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Modification of Cotton with Acrylonitrile by Radiation Polymerization

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INTRODUCTION

The use of ionizing radiation to prepare block and graft copolymers of various monomer-polymer combinations has produced a number of modified polymers of interest currently.[1-4] While a considerable amount of literature has been published on the modification of synthetic polymers with this technique, there appears to be much less information available on the modification of natural polymers.

With the recent interest in the modification of cotton fabric with various resins and other chemical treatments, it was decided to investigate the modification of cotton by radiation grafting techniques in an attempt to effect the desirable properties both of cellulose substrate and of synthetic polymers. Of particular interest was the radiation modification of cotton with acrylonitrile, and a comparison with the cyanoethylation of cotton in which acrylonitrile is made to react chemically with the cellulose.[5,6]

Radiation polymerization of acrylonitrile onto cotton yarn has been reported by Arthur et al.[7] who utilized zinc chloride as swelling medium. Pan[8] also attempted graft polymerization of acrylonitrile and other monomers onto cotton yarn. Recently Immergut and Huang[9] reported the modification of cotton by inclusion of monomer in the cellulose followed by gamma radiation, to polymerize the monomer. The grafting of styrene to cellulose by the preirradiation technique has been described by Kobayashi.[23] Some of the recent developments in graft copolymers of cellulose prepared by both radiation and chemical methods have been reviewed by Schwab et al.[24]

Other methods of modifying cellulose have involved the use of ozone or ultraviolet light to initiate the polymerization of monomers for graft copolymers.[10-12] A number of chemical modifications have also been used to form active or functional sites on the cellulose molecule which could be used to form graft copolymers[1,13]

The work reported here is primarily concerned with the radiation of cotton in dilute aqueous solutions of acrylonitrile,[25] to produce a polyacrylonitrile-modified cotton fabric having improved rot and mildew resistance, solvent resistance, and abrasion resistance. The effect of radiation and solution parameters on the extent of modification and on the physical properties of the modified fabric are presented.

EXPERIMENTAL

Radiation Source. Two radiation sources were used, a 2-m.e.v. Van de Graaff generator and a ^{60}Co gamma-ray source. A conveyor system was generally used with the Van de Graaff generator to permit multiple passes under the electron beam. The desired dose and dose rate were obtained by means of changes in beam current and number of passes. Gamma-ray irradiation was carried out by placing the samples at such a distance from the ^{60}Co source as to give the desired dose rate.

Material. Two grades of cotton fabric were used for the majority of the work reported, cotton sheeting No. 111, Daisy Belle cloth, 2.6 oz./sq. yd., and cotton sheeting No. 108, Class C bleached, 2.4 oz./sq. yd. In all cases where not specified, the sheeting No. 108 was used. Other materials are given in the following paragraphs.

Preliminary work indicated that the modification was not significantly affected by washing or scouring the fabric prior to radiation. Sufficient pretreatment of the fabric was simply rinsing in water and drying.

Monomers were distilled prior to use. Aqueous solutions were made with distilled water.

Procedure. In a typical procedure for the modification of cotton fabric with ^{60}Co radiation, the fabric was cut into strips or small sheets suitable for the subsequent determination of physical properties. The samples were rolled and placed in large-mouthed cylindrical jars, covered with the monomer solution, and capped. In most cases the system was purged with nitrogen. The amount of monomer solution was generally controlled to give a monomer cotton weight ratio of about 1:1. The bottles were then irradiated at the desired dose rate for a time sufficient to give the predetermined total dose. After irradiation the samples were washed thoroughly with water for removal of all homopolymer adhering to the surface, dried, and weighed under conditions of the initial weighings. The amount of pickup was calculated as

$$\% \text{ pickup} = [(P_f - P_0)/P_f]100$$

where P_f is the final weight of the fabric after modification and P_0 the initial weight.

The modification made with the Van de Graaff generator was carried out by placing the cotton sheets in glass trays, usually 6 × 8 in. sheets in 8 × 12 × 1 in. trays. The monomer solution was placed in the tray and then covered with a thin foil or plastic sheet, to prevent evaporation. The samples were irradiated with 2 m.e.v. electrons from the generator by being passed under the scanned beam in a conveyor system. The desired dose was obtained by adjusting the beam current and number of passes.

The treatment of the samples after irradiation was the same as described above.

The degree of voltage of the electrons imposes a limitation on the thickness of the sample to be irradiated and on the maximum efficiency of ionization throughout the material being irradiated. For water systems such as used in this work with a 2 m.e.v. source, the thickness of the total sample to be irradiated should be approximately 0.3 in. to give at least 60% of the maximum ionization throughout the sample. With higher-voltage electrons, greater thicknesses can be used.

