

Modification of Partially Carboxymethylated Cotton via Crafting with Acrylic Acid and Styrene Using Gamma Radiation

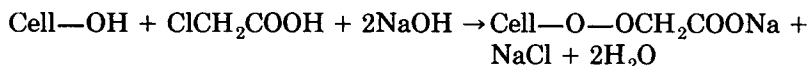
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Synopsis

Partially carboxymethylated cottons (PCMC) having 15.549, 27.409, and 46.834 meq —COOH/100 g cellulose as well as untreated cotton and alkali-treated cotton, which was prepared in an analogous manner to PCMC but, in the absence of monochloroacetic acid, were graft-copolymerized with either acrylic acid or styrene using gamma radiation under different conditions. Moisture regain and dyeing properties of the copolymers so obtained were investigated. It was found that the graft yield increases by increasing monomer concentration and radiation dose irrespective of the monomer or substrate used. Using water/methanol mixtures as polymerization media are advantageous for grafting of styrene onto the substrates in question. The graft yields of PCMCs are much lower than those of unmodified and alkali-treated cottons when they were grafted with acrylic acid. In case of styrene on the other hand, the graft yields for PCMCs are higher than the corresponding yields obtained with the unmodified and alkali-treated cottons. Poly(acrylic acid)-PCMC graft copolymers show much higher moisture regain than PCMCs particularly when the carboxylic groups of the graft were in the sodium form. The opposite holds true for polystyrene-PCMC graft copolymers which exhibit much lower moisture regain as compared with PCMCs. The color strength of PCMC dyed with direct or reactive dyes decreases significantly after being copolymerized with poly(acrylic acid) prior to dyeing. On the other hand, this copolymerization improves the affinity of PCMCs for the basic dye and brings about perceptible shade. Polystyrene-PCMC graft copolymers acquire higher color strength than the PCMC when dyed with direct, disperse, and basic dyes but lower color strength upon dyeing with the reactive dye. Also reported were the moisture regain and dyeability of unmodified and alkali-treated cotton before and after copolymerization with acrylic acid or styrene for comparison.

INTRODUCTION

Several publications¹⁻¹⁵ have dealt with preparation and properties of partially carboxymethylated cotton (PCMC). The latter may simply be prepared by padding the cotton cellulose with monochloroacetic acid or its sodium salt, followed by padding with sodium hydroxide.¹⁻³ The overall reaction may be written as follows:



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PCMC with a DS of about 0.05–0.15 retains the original fibrous nature and exhibits a number of potentially valuable properties, such as a crisp hand with a slightly starched feel, increased moisture regain, water absorbancy, water permeability, changed dyeing characteristics, increased resistance to soiling from aqueous dispersions, greater ease of soil removal, etc.^{4–7} Furthermore, detailed studies have been reported on the behavior of PCMC towards oxidation and hydrolysis,⁸ transfer printing,^{9,10} crosslinking,¹¹ thermal treatments,¹² and radiation treatments.¹³

Vinyl graft polymerization onto PCMC using tetravalent cerium¹⁴ or azobisisobutyronitrile¹⁵ as initiator has been studied in details. It was reported that the graft yield obtained with PCMC is significantly higher than that obtained with native cotton.

The present work is undertaken with a view of studying (a) graft polymerization of acrylic acid and styrene onto PCMCs using gamma radiation and (b) moisture regain and dyeing properties of the cotton graft copolymers so obtained.

EXPERIMENTAL

Materials

Cotton Fabric

Mill desized, scoured, bleached and mercerized plain weave (31 picks and 36 ends/cm), supplied by El-Nasr Spinning, Weaving and Knitting Co. was used.

Partially Carboxymethylated Cotton

Partially carboxymethylated cotton was prepared according to a procedure reported elsewhere² using 10N NaOH and sodium chloroacetate. Partially carboxymethylated cotton of various degree of substitution were obtained by using different concentrations of sodium chloroacetate ranging from 1N to 4N. The samples were then washed, neutralized, and washed again till free from any traces of chemicals and drying at room temperature.

Alkali-Treated Cotton

A control sample, namely, sodium-hydroxide-treated cotton, was prepared using NaOH (10N) and following the procedure mentioned above except that treatment with sodium salt of monochloroacetic acid was cancelled.

Dyestuffs

Four dyestuffs belonging to different classes were used. These dyes were: a direct dye, namely, Diamine Supra Turquoise Blue GL, supplied by Cassela, Italy; a reactive dye, namely, Remazol Brilliant Green CB, (C.I., Reactive Green 14), supplied by Hoechst, West Germany; a basic dye, namely, Sandocryl Orange B-3RLE, (C.I. Basic Orange 39), supplied by Sandoz, Switzerland; and a disperse dye, namely, Samaron Pink FRL (C.I. Disperse 91), supplied by Hoechst, West Germany.

Graft Copolymerization Procedures

Copolymerization with Acrylic Acid

Samples of cotton and modified cottons were grafted with acrylic using the mutual irradiation technique, that is, the samples were immersed in the monomer solution and exposed to gamma radiation. Five concentrations of acrylic acid, viz., 4, 8, 12, 16, and 20% in water were prepared. The monomer solutions containing samples were irradiated to 0.5, 1.5, and 2 Mrad. Irradiation to the required radiation doses has been carried out in the cobalt-60 Gamma Source (3600 ci) of the National Centre for Radiation Research and Technology (dose rate ranged from 25 to 20 rad/s). The unreacted monomer was removed by washing with water. The samples were then extracted with boiling water to remove the homopolymer, followed by drying. Extraction and drying were repeated till constant weight. The graft yield was expressed as meq $-\text{COOH}$ group/100 g cellulose.

