Grafting of Acrylate Monomers in Cotton Fabrics

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Synopsis

The graft copolymerization of acrylate monomers, methyl, ethyl, n-propyl, and n- or isobutyl, in cotton fabrics was carried out in the aqueous emulsion system by the ceric ion method.   The rate of grafting decreases with increasing length of the ester group. The maximum improvement of dry crease recovery, thus raising its value, increases with increasing graft-on shifts towards the higher extents of grafting, and with decreasing second-order transition temperature of graft polymer.   The improvement of wet crease recovery, equilibrated in the presence of a wetting agent, is always greater than that in the dry crease recovery even when the hydrophobic propyl or butyl acrylate-grafted cotton levels off with increasing graft-on.   The improvement of crease recovery was explained by the stabilization of the opened fiber structures by grafting with acrylates, especially those having bulky ester groups, the entangled crosslinking between the graft polymers or the graft polymers and cellulose chains, and the consequently developed elastomeric or swelling, elastomeric behaviors due to the segmental movements in the amorphous regions of graft copolymer.   Furthermore, from the measurements of water imbibition and repellency, moisture regains, tensile properties, stiffness, flex abrasion, and thermosetting properties, it has been concluded that the improvements of physical properties are remarkable in the propyl or butyl acrylate-grafted cotton.

INTRODUCTION

In order to improve the crease recovery, shrink-proofing, and dimensional stability of cotton fabrics, it has been accepted that the intermolecular covalent crosslinking is most effective.   Also, it has been found that crease recovery of cotton, especially in the dry state, can be improved by crosslinking in the unswollen state and the wet crease recovery greatly improved by crosslinking in the swollen state.   This principle has been utilized to obtain wash-wear cottons.

However, intermolecular crosslinking, especially in the unswollen state of cotton, is usually apt to be accompanied by much loss in tensile strength, breaking elongation, tear strength, and thermosetting ability.   Although these defects have been appreciably improved by the extraordinary efforts of many investigators, they appear to be unavoidable to some extent.   Particularly, it may be that the thermosetting property which is necessary to imparting permanent creases or pleats may be lost as a result of chemical crosslinking.

Recently, to overcome the above disadvantages and to obtain true wash-wear cotton fabrics, the recuring,[1] deferred curing,[2-4] or two-step cross-linking methods[5] have been proposed. However, these methods seem generally to be inconvenient for fabrics for home use applications.

We have investigated the graft copolymerization of cotton fabrics, which seems not to be accompanied so much by the above defects. The modification of cotton by graft copolymerization has been reported by many investigators, but little work has been done as regards grafting with various alkyl acrylates. Since grafting with styrene, methyl methacrylate, or acrylonitrile does not give simultaneously the desired specific properties,[6-8] we have tried grafting with alkyl acrylates forming graft polymer having second-order transition temperatures below room temperature.

EXPERIMENTAL

Materials

The cotton fabrics used were two samples of scoured and bleached broad-cloth (40's, W 55 × F 29 cm.) designated A and B. Most of acrylate monomers were commercial materials purified by the usual methods. n-Propyl and isobutyl acrylates were synthesized by an ester exchange reaction between methyl acrylate and n-propyl or isobutyl alcohol with the use of p-toluenesulfonic acid as the catalyst.

Grafting Procedure

Acrylate monomers used were methyl, ethyl, n-propyl, isobutyl, and n-butyl acrylates. In addition, occasionally styrene and methyl methacrylate were used for comparison. Graft copolymerization was carried out by the ceric ion method, in which ceric ammonium nitrate as the catalyst was used together with nitric acid.[9] As the reaction system, generally a 3% aqueous monomer solution emulsified with the cationic detergent APC (alkyl methylpyridinium chloride) was used at 30°C. The reaction of graft copolymerization was performed in air at atmospheric pressure, with degassing only before addition of the reaction liquor or bubbling in of nitrogen throughout the duration of reaction.

After the reaction period, the cotton fabrics were first washed with acetone, then water, and finally Soxhlet-extracted with acetone for about 20 hr. to remove the homopolymer as much as possible. To extract the polystyrene homopolymer, benzene was used. The extent of grafting was expressed as the weight per cent increase based on the original weight of the fabrics.

Physical Testing

The dry crease recovery of fabrics was measured by the Monsanto Wrinkle Recovery Tester at 65% R.H. and 20°C. The wet crease recovery was measured after being immersed for 15 min. at 40°C. in water containing

0.2% nonionic wetting agent and 0.2% sodium carbonate, washed lightly, and the excess water removed with filter paper. Occasionally, the effects of temperature and duration of water immersion on the wet crease recovery were investigated. For the sake of expediency, the crease recoveries were all measured only for the warp direction because it was found that the values for both warp and filling of untreated cotton fabrics were almost the same.

In order to determine the effect of the degree of swelling on the crease recovery of grafted cotton fabrics, the crease recovery was measured on the fabrics wetted with organic liquids such as methanol, ethanol, ethyl acetate, acetone, methyl ethyl ketone, dioxane, benzene, and n-hexane. The procedure was as follows. The specimens were immersed in water containing 0.2% nonionic wetting agent for about 48 hr. at room temperature and the water pressed out with filter paper. Some water was retained in the specimens, but it was repeatedly replaced, first with methanol and then the desired liquid, respectively; the procedure was repeated eight times, care being taken to allow sufficient time at each exchange. After removal of the excess liquid, the crease recovery was measured as usual.

The moisture content was measured at 65% R.H. and 20°C. Also, the water imbibition in water alone or in water containing 0.5% nonionic wetting agent was measured by pressing out the excess water with filter paper until approximately a constant weight was obtained.

The tensile strength and breaking elongation were determined with a Tensilon Tester, tear strength by the Elmendorf tester, stiffness by the Clark tester, and flex abrasion strength by the Custom Universal Wear Tester at 65% R.H. and 20°C.

The determination of the thermosetting property was performed as follows. The specimens (W 4 × F 1.5 cm.) were immersed for 10 min. at 40°C. in water containing 0.2% nonionic wetting agent, the excess water pressed out with filter paper, and the fabric doubled as in the crease recovery measurement and iron-pressed for 90 sec. at 165–175°C. The heat-pleated specimens were allowed to hang free along a fine steel wire which was spun in the water containing the same wetting agent as above at 40°C., allowed to open for 10 min., and air-dried overnight at 65% R.H. and 20°C. Then, the angle of opening was measured.

Also, water-repellency and laundering tests were carried out briefly by the sinking method and Launder-Ometer, respectively.

RESULTS AND DISCUSSION

Rate of Grafting

The effect of reaction time on the extent of grafting of methyl, ethyl, n-propyl, and n-butyl acrylates was investigated at 30°C. The composition of reaction liquor was 3% monomer, 0.5% cationic detergent, and 0.01 mole/l. of nitric acid. The concentration of ceric ion was 0.001 mole/l. for methyl or ethyl acrylate and 0.005 mole/l. for n-propyl or n-butyl acrylate.

