

Wrinkle-Resistant Cotton by Photoinitiated Reaction with Glycidyl Methacrylate Followed by Crosslinking Reactions*

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Synopsis

A wrinkle-resistant cotton fabric was produced by photoinitiated free-radical reaction of a glycidyl methacrylate monomer from a methanol-water solution to form a poly(glycidyl methacrylate) copolymer, followed by crosslinking reactions of oxirane groups of the copolymer with cellulose. The product had increased conditioned and wet recovery angles and retained breaking and tearing strengths and stiffness values in the ranges normally obtained for wrinkle-resistant cottons. The effects of these reactions on the fiber structure were determined by transmission electron microscopy. The modified fibers were resistant to dissolution in cupriethylenediamine dihydroxide.

INTRODUCTION

The development of processes for crosslinking of cellulose in cotton fabrics to impart wrinkle resistance continues to be of interest.¹ *N*-Methylolacrylamide²⁻⁶ and glycidyl methacrylate⁷⁻⁹ monomers have been used as crosslinking reagents for cellulose. In one experiment, graft polymerization reaction of a monomer with cellulose is initiated. Then, pendant groups, methylol groups on poly(*N*-methylolacrylamide) and oxirane groups on poly(glycidyl methacrylate) (PGMA), are reacted with cellulose. The three-dimensional structure formed imparts wrinkle resistance to the fabric.^{4,7} High-energy radiation has been used as a free-radical initiator in these processes.^{7,8} Near-ultraviolet radiation has also been used to initiate graft polymerization of vinyl monomers with cellulose.^{2-4,9-14} *N*-Methylolacrylamide was used in these processes to impart wrinkle resistance to cotton fabrics.⁴

This report deals with ultraviolet-radiation-initiated reactions of a glycidyl methacrylate monomer from a water-methanol solution with cotton fabric, followed by reactions of the oxirane groups with cellulose to impart wrinkle resistance. Also reported are the effects of the solution composition, wavelength of ultraviolet light, type of inorganic catalyst, and other experimental factors on the reactions and on selected textile properties of the modified cotton fabrics.

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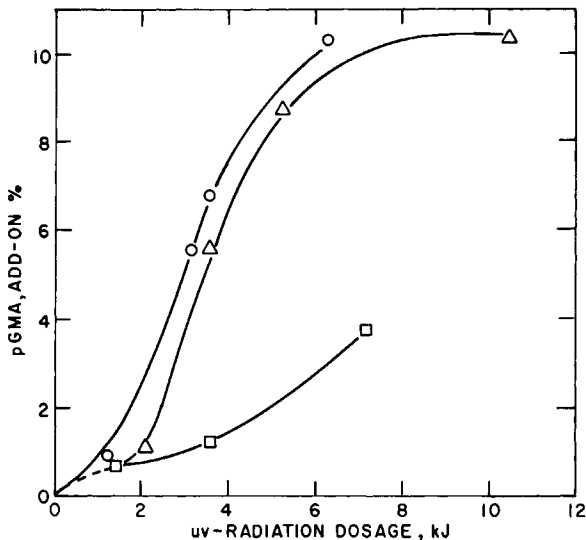


Fig. 1. Effects of wavelength of ultraviolet light on photoinitiated polymerization of glycidyl methacrylate (GMA) with cotton cellulose; cotton printcloth was padded with a solution that contained GMA (15%), methanol (55%), and water (30%) to a wet pickup of about 80% by weight and irradiated in a quartz container in an atmosphere of nitrogen. (Δ) 254 nm; (O) 300 nm; (\square) 350 nm.

EXPERIMENTAL

Materials

The cotton fabric, a commercial grey printcloth (0.109 kg/m², 3.15 × 3.15 threads/mm), was desized, alkali scoured, bleached, washed with water, and air dried. Samples of the fabrics were equilibrated overnight in air at about 298 K and 45% relative humidity to constant weight, as previously described.⁴

Glycidyl methacrylate (GMA), a commercial product, was obtained with inhibitor, about 50 ppm of 4-methoxyphenol. The inhibitor was removed by adsorption on activated alumina. Other chemicals were reagent grade.

Methods

The ultraviolet light source was a Rayonet photochemical reactor RPR-100, manufactured by the Southern New England Ultraviolet Company.* The reactor was equipped with a set of 16 tube lamps mounted vertically around the inside walls of a cylindrical chamber (0.25 m diameter and 0.38 m long). The reactor gave sources of radiant energy with about 85–90% of the light in the desired wavelength range. The reactor generated watts of ultraviolet energy as follows: 254 nm (35 W), 300 nm (21 W), and 350 nm (24 W).

