einer Annäherung der Wärmehärtungsfähigkeit an diejenige von unbehandelter Baumwolle bei etwa 35% Aufpfropfung. Die Charakteristik des Pfropfpolymeren sowie die chemische Vernetzung konnte praktisch nach Wunsch entwickelt werden.

Received February 19, 1965
Revised July 12, 1965
Prod. No. 1248