Physical Properties. The breaking strengths and elongation of the fabric were determined on $1^1/_2 \times 8$ in. strips with an Instron tester under controlled temperature and humidity conditions. Usually, ten samples were tested and averaged for each value reported. Other properties, such as moisture regain, abrasion resistance, etc., were determined with conventional textile testing procedures.

Soil burial evaluation of the fabric was carried out in a tropical chamber in accordance with U. S. Government Specification CCC-T-191b, test method 5762. The soil was of a consistency such that a sample of cotton duck was completely consumed in 7–10 days. The chamber was maintained at 86°F. and a relative humidity of 98%.

Inoculation tests with cellulose-degrading fungi were carried out as given in U. S. Government Spec. CCC-T-1911b, test methods 5760 and 5751.

RESULTS AND DISCUSSION

Effect of Ionizing Radiation on Strength Properties of Cotton Fabric

It has been reported that the predominant effect of radiation on cellulosic materials is one of degradation. Charlesby[14] has studied the viscosity of irradiated cellulose which indicates a degradation with increasing dose. A number of studies have been carried out to determine the loss in physical properties of cotton yarn and fabric as a result of ionizing radiation.[15,17] For the purpose of determining the effect of radiation on the physical properties of the cotton fabric, under conditions similar to those used in the radiation grafting experiments reported here, its breaking strength and elongation was determined as a function of dose and radiation media. In Table I are given the properties of the cotton sheeting after irradiation in air, nitrogen, and water with ^{60}Co gamma-radiation up to 25 Mrads. Below approximately 2 Mrads the properties of the cotton are not significantly affected. The irradiation medium also did not appear to influence the change in properties observed with increasing dose. There appears to be a slight increase in breaking strength with a dose of about 1 Mrad. A similar effect was also noted on irradiated cotton yarn and may be worthy of further investigation.

As a result of the above observations and as insurance against any del-

TABLE I

Effect of Dose and Media on Physical Properties of Irradiated Cotton Sheeting

	Air		Nitrogen		Water	
Dose, Mrad [a]	Breaking strength, lbs.	Elong., %	Breaking strength, lbs.	Elong., %	Breaking strength, lbs.	Elong., %
0	31.3	5.0				
0.5	32.4	5.3	31.4	5.1	36.1	6.0
1.0	32.9	5.4	31.4	5.1	37.3	6.1
5.0	27.2	4.4	28.0	4.6	29.8	5.0
10.0	21.6	3.6	23.3	3.9	24.7	4.4
25.0	15.9	2.8	16.0	2.8	16.6	3.4

[a] ^{60}Co radiation at 0.2 Mrads/hr.

eterious effect of radiation on the cotton, the dose used for most of the radiation modification was generally less than about 2 Mrads.

Mutual Radiation Polymerization Medium for Modification of Cotton

Two types of radiation grafting techniques are commonly employed for grafting of polymers, (*1*) the "mutual" technique, in which the polymer immersed in the monomer solution is subjected to radiation, and (*2*) the preirradiation technique, in which the polymer substrate is irradiated and then placed in the monomer for subsequent polymerization. A comparison of these two processes in the modification of cotton has indicated that only the mutual technique gave satisfactory results under the conditions considered here; very little, if any, modification has been obtained by preirradiation grafting. Irradiation in the presence of air or nitrogen, or in vacuum, did not appear to alter the ability of the cotton to be modified by the preirradiation grafting method.

Early work also showed that the presence of water was necessary to the carrying out of satisfactory radiation modification. This is presumably due in part to the solvating action of the water, which permits uniform wetting of the cellulose by the monomer, and in part to polymerization initiated by the radiolysis products of the medium. Acrylonitrile solutions in such dry solvents as methanol, ethanol, dimethylformamide, and dioxane gave essentially no pickup on cotton from 10% solution at 0.5 Mrads. With a 1:1 water–solvent mixture, modifications of 8–10% were obtained. In 7% aqueous solutions of acrylonitrile (maximum solubility at room temperature) pickups of 8–10% were obtained with very uniform modifications and no evidence of embedded homopolymer.

A recent Russian article has also indicated that the presence of water improved the ^{60}Co radiation grafting of acrylonitrile to cellulose.[18]

The mechanism of the modification of cellulose produced by mutual grafting has not been studied in detail owing to the complexity of the system. The polymerization is probably initiated by radiolysis products of the water and cellulose, resulting in some graft polymerization to the cellulose chain, homopolymer formed within the cellulose structure, and homopolymer formed in the solution phase.