Samples of fabric about 0.25 × 0.41 m were immersed in methanol–water solutions of GMA and crosslinking catalysts (as indicated in footnotes to the tables

* Names of companies or commercial products are given solely for the purpose of providing specific information; their mention does not imply recommendation or endorsement by the U.S. Department of Agriculture over others not mentioned.

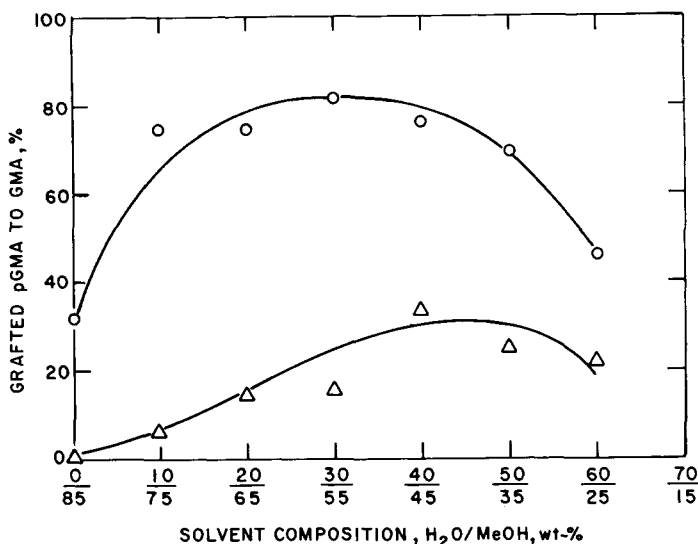


Fig. 2. Effects of solvent composition on photoinitiated polymerization of glycidyl methacrylate (GMA) with cotton cellulose; cotton printcloth was padded with a solution that contained GMA (15%), methanol (85- X %), and water (X %) to a wet pickup of about 80% by weight, and irradiated in a quartz container in an atmosphere of nitrogen with 300 nm light (Δ) 3.15 kJ ultraviolet-radiation dosage; (O) 6.3 kJ ultraviolet-radiation dosage.

and captions of the figures) at 298 K and padded to the desired wet pickup by a two-dip, two-nip process. The treated samples in wet pickup states were wrapped around and fastened to cylinders made of stainless-steel hardware cloth. The cylinders were about 0.41 m in circumference and 0.25 m long. These

TABLE I
Effects of Glycidyl Methacrylate Photoinitiated Polymerization and Crosslinking on Some Textile Properties of Cotton Printcloth^a

Reaction	GMA ^b reacted, add-on %	Grafted PGMA ^c to GMA, %	Breaking strength, N	Tearing strength, N	Wrinkle recovery angle, rad(W + F)		Stiffness, mN m
					Conditioned	Wet	
Control	—	—	215	8.2	3.33	3.04	0.0357
Cure ^d	(-1.0)	—	45	3.0	3.77	3.72	0.0384
UV ^e	6.2	78	200	6.9	4.03	4.08	0.0733
UV-cure ^f	4.4	55	52	2.4	4.19	3.98	0.0424
UV ^g	6.9	88	170	8.0	3.72	3.84	0.0583
UV-cure ^h	5.2	66	45	3.2	4.40	4.36	0.0489

^a Cotton printcloth was padded with a solution that contained glycidyl methacrylate (10%), Mg(BF₄)₂ (1%), methanol (43%), and water (46%) to a wet pickup of about 80% by weight.

^b GMA = glycidyl methacrylate.

^c PGMA = poly(glycidyl methacrylate).

^d Padded sample was dried on a frame in an air oven at 353 K for 480 sec, then cured at 423 K for 180 sec.

^e Padded sample was irradiated in a quartz container in an atmosphere of nitrogen with 300 nm light to a dosage of 12.6 kJ and then dried on a frame in an air oven at 353 K for 480 sec.

^f Sample from e was cured at 423 K for 180 sec.

^g Same as e except UV-radiation dosage was 37.8 kJ.

^h Sample from g cured at 423 K for 180 sec.

TABLE II
Effects of Type of Crosslinking Catalysts on Some Textile Properties of Cotton Printcloth
Containing Glycidyl Methacrylate^a