Copolymerization with Styrene

Samples of cotton and modified cottons were grafted with styrene under different conditions including monomer concentration, dose, and solvent composition. Three monomer concentrations, viz., 5, 10, and 20% were used. Varied methanol/water compositions (100% water, 20/80% MeOH/H₂O, and 100% MeOH) were employed. Samples immersed in the solvent-monomer mixtures were irradiated at 0.5 and 1.5 Mrad. The irradiated samples were first washed with water to remove the untreated monomer, followed by first air drying then oven drying at 105°C for 2 h. The styrene homopolymer was removed by benzene extraction for 40 h. The graft yield was calculated (on dry weight basis) as follows:

$$\text{Graft yield (\%)} = \frac{\text{wt grafted sample} - \text{wt ungrafted sample}}{\text{wt ungrafted sample}} \times 100$$

Dyeing Procedures

Detailed procedures for dyeing with the basic dye, reactive dye, direct dye, and disperse dye have been described elsewhere.¹⁶

Testing and Analysis

The carboxyl content was estimated according to a reported method.¹⁷ The moisture regain was determined by the vacuum desiccator method with sodium nitrate to give 65% relative humidity (RH) at $21 \pm 1^\circ\text{C}$.

The color strength measurements¹⁸ of the dyed substrates were done on automatic filter spectrophotometer. The relative color strength (expressed as K/S values) was determined by applying the Kubelka-Munk equation:¹⁹

$$\frac{K}{S} = \frac{(1 - R)^2}{2R} - \frac{(1 - R_0)^2}{2R_0} = A \cdot C$$

where R is the decimal fraction of the reflectance of the coloured fabric, R_0 is the decimal fraction of the reflectance of the uncolored fabric, K is the absorption coefficient, S is the scattering coefficient, C is the dye concentration, and A is a proportionality factor.

RESULTS AND DISCUSSION

Unmodified cotton (substrate I), alkali-treated cotton (substrate II) and PCMCs having 15.459, 27.409, and 46.834 meq $-\text{COOH}/100$ g cellulose (substrates III, IV, and V, respectively) were grafted-copolymerized with either acrylic acid or styrene using different monomer concentrations and radiation doses. This was done to clarify the effect of changes in the physical as well as chemical structure of cotton on graftability of the latter. Given below are the results of the copolymerization studies as well as those of the properties of the copolymers obtained along with their appropriate discussion.

Copolymerization with Acrylic Acid

Carboxymethyl Content

Table I shows the effect of the carboxymethyl content of PCMC on the graft yield. The latter is expressed as meq $-\text{COOH}/100$ g cellulose. It is observed that, for a given radiation dose and monomer concentration, the graft yields of PCMC are much lower than those of unmodified and alkali-treated cottons. Also the graft yields of PCMC decrease substantially as the carboxymethyl content increases. This is rather in contrast with previous reports,^{14,15} which disclosed higher grafting with PCMC using nonionizable vinyl monomers and gave opening up the cellulose structure with increased swellability of cotton as reasons for the higher grafting. With ionizable monomer such as acrylic acid, which is the case here, the situation is different. The carboxyl groups of PCMC ionize and produce negatively charged cellulose surfaces which repel the similarly charged monomer, i.e., acrylic acid. As a result, diffusion in and adsorption of monomer on PCMC are impeded, thereby leading to decreased grafting. Nevertheless, contribution of blocking of some of the cellulose hydroxyls, which act as sites for grafting, by introduction of the carboxymethyl groups in lowering the graft yield of PCMC cannot be excluded. Stated in other words, the effects of production of negative cellulose surfaces as well as blocking some of the cellulose hydroxyls by the carboxymethyl groups prevail over their effects on opening up the structure of cellulose with increased swellability, thereby decreasing graftability of PCMC toward acrylic acid.

Table I shows also that alkali-treated cotton shows higher graft yield than the unmodified cotton irrespective of the conditions of grafting. This could be associated with increased accessibility of cotton brought about by the alkali treatment.

It may be further noted that irradiation in the absence of acrylic acid of the unmodified cotton and alkali-treated cotton resulted in the creation of carboxyl content but with the certainty that the latter acquires higher carboxyl content than the former. This, again, could be interpreted in terms of higher accessibility and, therefore, higher susceptibility of alkali-treated cotton to

TABLE I
 Radiation-Induced Grafting of Acrylic Acid Onto Untreated Cotton (Substrate I), Alkali-Treated Cotton (Substrate II), and Partially Carboxymethylated Cottons
 (Substrates III-V) Using Different Monomer Concentrations at Varying Radiation Doses

Acrylic acid concentration (%)	Graft yield (mi eq —COOH/100 g cellulose) ^a														
	Substrate I			Substrate II			Substrate III			Substrate IV			Substrate V		
	a	b	c	a	b	c	a	b	c	a	b	c	a	b	c
None	0.622	0.854	1.080	1.652	2.051	2.202	15.549	15.120	14.823	27.409	27.000	26.672	46.834	45.000	45.000
4	14.29	21.513	25.661	19.128	27.009	26.589	9.521	11.572	5.521	2.037	24.531	2.069	0.375	17.672	00.00
8	20.52	33.261	35.753	22.619	43.069	44.968	14.595	30.531	30.340	10.721	28.687	22.502	6.941	26.250	15.60
12	25.72	45.567	53.145	31.794	55.589	73.228	29.310	45.342	40.591	18.373	60.366	40.612	14.210	36.78	31.880
16	49.54	68.015	72.824	65.151	70.341	78.938	50.230	83.542	50.111	39.830	81.651	18.801	26.229	59.501	39.576
20	62.95	75.272	80.472	70.533	78.477	88.392	60.951	99.892	79.312	49.757	95.947	71.490	33.555	78.340	50.720