The graft copolymerization was performed in air at atmospheric pressure except in the case of n-butyl acrylate, which was difficult to graft in the air; degassing was carried out only before addition of the reaction liquor.   These
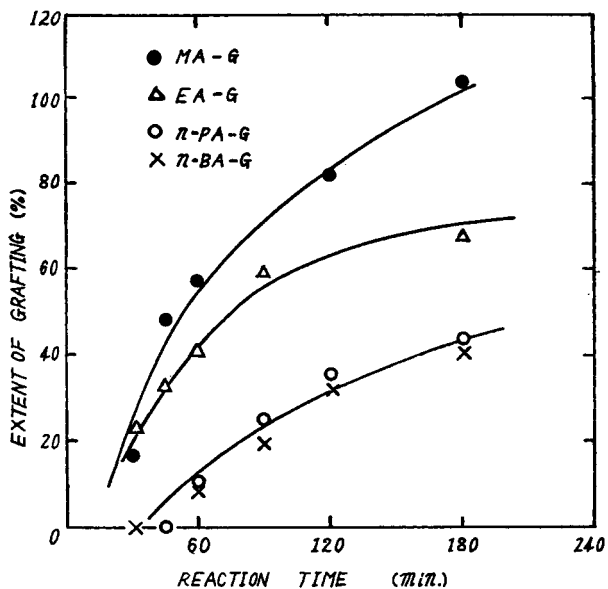

Fig. 1. Effects of reaction time on grafting of methyl, ethyl, n-propyl, and n-butyl acrylates in cotton (cotton A, monomer 3%, HNO$_3$ 0.01 mole/l., cationic detergent 0.5%, 30°C.).
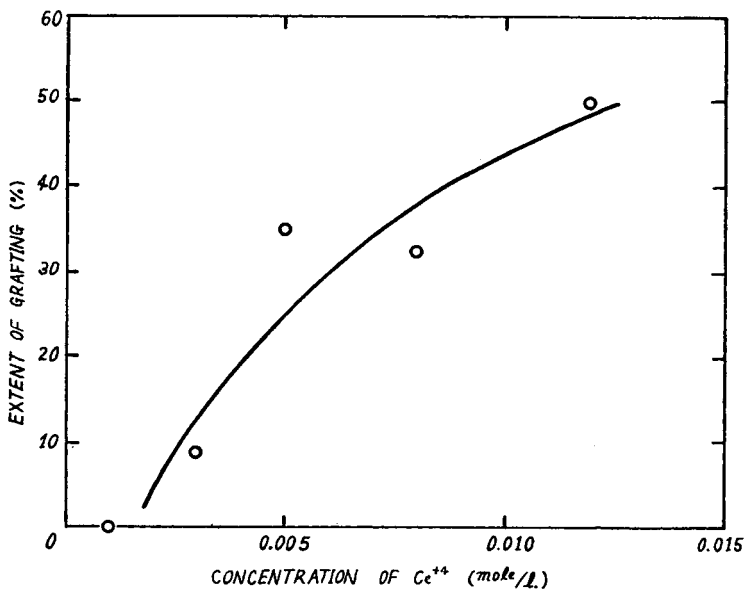

Fig. 2. Effects of concentration of ceric ion on grafting of n-propyl acrylate in cotton (cotton A, monomer 3%, HNO$_3$ 0.01 mole/l., cationic detergent 0.5%, 120 min., 30°C.).

results are shown in Figure 1. It can be seen that the rate of graft copolymerization decreases with increasing length of the ester group of the monomer. Flushing with gaseous nitrogen before addition of the reaction liquor
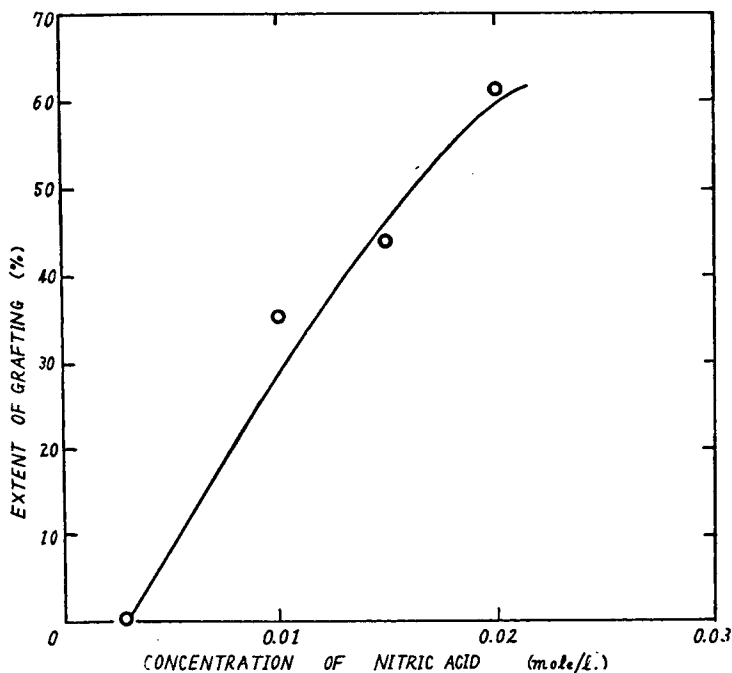

Fig. 3. Effects of concentration of nitric acid on grafting of n-propyl acrylate in cotton (cotton A, monomer 3%, Ce^{+4} 0.005 mole/l., cationic detergent 0.5%, 120 min., 30°C.).
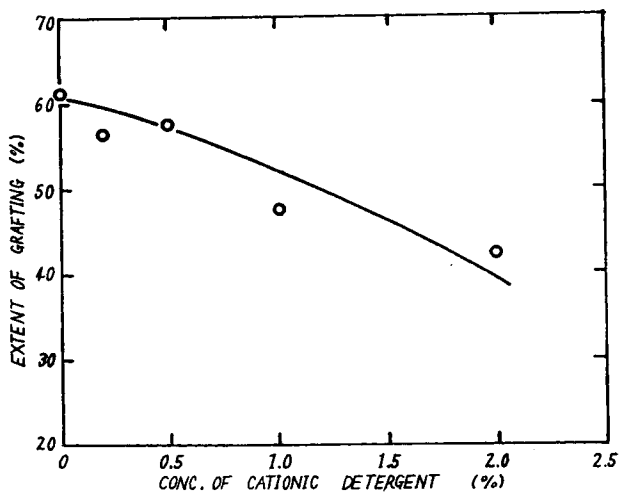

Fig. 4. Effects of concentration of cationic detergent on grafting of methyl acrylate (cotton A, monomer 3%, Ce^{+4} 0.001 mole/l., HNO$_3$ 0.01 mole/l., 60 min., 30°C.).

and bubbling in of nitrogen throughout the duration of reaction further increased the reactivity of n-butyl acrylate.

The effects of the temperature grafting and concentration of monomer, ceric ion, and nitric acid on the extent of grafting were studied for various monomers. However, the results presented here will be limited to those for the grafting of n-propyl acrylate. Figures 2 and 3 show the effects of concentration of ceric ion and nitric acid on the extent of grafting respectively. Also, the effect of cationic detergent is to decrease the grafting of methyl acrylate, as shown in Figure 4.

The results for cotton fabrics grafted with various monomers at varying reaction conditions are given by the physical tests below.