Catalyst	Catalyst concen- tration, %	Reaction	GMA ^b reacted, add-on %	Breaking strength, N	Wrinkle recovery angle, rad(W + F)		Stiffness, mN m
					Condi- tioned	Wet	
—	—	Cure ^c	0.8	216	3.30	2.55	0.0424
—	—	UV ^d	9.2	224	3.30	2.83	0.0518
—	—	UV-cure ^e	10.7	219	3.39	2.91	0.0540
Mg(BF ₄) ₂	1	Cure ^c	(-0.3)	66	3.37	3.75	0.0385
	1	UV ^d	10.3	218	3.21	3.07	0.0790
	1	UV-cure ^e	9.4	60	4.33	4.00	0.0470
Mg(ClO ₄) ₂	1	Cure ^c	0.0	129	3.37	3.21	0.0414
	1	UV ^d	9.2	204	3.25	2.88	0.0546
	1	UV-cure ^e	9.6	150	3.56	3.21	0.0498
Zn(NO ₃) ₂	1.5	Cure ^c	(-0.2)	205	2.98	2.97	0.0424
	1.5	UV ^d	7.9	213	3.30	2.74	0.0507
	1.5	UV-cure ^e	8.4	175	3.05	3.05	0.0527
Al ₂ (SO ₄) ₃	2	Cure ^c	(-2.2)	45	3.14	3.16	0.0376
	2	UV ^d	9.6	211	3.12	2.72	0.0565
	2	UV-cure ^e	7.4	66	3.80	3.28	0.0414

^a Cotton printcloth was padded with a solution that contained glycidyl methacrylate (15%), methanol (40%), catalyst (X%), water (45-X%) to a wet pickup of about 80% by weight.

^b GMA = glycidyl methacrylate.

^c Padded sample was dried on a frame in an air oven at 353 K for 480 sec, then cured at 423 K for 180 sec.

^d Padded sample was irradiated in a quartz container in a nitrogen atmosphere with 300 nm light to a dosage of 6.3 kJ and then dried on a frame in an air oven at 353 K for 480 sec.

^e Sample from d cured at 423 K for 180 sec.

samples were placed in a quartz reactor vessel, the vessel was closed, and the atmosphere was exchanged with nitrogen. The vessel was placed in the reactor and photoirradiated. When wet fabrics are photoirradiated, polymerization of GMA occurs throughout the fiber structure.⁹ The ambient temperature of the reactor increased from about 296 to 318 K during the initial 300 sec of photoirradiation.

The samples were fastened to flat, rectangular frames during drying and crosslinking treatments that were conducted in ovens with mechanically circulated, heated air. Preliminary tests to determine the effects of curing temperature on wrinkle recovery angles of the fabrics were made over the range 378 to 448 K. Maximum increases in wrinkle recovery angles of the modified fabrics were obtained in the range 413–433 K. A curing temperature of 423 K was used.

After the desired ultraviolet reactions, cure reactions, and ultraviolet-cure reactions, the fabrics were washed in hot water (340 K) to remove unreacted monomer and other reagents and dried. After equilibration to constant weight at about 298 K and 45% relative humidity, the increase in weight of modified fabric, compared with the weight of an equivalent sample of unmodified fabric, was recorded as monomer or polymer add-on. The efficiency of conversion of GMA to poly(glycidyl methacrylate) (PGMA) was calculated from the compo-

TABLE III
Effects of Type of Crosslinking Catalysts and After-Curing Wash on Some Textile Properties of Cotton Printcloth Containing Poly(Glycidyl Methacrylate)^a

Catalyst	Catalyst concentration, %	Wash after cure ^b	PGMA ^c reacted, add-on %	Breaking strength, N	Wrinkle recovery angle, rad(W + F) Conditioned
—	—	no cure-no wash	12.3	239	3.32
—	—	no cure-wash	8.6	224	3.65
—	—	cure-no wash	12.3	219	3.63
Mg(BF ₄) ₂	1	cure-no wash	12.5	48	4.33
	1	cure-wash	11.3	44	4.15
Mg(ClO ₄) ₂	1	cure-no wash	12.5	174	3.94
	1	cure-wash	11.3	163	3.54
—	—	—	—	215	3.33

^a Cotton printcloth was padded with a solution that contained glycidyl methacrylate (15%), methanol (55%), catalyst ($X\%$), and water ($30-X\%$) to a wet pickup of about 80% by weight; the padded sample was irradiated in a quartz container in an atmosphere of nitrogen with 300 nm light to a dosage of 6.3 kJ and dried on a frame in an air oven at 353 K for 480 sec.

^b Sample from a was cured at 423 K for 180 sec; some of these samples were given an after-wash as described in the text.

^c PGMA = poly(glycidyl methacrylate).

sition of the solution, the wet pickup of solution on the fabric, and the weight add-on of PGMA.