^a a, 0.5 Mrad; b, 1.5 Mrad; c, 2 M rad; graft yield = the total meq —COOH/100 g cellulose after grafting. The initial meq —COOH/100 g cellulose before grafting. Substrate III = 15.549 meq —COOH/100 g cellulose; substrate IV = 27.409 meq —COOH/100 g cellulose; substrate V = 46.834 meq —COOH/100 g cellulose.

radiation. With PCMC, on the other hand, there is a tendency that the carboxyl content increases at high radiation doses and decreases at lower doses, indicating concurrent creation of carboxyl groups and decarboxylation during irradiation in the absence of the monomer as detailed elsewhere.¹³

Acrylic Acid Concentration

Table I shows the effect of acrylic acid concentration on the graft yield. Obviously, for a given radiation dose, the graft yield increases significantly by increasing the acrylic acid concentration. This is observed regardless of the substrate used. Since the sites for grafting on the five substrates, i.e., the cellulose hydroxyls, are immobile, the graft polymerization reaction would rely on the amount of monomer available in the vicinity of the substrate. It is logical that availability of monomer in the proximity of the substrate increases by increasing monomer concentration thereby giving rise to increased graft yields.

Radiation Dosage

Table I shows the effect of radiation dose on the graft yields obtained with the five substrates in question. It is observed that increasing the radiation dose from 0.5 to 1.5 Mrad causes a significant enhancement in the graft yield. Increasing the radiation dose to 2.0 Mrad is accompanied by further enhancement in the graft yield only in case of the unmodified and alkali-treated cottons. In case of PCMC increasing the dose to 2.0 Mrad decreases the graft yield. This suggests that at higher radiation dose (i.e., 2 Mrad), PCMC undergoes decarboxylation and that factors associated with decarboxylation act in favour of termination processes.

Moisture Regain and Dyeability of Poly(acrylic Acid)-PCMC Graft Copolymers

Moisture Regain

Table II shows the moisture regain of unmodified cotton (substrate I), alkali-treated cotton (substrate II), and PCMCs having 15.549, 27.409, and 46.834 meq $-\text{COOH}/100$ g cellulose (substrates III, IV, and V, respectively) before and after these substrates were copolymerized with poly(acrylic acid). It is seen that, before copolymerization, the moisture regain of the five substrates varies substantially. Substrate II acquires higher moisture regain than substrate I by virtue of greater accessibility of the former than the latter. It is understandable that alkali treatment is accompanied by enhancement in the accessibility of cotton cellulose. A similar situation is encountered with PCMCs (substrates III-V) whose moisture regain not only exceeds that of substrate I but also that of substrate II. The higher moisture regain of PCMCs than the untreated and alkali-treated cottons could be attributed to two factors: (1) increasing accessibility of cotton under the influence of the alkaline environment during partial carboxymethylation and (2) factors associated with the presence of carboxymethyl groups in the molecular structure

TABLE II
Moisture Regain of Unmodified Cotton (Substrate I), Alkali-Treated Cotton (Substrate II), and Partially Carboxymethylated Cottons
(Substrates III-V) before and after Graft Polymerization with Acrylic Acid^a

Substrate I			Substrate II			Substrate III			Substrate IV			Substrate V		
G	MR		G	MR		G	MR		G	MR		G	MR	
0.00	5.974		0.00	6.945		0.00	7.196 (7.281)		0.00	7.690 (9.066)		0.00	8.496 (9.457)	
22.656	7.00 (7.510)		27.009	7.460 (9.198)		11.572	7.456 (7.641)		24.531	7.920 (10.093)		17.672	8.722 (10.378)	
35.406	7.721 (7.940)		43.069	7.602 (9.621)		30.531	7.561 (10.112)		28.687	8.748 (11.321)		26.250	8.849 (12.012)	
52.126	7.854 (8.763)		55.589	7.809 (10.541)		45.342	7.341 (11.098)		60.366	8.362 (11.269)		29.925	8.974 (13.475)	
80.156	7.598 (8.887)		98.859	8.019 (9.541)		83.542	7.931 (11.821)		81.651	8.421 (12.801)		59.501	9.188 (13.512)	
92.916	7.768 (9.033)		112.378	8.120 (11.941)		99.892	8.051 (12.111)		95.947	8.542 (13.149)		78.340	10.213 (13.497)	

^aG = graft yield (meq -COOH/100 g cellulose); MR = % moisture regain; substrate III = 15.549 meq -COOH/100 g cellulose; substrate IV = 27.409 meq -COOH/100 g cellulose; substrate V, 46.834 meq -COOH/100 g cellulose. Data between brackets represent moisture regain of the sodium salt of the grafted substrates.

of cellulose, such as opening up the cellulose structure, increasing hydrophilicity, and decreasing crystallinity.²⁰

Table II shows that graft copolymerization of substrates I–V with poly(acrylic acid) causes further improvement in their moisture regain. Nevertheless, the magnitude of moisture regain depends upon the percent graft and its form as well as original nature of the substrate. The moisture regain increases by increasing the level of grafting within the range studied. Moreover, the sodium salt of the graft induces much higher moisture regain as compared with its hydrogen form. This is observed irrespective of the substrate used. However, both effects, i.e., the level of grafting and the form of the graft, are more pronounced with substrates bearing higher carboxymethyl contents such as substrate V.