Dry Crease Recovery

The dry crease recovery at varying graft-ons of various acrylates and styrene is shown in Figure 5. In general, a maximum improvement of dry crease recovery is exhibited, and the value of the maximum and the corresponding extent of grafting depend on the kind of acrylate monomer used. In the n-alkyl acrylate series, the maximum improvement of crease recovery appears to increase with decreasing second-order transition temperature of the homopolymer, and the corresponding graft-on shifts towards higher extents of grafting, as summarized in Table I. The dry crease recovery of styrene-grafted cotton is not improved so much, which may be attributed to the higher second-order transition temperature of polystyrene. Fur-
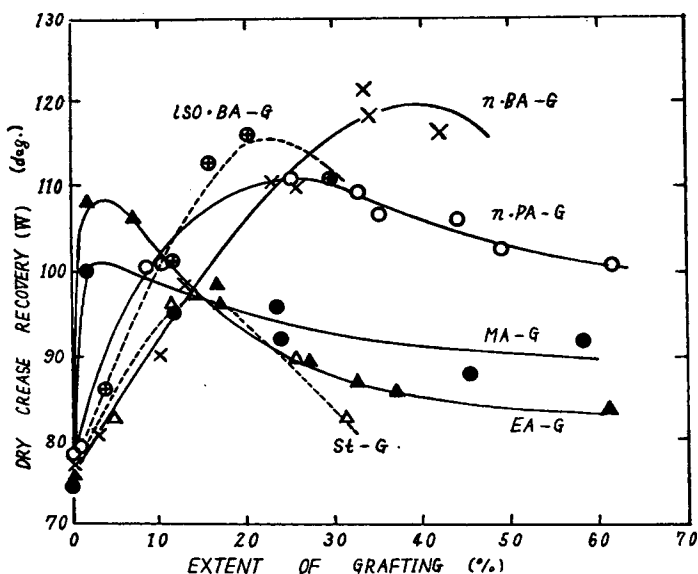

Fig. 5. Dry crease recovery at varying graft-on of various acrylates and styrene (methyl, ethyl, n-propyl, and n-butyl acrylates: cotton A; isobutyl acrylate and styrene: cotton B).

TABLE I

Maximum Values of Dry Crease Recovery, the Corresponding Graft-On of Grafted Cotton Fabrics with Various Acrylates or Styrene, and Second-Order Transition Temperature of Homopolymers

Sample	Maximum value of dry crease recovery (W)	Extent of grafting at maximum value of dry crease recovery, %	Second-order transition temperature of homopolymer, °C.[a]
Untreated cotton A	78°	—	—
Cotton A grafted with			
Methyl acrylate	100°	2	9
Ethyl acrylate	108°	5	−22
n-Propyl acrylate	110°	25	−51.5
n-Butyl acrylate	120°	35	−56
Untreated cotton B	77°	—	—
Cotton B grafted with			
Isobutyl acrylate	115°	20	−24
Styrene	97°	15	100

[a] Data of Wiley and Brauer,[10] Wood,[11] and Rehberg and Fisher.[12]

thermore, it is interesting that in the region of lower grafting, the softer the acrylate graft polymer becomes, the greater the amount of graft-on required to obtain the same improvement of crease recovery.

Acrylate polymers may perhaps be grafted most in the amorphous region of cotton fibers which have been swollen in an aqueous media; this treatment gives an open structure to the fibers, increasing the distance between crystal regions or breaking the secondary bonds in the amorphous regions. Hence, it might be considered that entanglements between the graft polymer chains and between graft polymer and cellulose chains exist to some extent. In elastomeric polymers consisting of three-dimensional networks, such as a weak vulcanized rubber, the molecular entanglements behave like chemical crosslinkages.[13] Thus, it is quite possible that in the graft copolymers, such molecular entanglements might play the role of crosslinks to certain extent. Although the entanglements between the graft polymer and cellulose chains may have an important role especially in the polar or hydrophilic graft polymer, evaluation is difficult at the present.

The results of viscoelastic measurements of Tobolsky and Takahashi,[14] show that the extent of molecular entanglements of poly(methyl acrylate) is much greater than that of poly(butyl acrylate), as shown in Table II. Thus, when softer acrylate polymers with fewer entanglements are grafted to cellulose molecules, it would be expected that the efficiency of grafting on the improvement of crease recovery becomes smaller, while graft-ons to a higher extent give a significant improvement of the dry crease recovery, with the development of elastomeric behavior as in weakly crosslinked polymer. The maximum improvement of the dry crease recovery at increasing graft-on is considered to be due to the restriction of segmental

TABLE II
Dry and Wet Crease Recovery at about 30% Graft-On of Various Acrylates or
Styrene and Number of Links between Entanglements of Homopolymer

| Sample | Crease recovery (W) | | No. of links between entanglements of homopolymer $\times 10^2$ [a] |
	Dry	Wet, equilibrated	
Untreated cotton A	78°	55°	—
Cotton A grafted with			
Methyl acrylate	93°	105°	1.65
Ethyl acrylate	88°	114°	—
n-Propyl acrylate	110°	120°	—
n-Butyl acrylate	116°	126°	2.38
Untreated cotton B	77°	74°	—
Cotton B grafted with			
Isobutyl acrylate	110°	145°	—
Methyl methacrylate	98°	102°	1.24
Styrene	83°	90°	3.71

[a] Data of Tobolsky and Takahashi.[14]

movements of molecules including graft and cellulose chains by increased entanglements, not only between graft polymer chains but also between graft polymer and cellulose chains. Also, it should be noted that the crease recovery imparted by grafting of the relatively hydrophilic methyl or ethyl acrylate becomes rapidly poorer at lower extents of graft-on. In these graft copolymers, since relatively good compatibility is expected between the graft polymer and cellulose chains, the entanglements might presumably occur readily between graft polymer chains and also between graft polymer and cellulose chains, and this would restrict the segmental movements of molecules, thus rapidly depressing the elastomeric behavior.

Tobolsky and Takahashi showed the chain entanglements of polystyrene to be less but of the same order as that of poly(butyl acrylate) (Table II). Nevertheless, the styrene-grafted cotton gives a comparatively smaller improvement of crease recovery. This may perhaps be due to the greater rigidity of polystyrene as a result of the stronger dispersion force and/or the smaller flexibility of molecular chain due to the presence of the side chain on the benzene nucleus. Also, as shown in Table II, cotton grafted with methyl methacrylate shows comparatively less improvement of crease recovery, suggesting also greater rigidity because of the greater number of entanglements and/or the lower molecular flexibility. For the qualitative considerations mentioned above, viscoelastic measurements on grafted cotton will be necessary, though some work has been recently reported by Arthur et al.[8]

Wet Crease Recovery

In cotton fabrics grafted with methyl or ethyl acrylate, the usual method was sufficient to obtain the equilibrated wet crease recovery. However, as
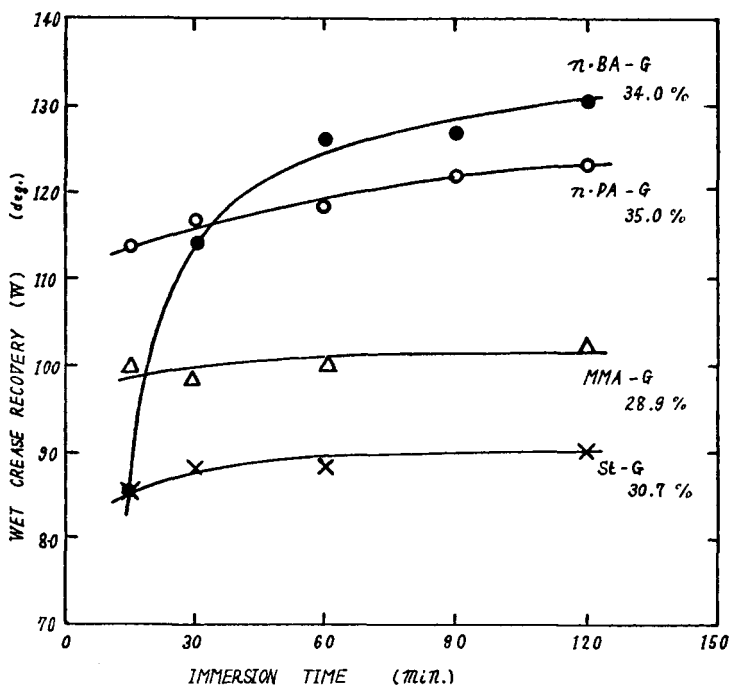
Fig. 6. Effect of immersion time in water containing 0.2% nonionic wetting agent at 40°C. on wet crease recovery of cotton grafted with n-propyl and n-butyl acrylates (cotton A) and methyl methacrylate and styrene (cotton B).

shown in Figures 6 and 8, in the cotton fabrics grafted with n-propyl, iso-butyl, and n-butyl acrylates, methyl methacrylate, or styrene, especially in the three former, the equilibrated value of wet crease recovery could not be obtained by the usual method because of their hydrophobic properties. Therefore, in the determination of wet crease recovery of the grafted cotton fabrics with these hydrophobic monomers a longer immersion time (about 2 hr.) was required. Most of hydrophobic properties imparted by grafting can be eliminated by slight subsequent formaldehyde crosslinking. In addition, the formaldehyde crosslinking results in further improvement of the crease recovery, both dry and wet. The details will be reported in a subsequent paper.