Physical properties of the fabrics were determined by ASTM methods for breaking strength,^{15a} tearing strength,^{15b} and conditioned and wet wrinkle recovery angles.^{15c} Stiffness was determined by the Federal Test Method Standard.¹⁶ Transmission electron microscopy (TEM) analyses¹⁷ were used to determine the location of PGMA within the fiber cross section, interaction between fiber and PGMA, and effects of ultraviolet-cure reactions on fiber structure. Infrared spectra of the samples were determined by the KBr disk technique.¹⁸

RESULTS AND DISCUSSION

The effects of the wavelength of ultraviolet light on photoinitiated polymerization of GMA with cotton cellulose are shown in Figure 1. The effects of light on PGMA add-on were $300 > 254 > 350$ nm. After an induction period, the rate of polymerization of GMA was about equal for samples irradiated with 254 and 300 nm light. However, complete conversion of GMA to PGMA, at about 10% add-on, was reached at a lower ultraviolet-radiation dosage with 300 nm light.

If the padded cotton printcloth was irradiated in air, conversion of GMA to PGMA did not occur. Removal of the inhibitor, 4-methoxyphenol, from GMA before irradiation reduced the induction period; however, at ultraviolet-radiation dosages greater than about 6 kJ, conversion of GMA to PGMA was about the same in the presence or absence of 4-methoxyphenol. Addition of diacetyl to the GMA solution before padding onto cotton printcloth increased both the rate and efficiency of the conversion of GMA to PGMA. For example, solutions that contained diacetyl:GMA = 1:100 molar ratio at an ultraviolet-radiation dosage

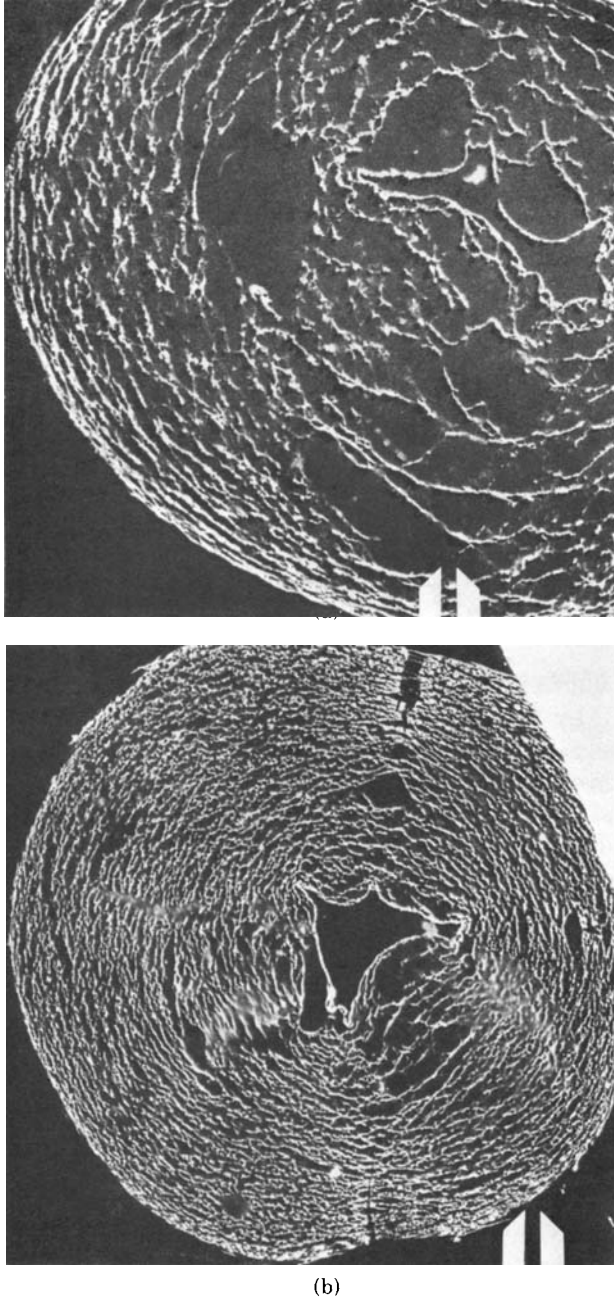


Fig. 3. Transmission electron micrographs of sections of cotton fibers from printcloth treated with poly(glycidyl methacrylate) (PGMA). (a) Expansion of section of untreated fiber; (b) expansion of section of fiber that contained PGMA (10.3% add-on); (c) expansion of section of fiber that contained PGMA (9.4% add-on) and $\text{Mg}(\text{BF}_4)_2$ (1%) and was dried and then cured at 423 K for 180 sec.

of 3.15 kJ had an efficiency of conversion of GMA to PGMA of about 96%; in the absence of diacetyl conversion was only about 16%.