At any event, enhancement in moisture regain by introducing poly(acrylic acid) in the molecular structure of any substrates in question is a direct consequence of the hydrophilic environment created in the cellulose structure by the graft particularly when the latter is in the sodium form.

Dyeing with Basic Dye

It is well known that basic or cationic dyes are the most widely used dyes for acrylic fibers. Cellulose fibers have, for practical purposes, no affinity for basic dyes,²¹ and even those which are adsorbed have low wet fastness. For adsorption, the fiber must possess acidic groups. With this in mind, the five substrates in question before and after copolymerization with poly(acrylic acid) were dyed under identical conditions with a basic dye, namely, Sandocryl Orange B-3RLE. Results of the color strength, expressed as K/S , of the dyeings obtained are summarized in Table III.

Considering the results of color strength before copolymerization, despite their low values, one would realize that PCMCs show higher color strength than the ungrafted and alkali-treated cottons. Furthermore, the color strength is higher the higher carboxymethyl content of PCMC. This is rather expected since introduction of carboxymethyl groups in the molecular structure of cotton impart to the latter the acidic properties, thereby inducing dyeability with the basic dye.

Table III reveals that graft copolymerization of the five substrates with poly(acrylic acid) not only improves their affinity for the dye in question but also brings about a significant perceptible shade. As is evident, the magnitude of color strength is quite substantial irrespective of the substrate used, and the color strength increases by increasing the magnitude of grafting due to abundance of carboxylic group—at higher graft yield—which permit the copolymer to react with the dye through ionic bonding. Nevertheless, at roughly equal graft yields, the color strength of PCMC is exceedingly higher than those of ungrafted and alkali-treated cottons even after subtracting the original color strength. This could be associated with the more open structure and higher swellability of PCMC due to presence of the hydrophilic carboxymethyl groups. Opening up the cotton structure coupled with swellability would provide a favorable environment for dye diffusion and adsorption which are prerequisite for the dyeing process.

TABLE III
 Behavior of Untreated Cotton, Alkali-Treated Cotton, and Partially Carboxymethylated Cottons before and after Grafting
 with Acrylic Acid towards Dyeing with Basic Dye^a

Substrate I		Substrate II		Substrate III		Substrate IV		Substrate V	
G	K/S	G	K/S	G	K/S	G	K/S	G	K/S
0.00	0.125	0.00	0.185	0.00	0.383	0.00	0.593	0.00	1.163
14.29	1.195	19.140	1.542	9.521	1.679	2.037	2.150	0.375	2.800
20.52	1.656	22.619	3.330	14.595	3.009	10.721	3.520	6.941	4.150
25.72	2.850	41.057	3.860	29.310	3.514	18.373	3.950	14.210	4.730
49.54	3.440	65.151	4.26	50.23	3.613	39.830	4.54	26.229	5.07
62.95	3.600	69.99	4.640	60.951	4.700	49.757	4.86	33.555	5.530

^aSubstrate I = unmodified cotton; substrate II = alkali-treated cotton; substrates III-V = partially carboxymethylated cotton having 15.549, 27.409, and 46.834 meq —COOH/100 g cellulose, respectively; G = graft yield (meq —COOH/100 g cellulose); Basic dye, Sandocryl Orange B-3RLE; dye concn 4%; dyeing temp, boiling; duration of dyeing, 60 min; liquor ratio, 1:30.

Dyeing with Reactive Dye

It has been established that reactive dyes have good affinity towards cotton fabrics, in which dyeing proceeds through chemical bonding between the hydroxyl groups of cellulose and the dye.²² Hence availability and accessibility of the cellulose hydroxyls are not only essential but rather a deciding factor in dyeing cotton with reactive dyes. With this in mind, ungrafted cotton (substrate I), alkali-treated cotton (substrate II), and PCMCs (substrates III–V) before and after copolymerization with poly(acrylic acid) were dyed under identical conditions with a reactive dye, namely, Remazol Brilliant Green CB. Results of the color strength of the dyeings obtained are set out in Table IV.

It is seen (Table IV) that the color strength of the five substrates before copolymerization follows the order:

substrate II > substrate I > substrate III > substrate IV > substrate V

This order signifies that while alkali treatment of cotton enhances somewhat its affinity for the dye, partial carboxymethylation decreases this affinity. Furthermore, the affinity for the dye decreases as the carboxymethyl content of PCMC increases.

The marginal enhancement in color strength brought about by alkali treatment of cotton prior to dyeing seems to be a manifestation of greater accessibility of the alkali-treated cotton (substrate II) than the unmodified cotton (substrate I). On the other hand, the decrement in color strength brought about by partial carboxymethylation could be associated with two main reasons: (a) blocking some cellulose hydroxyls which represent the functional centers for the dye molecules and (b) creation of negatively charged cellulose surfaces—as a result of ionization of the carboxymethyl groups—which repel the similarly charged dye ions during dyeing.

Table IV shows also that when the five substrates were copolymerized with poly(acrylic acid), their color strength decreases significantly but still persists in the above order. This could be ascribed to ionization of the carboxylic groups of the graft during dyeing. Ionization results in substrates with negative surfaces which repel the dye anions.