The wet crease recovery at varying graft-ons of methyl, ethyl, n-propyl, and n-butyl acrylates is illustrated in Figure 7. It is shown that generally, wet crease recovery tends to level off with increasing graft-on, suggesting the existence of a maximum at much greater graft-on than that of the dry crease recovery; the softer the graft polymer becomes, the greater becomes the wet crease recovery of grafted cotton fabrics. The wet crease recovery of cotton fabrics grafted with isobutyl acrylate or styrene is shown in Figure 8. It is peculiar that the styrene-grafted cotton does not improve so much in wet crease recovery, the maximum value at the lower
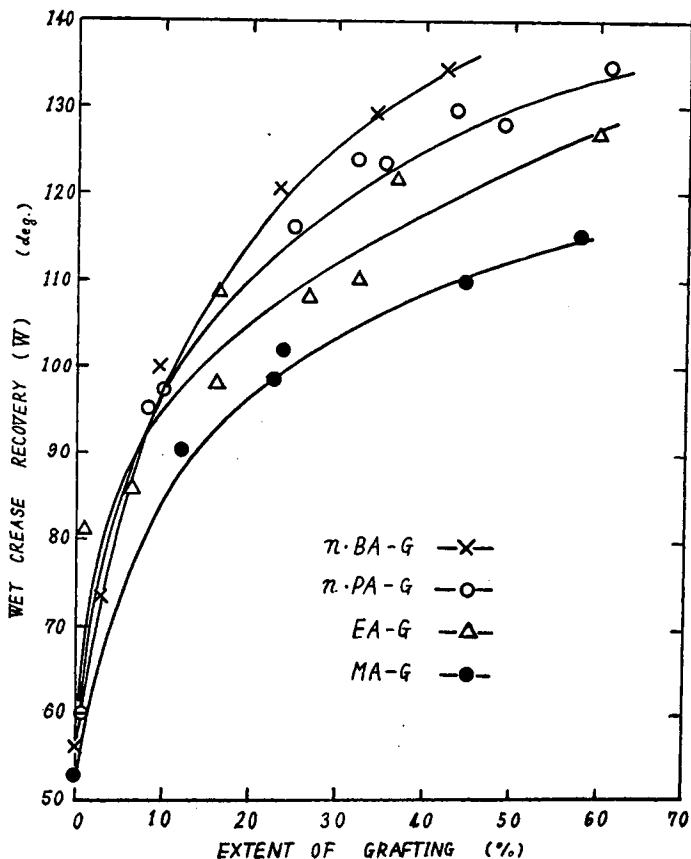
Fig. 7. Equilibrated wet crease recovery at varying graft-on of various acrylates (cotton A).

grafting being about 15% that for the dry crease recovery. Table II shows the comparison of the dry and wet crease recovery at about 30% graft-on of various acrylates.   It is important to note that the equilibrated wet crease recovery of grafted cotton fabrics is always greater than the dry crease recovery.   The behaviors of wet crease recovery of grafted cotton fabrics appear to be similar to the well-known behaviors of chemically crosslinked cotton in the swollen state.   Considering the open structure stabilized by grafting and the molecular entanglements in graft copolymers as mentioned above, this is quite reasonable.

To clarify the above similarity, the effect of temperature on the wet crease recovery was investigated.   The samples used were chemically crosslinked cotton fabrics which were formaldehyde-crosslinked by curing; semi-dry(Form-D), and wet(Form-W) methods were used.[15,16]   The content of bound formaldehyde was 0.30–0.33%.   First, the specimens were immersed in water containing 0.2% nonionic detergent at 50°C. and then at the desired temperature (5–80°C.) for 2 hr.   After being doubled under
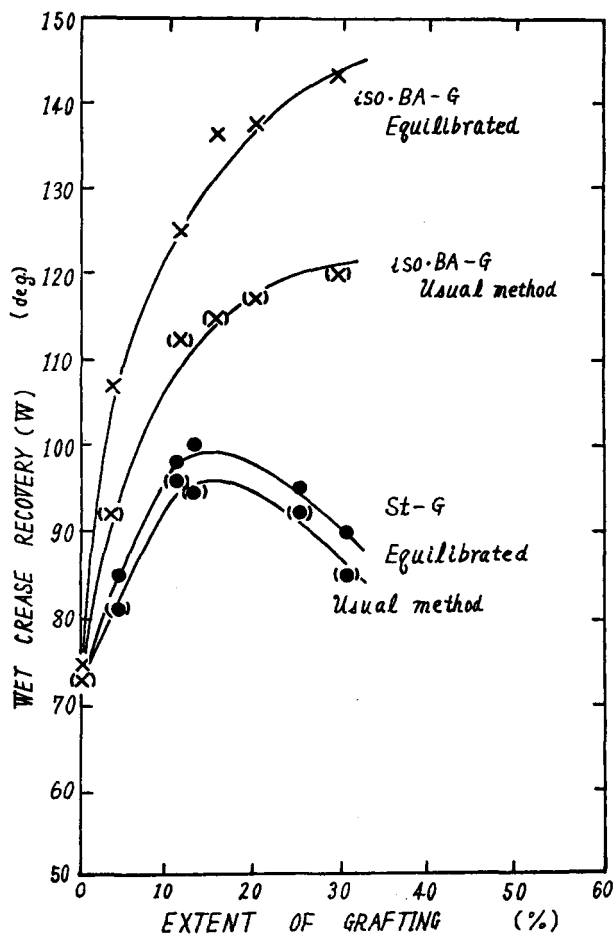
Fig. 8. Effects of graft-on and immersion time on wet crease recovery of cotton grafted with isobutyl acrylate and styrene (cotton B).