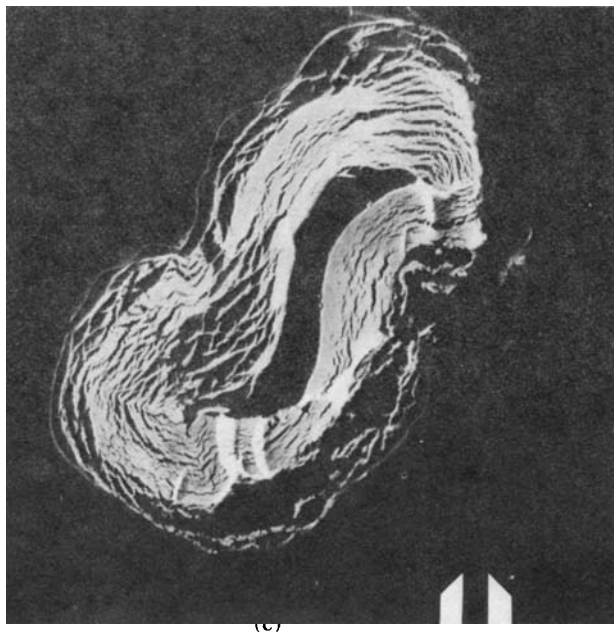
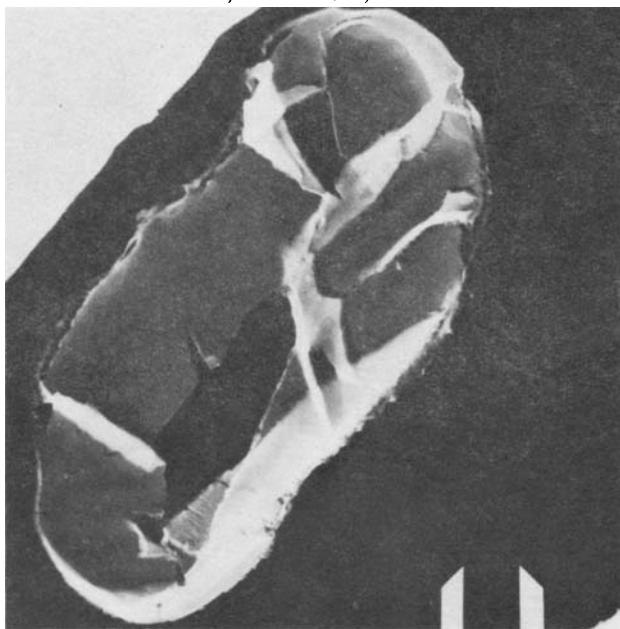


Fig. 3. (Continued from previous page.)

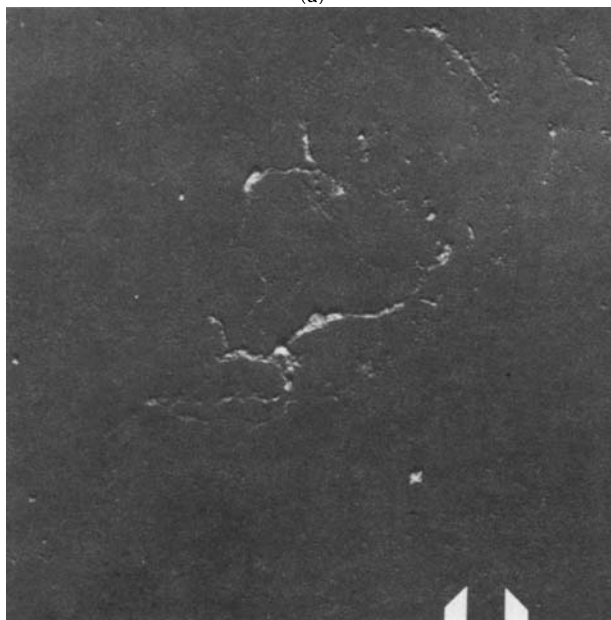
The effects of solvent composition on photoinitiated polymerization of GMA with cotton cellulose are shown in Figure 2. At an ultraviolet-radiation dosage of about 6.3 kJ, a maximum of 70–80% conversion of GMA to PGMA occurred when the composition of the solution ranged from GMA(15%)—CH₃OH(75%)—H₂O(10%) to GMA(15%)—CH₃OH(35%)—H₂O(50%). At a lower ultraviolet-radiation dosage of 3.15 kJ, a maximum of 25–30% conversion of GMA to PGMA occurred when the solution contained 40–50% water. When the water content of the solution was greater than about 55%, the solution separated into phases.

The effects of the sequences of the photoinitiated polymerization and crosslinking reactions of GMA with cellulose, in which Mg(BF₄)₂ catalyst was used, on some textile properties of cotton printcloth are shown in Table I. In the photoinitiated reaction, GMA is copolymerized with cotton fabric, so that PGMA graft copolymer with high molecular weight and pendant oxirane groups is covalently linked to cellulose. In the cure reaction, crosslinking reactions between oxirane groups and cellulose are initiated. Fabrics prepared by photoinitiated reactions had higher wrinkle recovery angles and stiffnesses and lower breaking and tearing strengths than unmodified fabrics. In the cure reactions, crosslinking of cellulose through oxirane groups further increased wrinkle recovery angles but decreased breaking and tearing strengths and stiffnesses of fabrics that contained PGMA.