Dyeing with Direct Dye

The binding forces between direct dye and cellulose are purely physical since the latter has no polar groups capable of salt linkages. There is also evidence that the hydroxyl groups play a significant part, because when cotton was acetylated its affinity for direct dyes was removed.²¹

Table V shows the color strength obtained with unmodified cotton (substrate I), alkali-treated cotton (substrate II), and PCMCs (substrates III–V) before and after copolymerization when a direct dye, namely, Diamine Supra Turquoise Blue GL was used. It is observed that, before copolymerization, the color strength for the unmodified cotton is much higher than for PCMCs, particularly those having high carboxymethyl contents. Alkali-treated cotton, on the other hand, acquires a lower color strength than that of the unmodified

TABLE IV
 Behavior of Untreated Cotton, Alkali-Treated Cotton, and Partially Carboxymethylated Cottons before and after Grafting
 with Acrylic Acid towards Dyeing with Reactive Dye^a

Substrate I		Substrate II		Substrate III		Substrate IV		Substrate V	
G	K/S	G	K/S	G	K/S	G	K/S	G	K/S
0.00	1.298	0.00	1.393	0.00	0.957	0.00	0.718	0.00	0.672
21.51	1.198	27.009	1.195	11.572	0.910	24.531	0.736	17.672	0.600
33.26	0.956	43.069	0.921	30.531	0.853	28.687	0.685	26.250	0.585
45.56	0.810	55.589	0.718	45.342	0.625	60.366	0.546	29.925	0.527
68.01	0.752	70.341	0.682	83.542	0.582	81.651	0.500	59.501	0.473
75.27	0.682	79.56	0.593	99.892	0.500	95.947	0.466	78.340	0.398

^aSubstrate I = unmodified cotton; substrate II = alkali-treated cotton; substrates III-V = partially carboxymethylated cotton having 15.549, 27.409, and 46.834 meq -COOH/100 g cellulose; G = graft yield (meq -COOH/100 g cellulose. Reactive dye, Remazol Brilliant Green CB; dye concn, 4%; dye temp, 60°C; duration of dyeing, 90 min; liquor ratio, 1:20.

TABLE V
 Behavior of Untreated Cotton, Alkali-Treated Cotton, and Partially Carboxymethylated Cottons before and after Grafting
 with Acrylic Acid towards Dyeing with Direct Dye^a

Substrate I		Substrate II		Substrate III		Substrate IV		Substrate V	
G	K/S	G	K/S	G	K/S	G	K/S	G	K/S
0.00	1.305	0.00	0.993	0.00	0.543	0.00	0.356	0.00	0.247
21.51	0.932	27.009	0.641	11.572	0.520	24.531	0.330	17.672	0.227
33.26	0.710	43.069	0.494	30.531	0.482	28.687	0.311	26.250	0.233
45.56	0.633	55.589	0.432	45.342	0.411	60.366	0.253	29.925	0.220
68.01	0.550	70.341	0.378	83.542	0.356	81.651	0.240	59.501	0.203
75.27	0.461	79.56	0.385	99.892	0.300	95.947	0.246	78.340	0.240

^aSubstrate I = unmodified cotton; substrate II = alkali-treated cotton; substrates III-V = partially carboxymethylated cottons having 15.549, 27.409, and 46.834 meq $-\text{COOH}/100$ g cellulose; G, graft yield (meq $-\text{COOH}/100$ g cellulose. Direct dye, Diamine Supra Turquoise Blue GL; dye concn, 4%; dyeing temp, boiling; duration of dyeing, 100 min; liquor ratio, 1 : 30.

cotton, indicating that increased accessibility of cotton by alkali treatment is not reflected on color strength upon dyeing with this particular dye.

The decreased color strength by increasing the carboxymethyl content of PCMC is a direct consequence of ionization of the carboxymethyl groups. This ionization brings about a negatively charged fiber surface which repels the similarly charged dye anions. It is the same reason which accounts for the significant decrement in color strength when the five substrates were graft-copolymerized with poly(acrylic acid). As is evident, the color strength decreases drastically by introducing a graft containing ionizable carboxylic groups in the molecular structure of the five substrates. Furthermore, the color strength decreases as the graft yield increases, though most of the decrement in color strength is caused by merely producing a relatively small amount of the graft in the molecular structure of these substrates.

Copolymerization with Styrene

Carboxymethyl Content

Table VI shows the dependence of the graft yield obtained with styrene on the carboxymethyl content of the PCMC. It is seen that for a given set of polymerization conditions (i.e., certain radiation dose, monomer concentration, and polymerization medium) the graft yield increases by increasing the carboxymethyl content within the range studied. Furthermore, the graft yields for PCMCs are higher than the corresponding yields obtained with the unmodified cotton and alkali-treated cotton, in accordance with previous reports,^{14,15} which ascribed this to the presence of the carboxymethyl groups in the molecular structure of cotton. These groups open up the cellulose structure and increases its swellability, thereby enhancing diffusion and adsorption of monomer. Due to its nonionizable nature, styrene, unlike acrylic acid, is not affected by the negatively charged cellulose surfaces brought about by ionization of the carboxymethyl groups. The favorable effect of increased accessibility of cotton grafting by partial carboxymethylation seems to dominate the adverse effect caused by blocking some of the cellulose hydroxyls in case of styrene. This would account for the contradiction observed when the dependence of the graft yields for styrene on the carboxymethyl content is compared with that of acrylic acid discussed before.

It is as well to note that, for a given set of polymerization condition, alkali-treated cotton exhibits higher graft yield than the unmodified cottons (Table VI). This is in accordance with the result of acrylic acid presented previously and could be explained on similar basis.