loading of 500 g. for 5 min. in air, the specimens were hung along the wire spun in water of the desired temperature, and allowed to open for 10 min. The angle of opening was measured in the water. The results obtained are shown in Figure 9. It is generally found that the grafted cotton and the formaldehyde-crosslinked cotton increase in wet crease recovery to a greater extent with increasing temperature than untreated or mercerized cotton. Particularly, it should be noted that a comparatively simple temperature dependency for the wet crease recovery is present in the acrylate-grafted cotton and the formaldehyde-crosslinked cotton in a swollen state. As expected, this suggests a similarity in swelling, elastomeric behavior of both. On the other hand, it is interesting that the formaldehyde-crosslinked cotton fabrics obtained by semi-dry and curing methods show a characteristic temperature dependence in which a transition takes
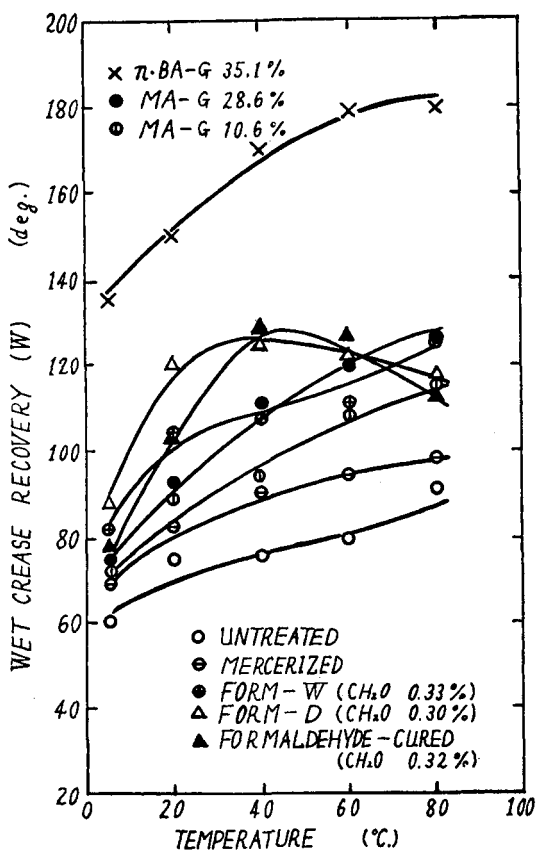
Fig. 9. Effect of temperature on wet crease recovery of fabrics formaldehyde-cross-linked by curing, semi-dry (Form-D), and wet (Form-W) methods, grafted with methyl or n-butyl acrylate, mercerized, and untreated cotton (cotton B).

TABLE III

Moisture Regains at about 30% Graft-On of Various Acrylates or Styrene
(65% R.H., 20°C.)

Sample	Extent of grafting, %	Moisture regains, %	Moisture content/ cellulose, %
Untreated cotton B	0	8.4	8.4
Cotton B grafted with			
Methyl acrylate	28.6	5.7	7.3
Ethyl acrylate	28.7	6.2	7.9
n-Butyl acrylate	29.4	5.7	7.4
Isobutyl acrylate	29.6	5.4	7.0
Methyl methacrylate	28.9	5.8	7.5
Styrene	30.7	5.9	7.3

place at 40–50°C. The transition temperature may perhaps be the temperature at which the hydrogen bonds in a higher lateral order of the amorphous region of cellulose are broken.[17] A similar situation has been found by Frick et al.[18] for the elastic strain at varying relative humidity.

Moisture Regains

Moisture regains of the grafted cotton fabrics with various acrylate are compared at about 30% graft-on in Table III. Generally, moisture regains decrease on grafting, but the decreases are almost independent of the kind of acrylate.

Water Imbibition

The effects of graft-on and wetting agent on the water imbibition calculated on the basis of the cellulose component is shown in Figure 10 and Table IV. In the cotton grafted with n-propyl or n-butyl acrylate, the water imbibition is significantly increased by the presence of 0.5% wetting agent, while in the grafted cotton with methyl or ethyl acrylate almost unaffected. This is in good agreement with the results of wet crease recovery mentioned above. A slight maximum of water imbibition appears, suggesting competition between the opening of the fiber structure and the imparting of hydrophobic property by grafting (see Fig. 10). Furthermore, it is interesting that the water imbibition seems to increase with increasing length of the acrylate ester group, indicating that the bulky group of ester plays a role in the opening of fiber structure to some extent.
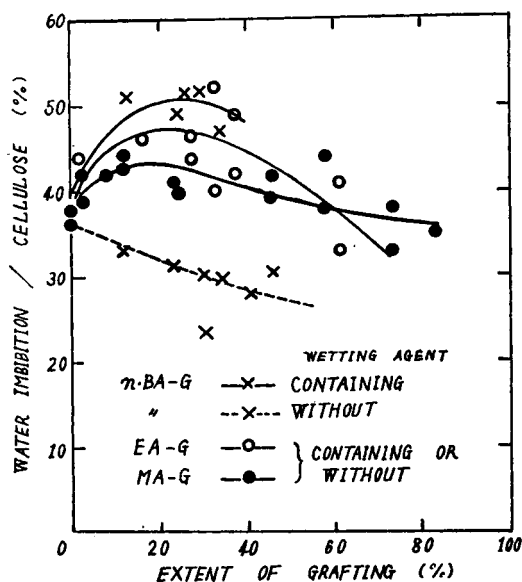

Fig. 10. Effect of graft-on and wetting agent on water imbibition per cellulose component for cotton grafted with methyl, ethyl, and n-butyl acrylates (cotton A).

TABLE IV
Water Imbibition at about 30% Graft-On of Various Acrylates or Styrene

| Sample | Extent of grafting, % | Water imbibition/cellulose, % | |
		Water	0.5% Nonionic wetting agent
Untreated cotton A	0	37.5	37.5
Cotton A grafted with			
Methyl acrylate	36.0	40.7	42.8
Ethyl acrylate	34.0	38.8	41.5
n-Propyl acrylate	35.0	30.4	46.3
n-Butyl acrylate	34.0	27.5	54.3
Untreated cotton B	0	—	36.6
Cotton B grafted with			
n-Butyl acrylate	29.4	—	51.5
Isobutyl acrylate	29.6	—	50.2
Methyl methacrylate	28.9	—	50.6
Styrene	30.7	—	42.5

The polymer radical on the cellulose molecule may be predominantly generated by the abstraction of hydrogen atoms at the α-positions by the OH, especially primary OH groups taking place in graft copolymerization.[19] Then, even if grafted, a greater part of the OH groups of cellulose may presumably remain in the latent state and imbedded within the graft copolymers. This structure also may contribute to imbibition of water within the grafted fiber by the wetting agent, even in the presence of the hydrophobic ester groups.

From the above considerations, it may be concluded that the opened structure of cotton fiber is stabilized by the graft polymer, especially those bulky ester groups, and consequently the capacity for water imbibition increases. This also may perhaps permit the cellulose molecules to attain greater flexibility in the wet state than untreated cotton. So, when the entanglement crosslinking of softer graft polymers is present to an appropriate extent, the swelling elastomeric behavior would be expected to be displayed, improving the wet crease recovery.

Organic Liquid Wet Crease Recovery

In order to ascertain the existence and role of entanglements in graft copolymers, the wet crease recovery with various organic liquids was measured. In the view of the considerations mentioned above, when grafted cotton fabrics are wetted with a liquid having a solvent or swelling power smaller for acrylate graft polymer and greater for cellulose, a greater crease recovery may be expected. The results obtained are shown in Table V, together with the number of revolutions of cotton yarn determined by Carra et al.[20] to give a measure of swelling power for untreated cellulose fiber.