The effects of the types of crosslinking catalyst and sequences of reactions on some textile properties of cotton printcloth are shown in Table II. When the cure reactions were conducted with only monomeric GMA present, there was no improvement in the textile properties of the fabrics. The amount of monomeric GMA reacted was low. Fabrics prepared by the ultraviolet-cure reaction had textile properties that depended on the catalyst. The catalyst concentra-



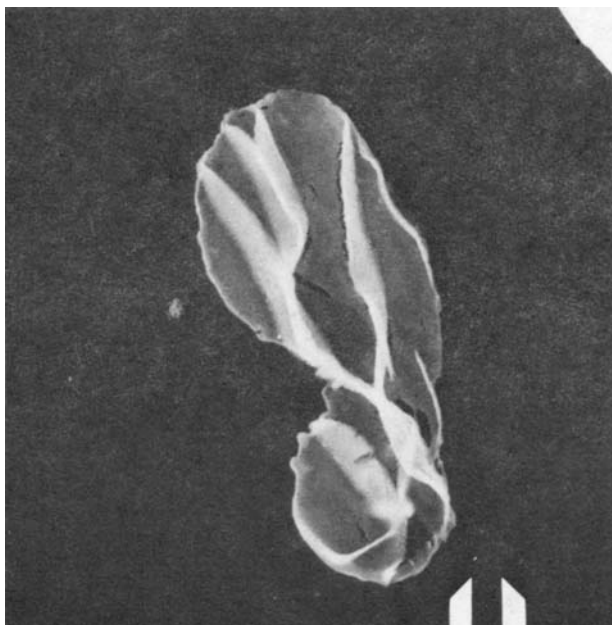
(a)



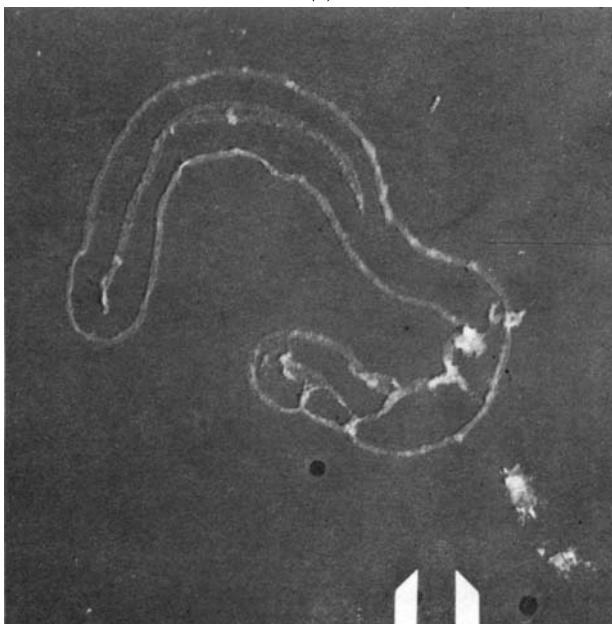
(b)

Fig. 4. Transmission electron micrographs of sections of cotton fibers from printcloth treated with glycidyl methacrylate. (a) Section of untreated fiber; (b) section a immersed in 0.5M cupriethylenediamine dihydroxide (CED) for 1.8 ksec; (c) section of fiber treated with a solution of GMA (15%), methanol (55%), water (29%), and $\text{Mg}(\text{BF}_4)_2$ (1%) to a wet pickup of about 80% by weight and then dried and cured at 423 K for 180 sec; (d) section c immersed in 0.5M CED for 1.8 ksec.

tions were reported to be optimum concentrations for reacting oxirane groups with cotton. Fabrics prepared by the ultraviolet-cure reaction in which $\text{Mg}(\text{BF}_4)_2$ was the catalyst had increased wrinkle recovery angles, decreased



(c)