Styrene Concentration

Table VI shows the effect of styrene concentration on the graft yields when the said five substrates were grafted under different conditions. As is evident, increasing styrene concentration is accompanied by a significant enhancement in the graft yield. This is observed irrespective of the substrate, polymerization medium, and radiation dose used (Table VI). However, the nature of the substrate does affect the magnitude of grafting as already indicated. Polymerization medium and radiation dose exert also a significant influence on the magnitude of grafting, as will be shown later.

TABLE VI
Radiation-Induced Grafting of Styrene onto Unmodified Cotton (Substrate I), Alkali-Treated Cotton (Substrate II),
and Partially Carboxymethylated Cottons (Substrates III-V) under Different Conditions^a

Solvent composition (%)	Styrene monomer (%)	Graft yield (%)									
		Substrate I		Substrate II		Substrate III		Substrate IV		Substrate V	
		a	b	a	b	a	b	a	b	a	b
100(H ₂ O)	5	5.09	6.91	6.57	8.61	8.29	9.55	9.52	10.15	9.28	10.27
	10	7.72	8.79	9.25	9.87	10.34	10.89	11.89	12.67	12.67	12.58
	20	10.01	12.78	12.98	13.17	12.89	13.47	14.81	14.45	14.49	14.60
20/80 (MeOH/H ₂ O)	5	7.11	7.65	6.62	9.13	9.23	10.38	10.10	11.54	10.75	11.75
	10	12.35	13.57	13.50	15.50	15.46	17.20	17.35	15.78	17.50	18.19
	20	17.72	18.40	20.36	21.72	20.76	22.14	22.27	23.97	25.26	26.29
60/40 (MeOH/H ₂ O)	5	8.51	9.60	14.64	16.53	16.32	18.83	24.09	22.78	27.41	26.80
	10	18.15	19.02	28.65	25.37	26.60	28.03	37.82	40.78	40.90	45.70
	20	26.84	30.85	46.65	55.76	52.81	56.62	54.60	56.99	55.01	58.72
100(MeOH)	5	1.35	2.06	1.52	6.52	8.06	10.78	11.15	14.35	13.13	15.12
	10	10.54	16.00	15.77	23.18	23.93	26.90	24.86	37.92	25.61	41.98
	20	32.68	43.79	53.93	57.27	55.53	58.44	56.38	59.78	56.71	60.70

^a a, 0.5 Mrad; b, 1.5 Mrad; substrate III = 15.549 meq —COOH/100 g cellulose; substrate IV = 27.409 meq —COOH/100 g cellulose; substrate V = 46.834 meq —COOH/100 g cellulose.

The higher graft yields obtained upon using increased styrene concentration could be explained on the basis of the gel effect²² as well as greater availability of styrene molecules in the proximity of the cellulose. The gel effect is brought about by the solubility of polystyrene in its own monomer as the styrene concentration increases. As a result, termination of the growing grafted chain radicals by coupling is hindered, thereby leading to increased grafting. Cellulose hydroxyls and cellulose macroradicals formed thereon are immobile. Their reaction with styrene to form ultimately a graft copolymer would certainly depend on the availability of monomer molecules in their vicinity. As expected, the monomer molecules would be more available at higher styrene concentrations and hence increased grafting.

Radiation Dosage

Table VI shows the graft yield obtained when styrene was grafted onto the five substrates in question at two radiation doses, viz., 0.5 and 1.5 Mrad. Obviously, the graft yields at 1.5 Mrad are higher than those at 0.5 Mrad, depending upon the polymerization medium, monomer concentration, and nature of the substrate. The higher graft yields observed at 1.5 Mrad than at 0.5 Mrad could be associated with creation of more free radical sites on the substrate backbone. It is understandable that formation of these macroradicals is a prerequisite for grafting.

Polymerization Medium

Previous studies²³ have dealt with the role of solvents in mutual irradiation grafting of monomers onto cellulose. These studies have disclosed that the presence of solvent brings about a substantially increased grafting level when compared with irradiation of cellulose and monomer alone.

Table VI shows the effect of water/methanol mixtures on the graft yield. It is seen that, for a given radiation dose and monomer concentration, the graft yield obtained with methanol/water mixture at a ratio of 20:80 is much higher than that obtained in the pure aqueous polymerization medium. Further improvement in the graft yield could be achieved upon using methanol/water mixture at a ratio of 60:40 or only methanol, provided that styrene is used at a concentration of 20%. Below this concentration, the graft yields are lower than their corresponding yields for methanol/water mixtures.

The favorable effect of methanol on the graft yield could be associated with the interaction of methanol with both styrene and the activated cellulose, leading to an increment in the accessibility of activated sites to styrene. That is, more free radicals are produced in methanol than in styrene, and the interaction of activated methanol with styrene may have increased the effectiveness (reactivity) of styrene. This situation seems to be valid at all styrene concentrations in methanol/water mixtures and only at the highest styrene concentration (20%) in 100% methanol. Using the latter along with lower concentrations of styrene seems to offset the effectiveness of styrene through abundance of methanol-free radicals, which may participate in termination processes rather than activation.

Moisture Regain and Dyeability of Polystyrene-PCMC Graft Copolymers

Moisture Regain

Table VII shows variations of the moisture regain of the five substrates under investigation with the graft yields. As is evident, the moisture regain decreases as the graft yield increases. This is observed regardless of the substrate used. However, there is a tendency that the decrement in moisture regain by increasing the graft yield is more pronounced in case of PCMCs than unmodified and alkali-treated cottons. This tendency could be associated with differences in nature between these five substrates. Such differences would be reflected on molecular weight and molecular weight distribution of the graft as well as frequency of branching, which, in turn, affect the accessibility of cotton cellulose. At any event, however, the observed lower moisture regain is a direct consequence of the hydrophobic environment brought about by the presence of polystyrene graft in the structure of cellulosic substrate.