Acrylate-grafted cotton fabrics wetted with ethanol or methanol show almost the same increase in crease recovery as those wetted with water while

TABLE V
Organic Liquid Wet Crease Recovery at about 30% Graft-On of Methyl, Ethyl, and n-Butyl Acrylates

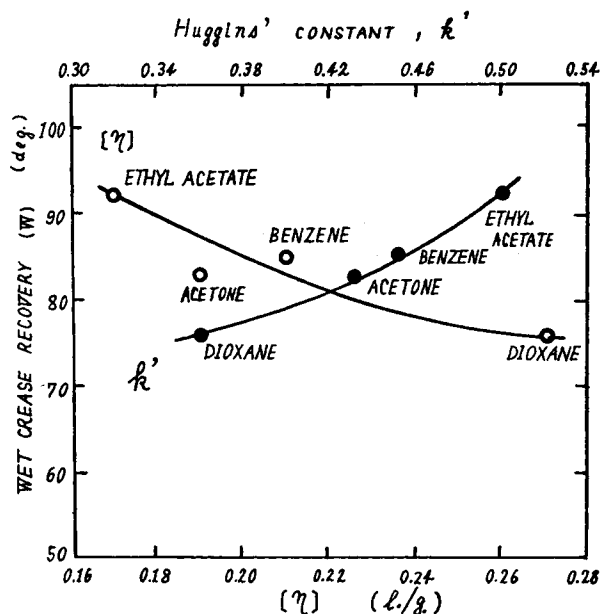|	Wet crease recovery (W)				No. of revolutions for untreated cotton yarn[a]
Organic liquid	Methyl acrylate, 32.8% graft-on	Ethyl acrylate, 30.3% graft-on	n-Butyl acrylate, 29.3% graft-on	Un- treated cotton	
Nonsolvents or poor solvents for acrylate polymers					
Water	106°	124°	129°	67°	24
Methanol	108°	120°	131°	89°	4
Ethanol	130°	129°	130°	93°	8
n-Hexane	85°	99°	87°	90°	—
Solvents for acrylate polymers					
Ethyl acetate	92°	91°	94°	93°	<1
Acetone	83°	92°	115°	82°	6
Methyl ethyl ketone	97°	97°	80°	85°	6
Dioxane	76°	80°	76°	70°	7
Benzene	85°	87°	89°	78°	—

[a] Data of Carra et al.[20]

Fig. 11. Relation between organic liquid wet crease recovery of grafted cotton with methyl acrylate and Huggins' constant or intrinsic viscosity of poly(methyl acrylate) (cotton A).

the grafted cotton fabrics wetted with ethyl acetate, acetone, methyl ethyl ketone, dioxane, or benzene show a smaller crease recovery. This is as expected, as the former are very poor solvents for acrylate polymers and fair swelling agents for cellulose, while the latter are fair solvents for acrylate polymers, though some of them seem to have some swelling power for cellulose, from the Carra's number of revolutions.

In order to clarify the effect of the solvent power for acrylate polymers on the crease recovery of grafted cotton, Huggins' constant and intrinsic viscosity of poly(methyl acrylate) or poly(ethyl acrylate) homopolymer,
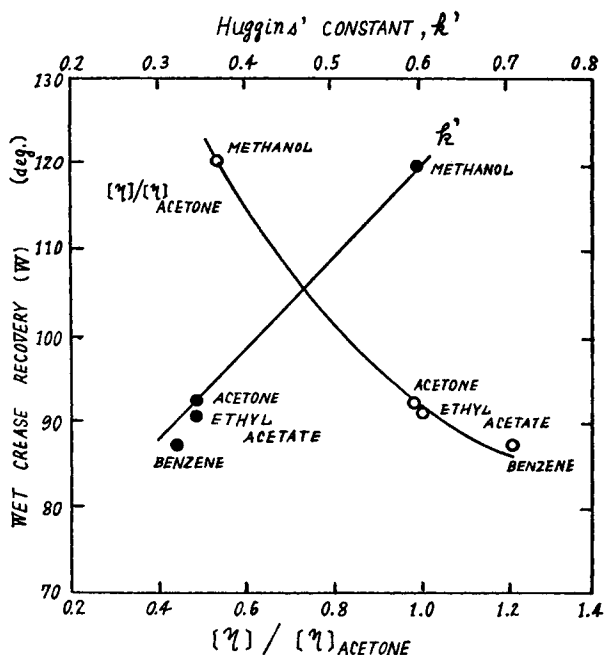

Fig. 12. Relation between organic liquid wet crease recovery of grafted cotton with ethyl acrylate and Huggins' constant or $[\eta]_{solvent}/[\eta]_{acetone}$ of poly(ethyl acrylate) (cotton A).

determined by Suzuki et al.[21] and Hachihama et al.[22] were plotted in Figures 11 and 12. It is known that the lower the solvent power for acrylate polymer, the greater the crease recovery of grafted cotton fabrics, indicating that the entanglement crosslinking of graft polymers plays an important role in the crease recovery on wetting with these liquids. However, it also should be noted that n-hexane as nonsolvent for acrylate polymers gives lower crease recovery, which may be due to the absence of swelling power for cellulose. In addition, we have found that the wet crease recovery of cotton wet with water is not improved so much by grafting with hydrophilic acrylamide. On the whole, the results obtained by experiment are as expected.

After all, the wet crease recovery of acrylate-grafted cotton fabrics might be fairly well explained by the entanglement crosslinking of graft polymers and the swelling, elastomeric behavior of cellulose.

Tensile Strength and Breaking Elongation

Tensile strength and breaking elongation of the grafted cotton fabrics are shown in Table VI. Tensile strength seems to be decreased slightly by the grafting of acrylates, especially that giving soft polymers. In contrast with the chemical crosslinking, it is remarkable that the grafting of acrylates gives very little loss of tensile strength, even at extents of grafting as high as about 30%. The breaking elongation, in general, is increased appreciably by the grafting of acrylates.

TABLE VI

Tensile Strength, Breaking Elongation, and Tear Strength at about 30% Graft-On of Various Acrylates or Styrene

Sample	Extent of grafting, %	Tensile strength, kg./cm.	Breaking elonga- tion, %	Tear strength, Elmendorf units
Untreated cotton A	0	12.7	14.2	37.0
Cotton A grafted with				
Methyl acrylate	24.1	13.7	24.8	27.5
Ethyl acrylate	32.4	13.5	28.0	31.7
n-Propyl acrylate	32.5	12.0	27.4	34.4
n-Butyl acrylate	34.0	11.0	27.2	33.8
Untreated cotton B with	0	12.0	11.0	32.5
Ethyl acrylate	27.8	11.1	25.0	32.0
n-Butyl acrylate	29.4	10.3	22.0	32.5
Isobutyl acrylate	29.6	10.8	18.0	30.0
Methyl methacrylate	28.9	11.2	8.5	26.0
Styrene	30.7	11.8	20.0	31.0

Tear Strength

Tear strength of grafted cotton fabrics decreases to some extent, especially in the grafting of acrylates giving hard polymers, as shown in Table VI.

The logarithmic relation between the tear strength and the extent of grafting of normal alkyl acrylates is shown in Figure 13. Assuming that the relation is approximately linear, the following equation is obtained:

$$T = \alpha G^{-k}$$

where T is the tear strength in Elmendorf units, G is the extent of grafting in per cent, k is a constant giving loss index of tear strength by graft-on, and α is a constant for the tear strength at 1% graft-on. The values for α and k obtained graphically are shown in Table VII. The softer the graft polymer, the lower the value of k, as shown in Figure 14. It is noteworthy
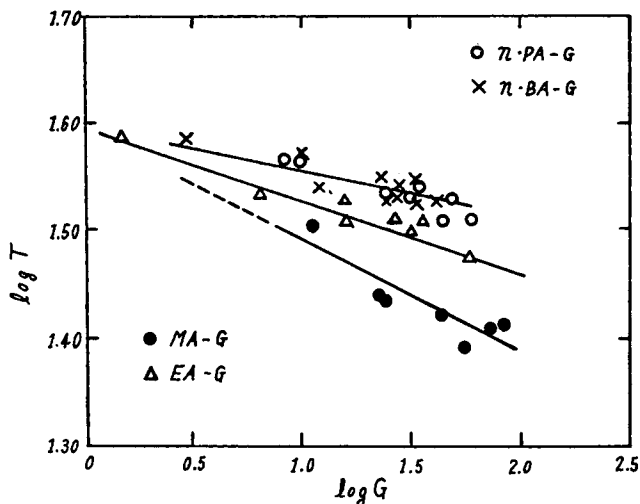
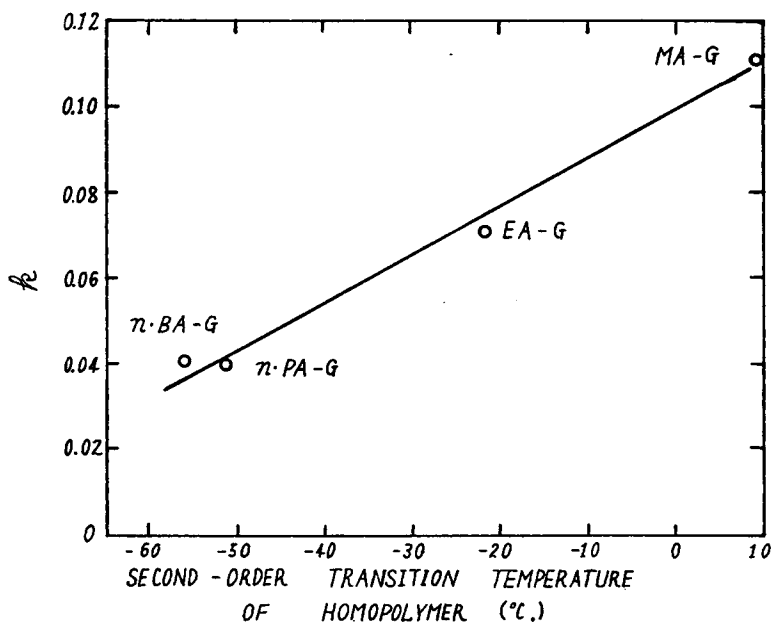Fig. 13. Logarithmic relation between tear strength and graft-on of normal alkyl acrylates (cotton A).

Fig. 14. Relation between loss index of tear strength k of cotton grafted with normal alkyl acrylates and second-order transition temperature of polyacrylates.

that the tear strength of the grafted cotton with n-propyl or n-butyl acrylate remains about 91–93% of that of original cotton, even at about 35% graft-on. Also, it is interesting that the styrene-grafted cotton shows greater tear strength than the methyl methacrylate- or methyl acrylate-grafted cotton. This fact will be discussed later.

TABLE VII
Values of α and k in $T = \alpha G^{-k}$ for Acrylate-Grafted Cotton Fabrics

Grafted monomer	α, Elmendorf units	k
Methyl acrylate	39.0	0.11
Ethyl acrylate	39.0	0.07
n-Propyl acrylate	39.0	0.04
n-Butyl acrylate	39.0	0.04

Stiffness

The Clark stiffness of grafted cotton fabrics having about 30% graft-on was measured. The results obtained are shown in Table VIII. In gen-
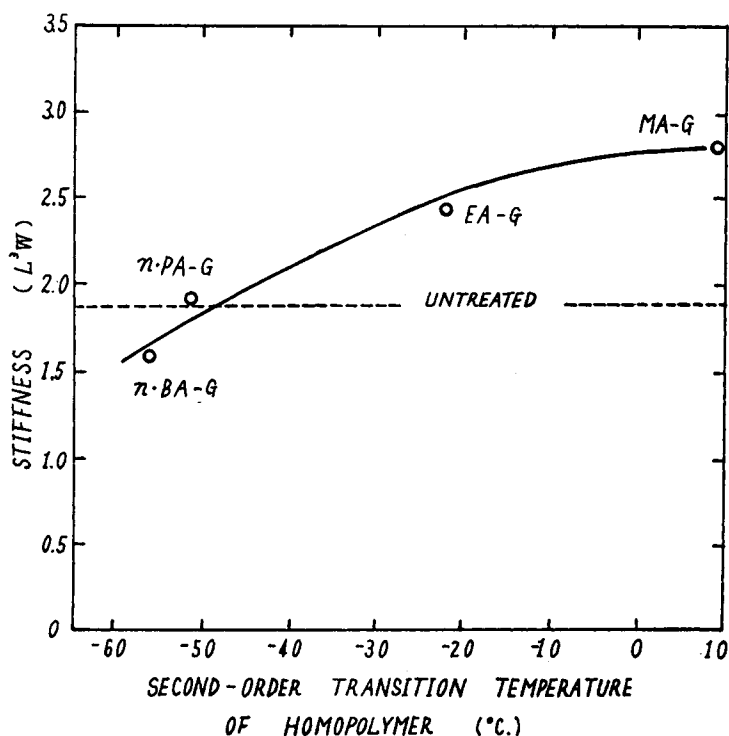

Fig. 15. Relation between Clark stiffness of grafted cotton with normal alkyl acrylates and second-order transition temperature of polyacrylate.

eral, the stiffness of grafted cotton with normal alkyl acrylates increases with increase of the second-order transition temperature of the graft polymer, as shown in Figure 15.

TABLE VIII
Clark Stiffness at about 30% Graft-On of Various Acrylates or Styrene

Sample	Extent of grafting, %	Clark stiffness, L^3W, g.-cm.[a]
Untreated cotton A	0	1.87
Cotton A grafted with		
Methyl acrylate	36.0	2.80
Ethyl acrylate	34.0	2.40
n-Propyl acrylate	35.0	1.88
n-Butyl acrylate	34.0	1.60
Untreated cotton B	0	4.25
Cotton B grafted with		
Ethyl acrylate	27.8	1.83
n-Butyl acrylate	29.4	1.50
Isobutyl acrylate	29.6	1.72
Methyl methacrylate	28.9	3.55
Styrene	30.7	3.25

[a] L = critical length in cm., W = weight in g./cm.[2].

Flex Abrasion

Flex abrasion strength of grafted cotton fabrics having about 30% graft-on was measured.   The results obtained are shown in Table IX.   It seems that the grafting is not accompanied by much loss of flex abrasion strength among the n-alkyl acrylates.

TABLE IX
Flex Abrasion Strength at about 30% Graft-On of Various Acrylates

Sample	Extent of grafting, %	Flex abrasion strength, number of cycles
Untreated cotton A	0	483
Cotton A grafted with		
Methyl acrylate	26.6	409
Ethyl acrylate	31.8	560
n-Propyl acrylate	25.2	459
n-Butyl acrylate	31.2	421

Thermosetting Property

The angle of opening of heat-pleated specimens was measured.   The results obtained are shown in Table X.   Generally, the thermosetting ability is improved by acrylate grafting.   Also, the thermosetting property increases with increasing softness of acrylate graft polymer.   It is specially noteworthy that the thermo setting ability of the cotton grafted with n-butyl acrylate is approximately the same as that of a synthetic polyester

TABLE X
Angle of Opening of Heat-Pleated Cotton Fabrics at about 30% Graft-On of
Various Acrylates or Styrene

Sample	Extent of grafting, %	Angle of opening
Untreated cotton A	0	37.5°
Cotton A grafted with		
Methyl acrylate	36.0	33.0°
Ethyl acrylate	34.0	33.5°
n-Propyl acrylate	35.0	28.7°
n-Butyl acrylate	34.0	24.3°
Synthetic polyester fiber (Tetoron)	—	25.5°
Acetate fiber (normal)	—	5.5°
Untreated cotton B	0	38.5°
Cotton B grafted with		
n-Butyl acrylate	29.4	25.0°
Isobutyl acrylate	29.6	30.0°
Methyl methacrylate	28.9	32.7°
Styrene	30.7	25.0°

fiber (Tetoron) at about 30% graft-on, though not as good as that of acetate fiber.