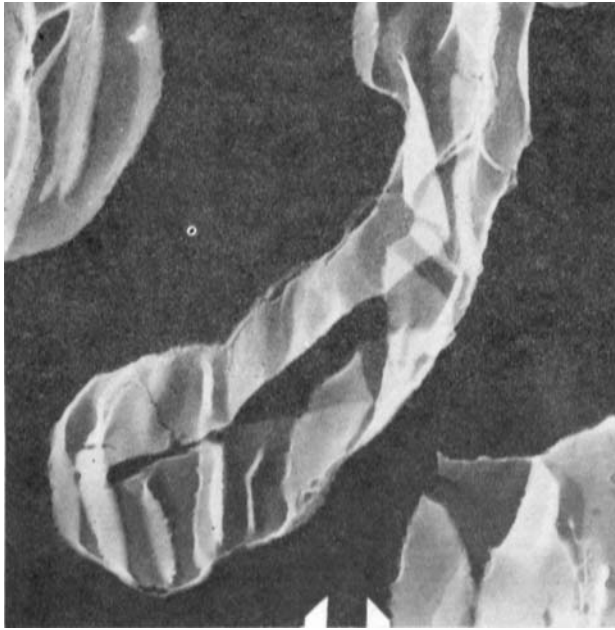


(d)

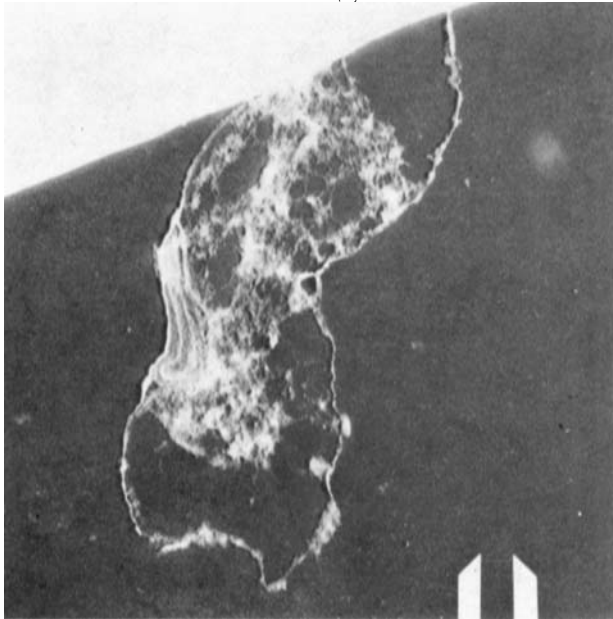
Fig. 4. (Continued from previous page.)

breaking strength, and decreased stiffness. The other catalysts $\text{Mg}(\text{ClO}_4)_2$, $\text{Zn}(\text{NO}_3)_2$, and $\text{Al}_2(\text{SO}_4)_3$, were not as effective as $\text{Mg}(\text{BF}_4)_2$ in increasing the wrinkle recovery angles of the modified fabrics.

The effects of the type of crosslinking catalysts and after-curing wash on some textile properties of cotton printcloth that contained PGMA are shown in Table III. Cure reactions increased the wrinkle recovery angles and decreased the



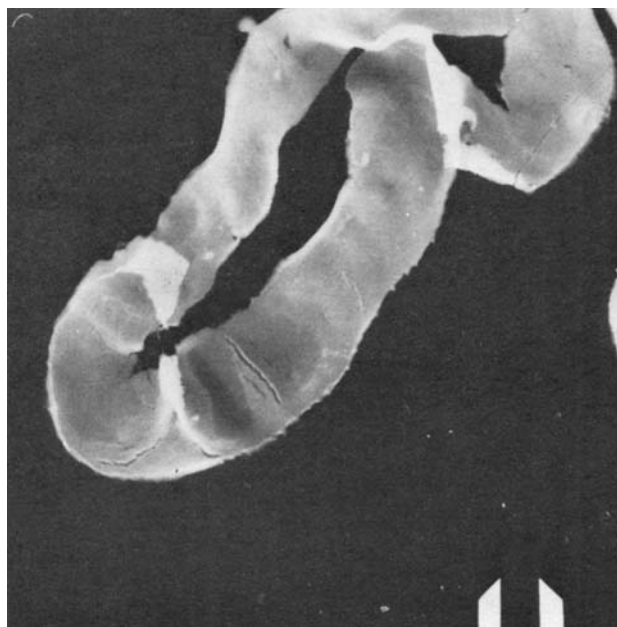
(a)



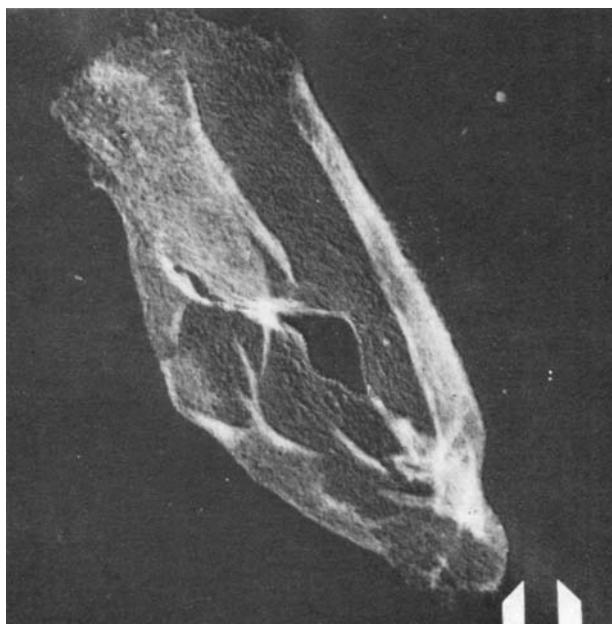
(b)