Dyeing with Basic Dye

Table VIII shows the color strength, expressed as K/S of the five substrates in question before and after copolymerization with polystyrene when they were dyed with a basic dye, namely, Sandocryl Orange B-3RLE. It is seen that the color strength increases significantly after grafting these substrates with polystyrene. Furthermore, the color strength increases by increasing the graft yield. This indicates that introducing polystyrene chains in the molecular structure of unmodified cotton, alkali-treated cotton, and PCMCs not only enhances the affinity of these substrates for the basic dye but also makes these substrates amenable to dyeing with this dye. Needless to say, the higher color strength observed with PCMCs as compared with unmodified and alkali-treated cottons is due to the presence of the carboxymethyl groups in the PCMCs which enables the latter to react with the basic dye via ionic bonding.

Dyeing with Disperse Dye

Unmodified cotton, alkali-treated cotton, and PCMCs before and after copolymerization with polystyrene were dyed with a disperse dye, namely, Samaron Pink FRL. Results of the color strength obtained are set out in Table IX. It is observed that none of the substrates used acquire practically acceptable color strength, though the latter is higher with unmodified and alkali-treated cottons than PCMCs. On the other hand, all the substrates under investigation have become amenable to dyeing with the said disperse dye after graft copolymerization with polystyrene. Furthermore, the color strength is higher the higher the graft yield. This is observed irrespective of the nature of the substrate before copolymerization. Nature of the substrate before copolymerization seems to have no significant effect on the dyeing properties of the copolymers using the said disperse dye.

Dyeing with Direct Dye

Table X shows the effect of graft copolymerization of the five substrates in question with polystyrene on dyeing with a direct dye, namely, Diamine

TABLE VII
Moisture Regain of Unmodified Cotton (Substrate I), Alkali-Treated Cotton (Substrate II), and Partially Carboxymethylated Cottons (Substrates III-V) before and after Graft Polymerization with Styrene^a

Substrate I	Substrate II		Substrate III		Substrate IV		Substrate V	
	MR	G	MR	G	MR	G	MR	G
0.00	5.974	0.00	7.311	0.00	7.196	0.00	7.690	0.00
8.51	5.098	14.64	5.927	16.32	6.951	24.09	7.792	27.41
18.15	5.055	28.65	5.189	26.60	5.931	37.82	5.416	40.90
26.84	3.613	46.65	3.781	52.81	5.003	54.60	4.634	55.01

^aG = graft yield (%); MR = % moisture regain; substrate III = 15.549 meq —COOH/100 g cellulose; substrate IV = 27.409 meq —COOH/100 g cellulose; substrate V = 46.834 meq —COOH/100 g cellulose.

TABLE VIII
Behavior of Unmodified Cotton, Alkali-Treated Cotton, and Partially Carboxymethylated Cottons before and after Grafting with Styrene towards Dyeing with Basic Dye^a

Substrate I	Substrate II		Substrate III		Substrate IV		Substrate V	
	K/S	G	K/S	G	K/S	G	K/S	G
0.00	0.125	0.00	0.220	0.00	0.527	0.00	0.540	0.00
5.09	1.838	6.57	2.59	8.29	2.52	9.52	2.62	9.28
7.11	1.961	6.62	2.54	9.23	2.85	10.10	3.09	10.75
8.51	2.06	14.64	3.26	16.32	3.68	24.09	3.95	27.41

^aSubstrate I = unmodified cotton; substrate II = alkali-treated cotton; substrates III-V = partially carboxymethylated cottons having 15.549, 27.409, and 46.834 meq —COOH/100 g cellulose, respectively; G, graft yield (meq —COOH/100 g cellulose. Basic dye, Sandocryl Orange B-3RLE; dye concn, 4%; dyeing temp, boiling; duration of dyeing, 60 min; liquor ratio, 1:30.

TABLE IX
Behavior of Unmodified Cotton, Alkali-Treated Cotton, and Partially Carboxymethylated Cottons before and after Grafting with Styrene towards Dyeing with Disperse Dye^a

Substrate I	Substrate II		Substrate III		Substrate IV		Substrate V	
	G	K/S	G	K/S	G	K/S	G	K/S
0.00	0.352	0.00	0.332	0.292	0.00	0.310	0.00	0.295
8.79	1.740	9.87	1.519	1.727	10.98	1.519	12.05	1.542
13.57	1.945	15.50	2.08	2.22	17.20	2.26	15.78	2.26
19.02	1.853	25.37	2.01	2.13	28.03	2.34	40.78	2.48

^aSubstrate I = unmodified cotton; substrate II = alkali-treated cotton; substrates III-V = partially carboxymethylated cottons having 15.549, 27.409, and 46.834 meq -COOH/100 g cellulose, respectively; G, graft yield (%). Disperse dye, Samaron Pink FRL; dye concn, 4%; dyeing temp, 95°C; duration of dyeing, 90 min; liquor ratio, 1:20.