Although polystyrene is a much harder polymer than n-butyl acrylate polymer, the styrene-grafted cotton fabrics have better thermosetting properties and tear strength than the cotton grafted with n-butyl acrylate.
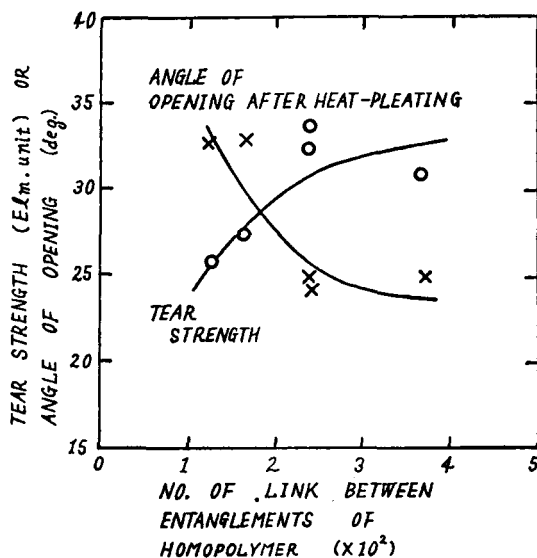

Fig. 16. Relation between tear strength or angle of opening after heat-pleating of grafted cotton with various acrylates or styrene, and number of links between entanglements of homopolymer.

On the other hand, although poly(methyl acrylate) is a much softer polymer than poly(methyl methacrylate), both grafted cotton fabrics show almost the same lower thermosetting properties and tear strength. No marked difference in the effect of ironing temperature could be found between the cottons grafted with styrene and n-butyl acrylate. Comparing the molecular entanglements of the amorphous polymers obtained by Tobolsky et al. in Table II, the thermosetting property and tear strength of grafted cotton fabrics seem to tend to become poorer with increasing extent of entanglements of graft polymers (see Fig. 16). These results are interesting, but require further investigation in detail.

Water Repellency

Water repellency was measured by the sinking method with the use of specimens of 1 cm.² and water containing 1% wetting agent at 60°C. The results obtained are shown in Table XI. The water repellency of the cotton fabrics grafted with n-butyl acrylate seems to be better than that of the styrene-grafted fabrics.

TABLE XI
Water Repellency at about 30% Graft-On of Various Acrylates or Styrene

Sample	Extent of grafting, %	Time required to sink, sec.
Untreated cotton B	0	1
Cotton B grafted with		
n-Butyl acrylate	29.4	720
Isobutyl acrylate	29.6	480
Methyl methacrylate	28.9	120
Styrene	30.7	240

TABLE XII
Laundering Test of the Cotton Fabrics Grafted with n-Butyl Acrylate

Sample	No. of laundering cycles	Crease recovery (W)		Tensile strength, kg./cm.	Breaking elongation, %	Tear strength, Elmendorf units
		Dry	Wet (equilibrium)			
Untreated cotton						
B	0	90°	79°	11.3	14.6	36.8
	10	87°	76°	12.2	12.3	40.5
Grafted cotton						
29.6% Graft-on	0	118°	150°	9.2	18.5	40.5
	10	117°	157°	9.2	16.9	40.8
41.7% Graft-on	0	104°	158°	9.9	19.4	38.8
	10	104°	159°	9.9	19.6	38.5

Laundering Test

The Launder-Ometer test was performed by use of specimens of W 12 × F 8 cm. fabrics and an aqueous 0.5% soap solution at 60°C. After laundering for 20 min., the fabrics were well rinsed with water, squeezed, and iron-dried before being resubjected to laundering. This laundering cycle was repeated ten times. The results obtained for cotton fabrics grafted with n-butyl acrylate of 29.6 and 41.7% graft-on are shown in Table XII. Although the alkaline hydrolysis of the ester groups of acrylate graft polymers was feared, almost no change in physical properties was seen.

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Résumé

La copolymérisation par greffage des acrylates de méthyle, éthyle, n-propyle et n- ou isobutyle sur les matériaux à base de coton, a été effectuée en émulsion aqueuse par la méthode à l'ion cérique. La vitesse de greffage diminue avec l'augmentation de la longueur du groupe ester. L'amélioration maximum dans le rétablissement du plissage à sec (ce qui augmente sa valeur) augmente avec l'augmentation du greffage, se déplace vers le maximum de greffage et augmente avec la diminution de la température de transi-

tion du second ordre du polymère greffé. L'amélioration dans le rétablissment du plissage humide, équilibré en présence d'un agent mouillant, est souvent plus importante que dans le cas du rétablissment du plissage à sec, même lorsque le coton greffé avec de l'acrylate de propyle ou de butyle hydrophobe s'applanit avec une augmentation du greffage. L'amélioration du rétablissement du plissage s'explique par la stabilisation des structures ouvertes de la fibre par greffage avec les acrylates, spécialement celles possédant des groupements esters volumineux par le pontage dense entre les polymères greffés ou les polymères greffés et les chaînes de cellulose, et par les comportements élastomères et élastomères gonflants dûs aux mouvements des segments dans les régions amorphes du copolymère greffé. De plus, à partir des mesures d'inhibition vis-à-vis de l'eau, d'humidification, des propriétés de tension, de rigidité, d'abrasion à la flexion et des propriétés thermodurcissables, on peut conclure que les améliorations des propriétés physiques sont remarquables pour le coton greffé à l'acrylate de propyle ou de butyle.

Zusammenfassung

Die Pfropfcopolymerisation von Acrylatmonomeren, Methyl, Äthyl, n-Propyl und n- oder Isobutyl, auf Baumwollgewebe wurde im wässrigen Emulsionssystem nach der Cerionenmethode ausgeführt. Die Pfropfgeschwindigkeit nimmt mit steigender Länge der Estergruppe ab. Die maximale Vergesserung der Trockenknitterfestigkeit nimmt mit steigender Pfropfung zu und verschiebt sich gegen einen höheren Pfropfungsgrad bei abnehmender Umwandlungstemperatur zweiter Ordnung der Pfropfpolymeren. Die Verbesserung der Nassknitterfestigkeit bei Gleichgewichtseinstellung in Gegenwart des Netzungsmittels ist immer grösser als dijenige der Trockenknitterfestigkeit, sogar bei Anwendung mit zunehmender Aufpfropfung bei hydrophober Propyl- oder Butylacrylatgepfropfter Baumwolle. Die Verbesserung der Knitterfestigkeit wurde durch eine Stabilisierung der offenen Faserstruktur durch aufpfropfung von Acrylaten besonders von solchen mit grossen Estergruppen durch Verschlingungsvernetzung zwischen Pfropfpolymeren oder den Pfropfpolymeren und Zelluloseketten und durch das auf diese Weise entwickelte elastische oder quellungselastische Verhalten auf Grund der Segmentbewegung in den amorphen Bereichen des Pfropfcopolymeren erklärt. Schliesslich konnte aus der Messung der Wasserimbibierung und -abstossung, Feuchtigkeitsaufnahme, der Zugeigenschaften, der Steifigkeit, Biegeabrieb und der Wärmehärtungseigenschaften geschlossen werden, dass die Verbesserung der physikalischen Eigenschaften bei der Propyl- oder Butylacrylat-gepfropften Baumwolle bemerkenswert ist.