Fig. 5. Transmission electron micrographs of sections of cotton fibers from printcloth treated with poly(glycidyl methacrylate) (PGMA). (a) Section of fiber treated with PGMA (10.3% add-on); (b) section a immersed in 0.5M cupriethylenediamine dihydroxide (CED) for 1.8 ksec; (c) section of fiber treated with PGMA (9.4% add-on) and $Mg(BF_4)_2$ (1%) and then dried and cured at 423 K for 180 sec; (d) section c immersed in 0.5M CED for 1.8 sec.

breaking strengths of the fabrics. An after-curing wash decreased both the wrinkle recovery angles and breaking strengths of the fabrics. The ultraviolet-cure reaction in which $Mg(BF_4)_2$ was the catalyst was more effective in in-



(c)



(d)

Fig. 5. (Continued from previous page.)

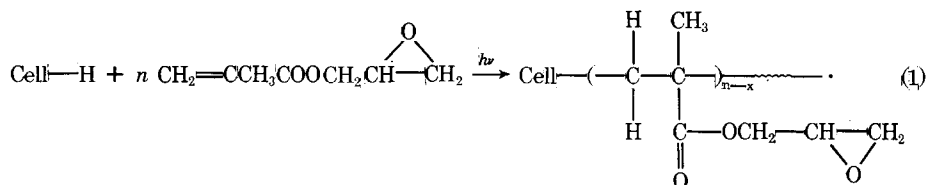
creasing the wrinkle recovery angles of the fabrics than reactions in which no catalyst or $\text{Mg}(\text{ClO}_4)_2$ was used.

Microscopical analyses of GMA-modified cotton printcloth by expansion techniques are shown in Figure 3. The ultraviolet reaction to form PGMA within the fibers gave products that could be expanded [Fig. 3(b)] in a manner similar to untreated fibers [Fig. 3(a)]. In the ultraviolet-cure reaction, some of the

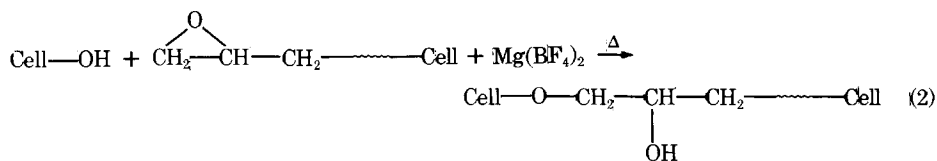
pendant oxirane groups of PGMA within the fibers were reacted with cellulose to form crosslinks and decreased the amount of lamellar expansion [Fig. 3(c)], compared with untreated [Fig. 3(a)] and PGMA reacted [Fig. 3(b)] fibers.

The resistances of cotton fibers from printcloth treated with GMA and PGMA to dissolution in 0.5*M* cupriethylenediamine dihydroxide (CED) are shown in Figures 4 and 5. The dissolution of untreated fiber [Fig. 4(a)] when immersed in CED is shown in Figure 4(b). The dissolution of fiber cured with monomeric GMA [Fig. 4(c)] in CED is shown in Figure 4(d). The resistance to dissolution of fiber reacted with PGMA [Fig. 5(a)] in CED is shown in Figure 5(b). The resistance to dissolution of fiber ultraviolet-cure reacted with PGMA [Fig. 5(c)] in CED is shown in Figure 5(d). Only fibers that had been ultraviolet reacted with GMA to form grafted PGMA with cellulose had resistance to dissolution in CED. Infrared spectra of fibers ultraviolet reacted with PGMA had bands associated with oxirane groups. After the ultraviolet-cure reactions of PGMA with cellulose, there were small changes in the infrared spectra.

The photoinitiated reaction of GMA with cellulose could occur as follows:



The cure reaction could initiate combination of some of the pendant oxirane groups with cellulose¹⁹ as follows:



This reaction would result in a three-dimensional crosslinked structure.

Wrinkle-resistant cotton fabrics with wrinkle recovery angles greater than 4 rad were prepared by ultraviolet-cure reactions with GMA at add-ons of 5–10%. Decreases in breaking and tearing strengths and increases in stiffnesses of the modified fabrics were in the range of textile properties normally obtained for wrinkle-resistant cotton fabrics prepared by other methods.

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