TABLE X
Behavior of Unmodified Cotton, Alkali-Treated Cotton, and Partially Carboxymethylated Cottons before and after Grafting with Styrene towards Dyeing with Direct Dye^a

Substrate I	Substrate II		Substrate III		Substrate IV		Substrate V	
	G	K/S	G	K/S	G	K/S	G	K/S
0.00	1.305	0.00	1.101	0.259	0.00	0.240	0.00	0.216
12.78	1.280	13.17	0.956	1.026	13.47	0.932	14.45	0.863
18.40	1.637	21.72	1.713	1.403	22.14	1.125	23.97	0.908
30.85	2.10	55.76	1.118	1.125	56.62	0.802	56.99	0.618

^aSubstrate I = unmodified cotton; substrate II = alkali-treated cotton; substrates III-V = partially carboxymethylated cottons having 15.549, 27.409, and 46.834 meq -COOH/100 g cellulose; G = graft yield (%). Direct dye, Diamine Supra Turquoise Blue GL; dye concn, 4%; dyeing temp, boiling; duration of dyeing, 100 min; liquor ratio, 1:30.

TABLE XI
 Behavior of Unmodified Cotton, Alkali-Treated Cotton, and Partially Carboxymethylated Cottons before and after Grafting
 with Styrene towards Dyeing with Reactive Dye^a

Substrate I		Substrate II		Substrate III		Substrate IV		Substrate V	
G	K/S	G	K/S	G	K/S	G	K/S	G	K/S
0.00	1.298	0.00	2.012	0.00	0.957	0.00	0.718	0.00	0.672
8.79	1.600	9.87	1.649	10.98	0.912	12.05	0.719	12.58	0.662
13.57	1.580	15.50	1.026	17.20	0.823	15.78	0.701	18.19	0.632
19.02	1.500	25.37	0.932	23.03	0.853	40.78	0.659	45.70	0.622

^aSubstrate I = unmodified cotton; substrate II = alkali-treated cotton; substrates III-V = partially carboxymethylated cottons having 15.549, 27.409, and 46.834 meq -COOH/100 g cellulose, respectively; G = graft yield (%). Reactive dye, Remazol Brilliant Green CB; dye concn, 4%; dyeing temp, 60°C; duration of dyeing, 90 min; liquor ratio, 1:20.

Supra Turquoise Blue GL. It is clear that copolymerization of the unmodified cotton, the alkali-treated cotton, and PCMCs with polystyrene enhances the ability of these substrates to dyeing with the said dye. Moreover, the color strength is determined by the magnitude of grafting regardless of the substrate used. Since there is no reason to believe that these copolymers acquire higher affinity for the dye, the enhanced color strength could be attributed to molecular disruption of the substrate by the graft. Such disruption would provide more resting places for accommodation of the dye molecules and aggregates, thereby improving the color strength.

Dyeing with Reactive Dye

Table XI shows the effect of introduction of polystyrene in the molecular structures of unmodified cotton, alkali-treated cotton, and PCMCs on their ability to dye with a reactive dye, namely, Remazol Brilliant Green CB. Evidently, the color strengths of unmodified and alkali-treated cottons decrease slightly after copolymerization with polystyrene. The same holds true for PCMCs. Blocking some of the cellulose hydroxyls (reactive centers for the dye) by the graft as well as creation of a hydrophobic environment unfavorable for dye affinity would account for this.

CONCLUSIONS

Unmodified cotton (substrate I), alkali-treated cotton (substrate II), and partially carboxymethylated cottons (PCMCs) having 15.459, 27.409, and 46.834 meq—COOH/100 cellulose (substrates III, IV, and V, respectively) were graft copolymerized with either acrylic acid or styrene using different monomer concentrations and radiation doses. Moisture regain and dyeing properties of the copolymers so obtained were also investigated.

Results of copolymerization with acrylic acid led to the following:

1. The graft yields of PCMC are much lower than those of unmodified and alkali-treated cottons; they decrease substantially as the carboxymethyl content of PCMC increases. Most probably the effects of production of negative cellulose surfaces as well as blocking some of the cellulose hydroxyls by the carboxymethyl groups prevail over their effects on opening up the structure of cellulose with increased swellability, thereby decreasing the graftability of PCMC toward the ionizable (negatively charged) acrylic acid monomer.

2. The graft yield increases significantly by increasing acrylic acid concentration irrespective of the substrate used.

3. The graft yield enhances significantly by increasing the radiation dose from 0.5 to 1.5 Mrad regardless of the substrate used. Increasing the radiation dose to 2.0 Mrad is accompanied by further enhancement in the graft yield only in case of unmodified and alkali-treated cottons; the graft yields of PCMCs decrease at 2.0 Mrad.

4. Moisture regain increases by copolymerization of the substrates in question with poly(acrylic acid). However, the magnitude of moisture regain depends upon the percent graft and its form as well as the original nature of the substrate.

5. Copolymerization of the five substrates in question with poly(acrylic acid) enhances their dyeability to basic dye. The opposite holds true for reactive and direct dyes.

Results of copolymerization of the said substrates with styrene led to the following:

6. The graft yield of PCMC is higher than those of unmodified and alkali-treated cottons. It increases by increasing the carboxymethyl content of PCMC.

7. The graft yield increases by increasing styrene concentration from 5 to 20% and radiation dose from 0.5 to 1.5 Mrad regardless of the substrate used.

8. Using water/methanol mixture at a ratio of 20:80 as polymerization medium is advantageous for grafting of styrene onto the substrates in question.

9. Copolymerization with polystyrene reduces the moisture regain irrespective of the substrate used but with the tendency that the original nature of the substrate and the percent graft determine the magnitude of moisture regain.

10. Copolymerization with polystyrene enhances the dyeability of the five substrates in question to basic and direct dyes and make them amenable to the disperse dye but decreases slightly the dyeability to the reactive dye.

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