Effect of Dose and Dose Rate on the Radiation Modification of Cotton with Acrylonitrile

The extent to which the cotton is modified will depend in part on the total dose and dose rate of the radiation. In Figure 1 is shown the effect of dose on pickup of acrylonitrile by cotton sheeting from a 7% solution of acrylonitrile. Data are given for both ^{60}Co radiation and high-energy electron radiation. The modification obtained under gamma-irradiation appears to reach a maximum of about 15% at a dose of 1–2 Mrads. The pickup obtained with electron irradiation is considerably lower at the low doses; however, at doses of 5 Mrads and above, the pickups from the two

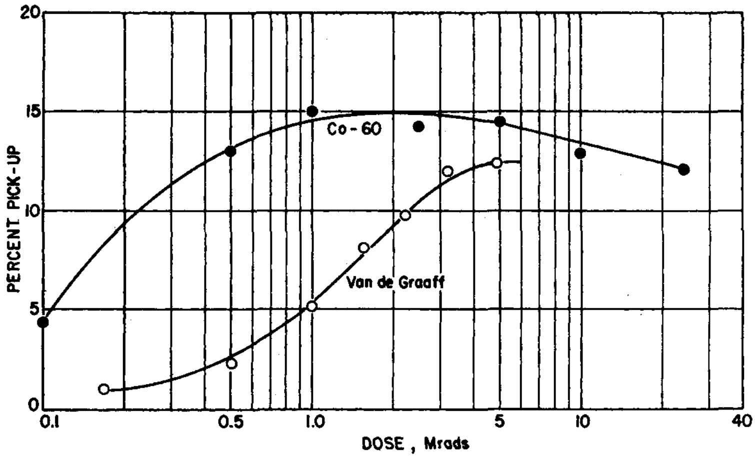

Fig. 1. Effect of dose on pickup of acrylonitrile by cotton.

sources are nearly the same. The difference in pickup observed at the low doses results from the difference in dose rate of the two radiation sources: the ^{60}Co radiation was carried out at 0.5 Mrads/hr., while the electron irradiation probably has an instantaneous dose rate many orders of magnitude higher than this. The dose rate effect appears to decrease with increasing dose. At the higher doses, the radiation time is longer and conversion is higher, which tends to minimize the dose rate effects.

To illustrate the effect of dose rate on the modification of cotton and conversion of monomer to polymer, a series of cotton samples in 7% acrylonitrile solution were irradiated at low dose rates from the Van de Graaff generator. The samples were placed 48 in. below the slit window and irradiated with the unscanned beam. The data are plotted in Figure 2 for a dose rate of 0.5–10 Mrads/hr. at a total dose of 0.5 Mrads. The rate was varied by changing the beam current. The modification is given as per cent conversion of monomer to polymer pickup by the cotton, and for this system is approximately the same as per cent pickup. A rate of about 2 Mrads/hr. and less does not greatly affect the pickup; dose with a rate increasing above 2 Mrad/hr. the pickup decreases nearly linearly with the log of dose rate.

Also shown in Figure 2 is the effect of dose rate on homopolymer formation in the aqueous phase, as well as the total conversion. At the low dose rates the amount of homopolymer formed is approximately twice that present as pickup. With increasing dose rate the homopolymer decreases to a greater extent than the pickup, resulting in a more favorable ratio of pickup-to-homopolymer formation. With the Van de Graaff generator and a scanned beam, giving much higher instantaneous dose rates than indicated in Figure 2, the amount of homopolymer formed can be reduced to less than 10% of the total polymer formed.

In addition to the above dose rate effects, the molecular weight of the

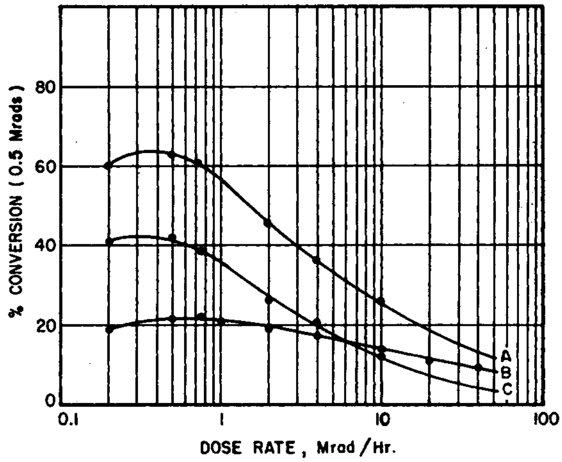

Fig. 2. Effect of dose rate on modification of cotton with acrylonitrile: (*A*) total conversion; (*B*) pickup by cotton; (*C*) homopolymer.

grafted or associated polyacrylonitrile is decreased with increasing dose rate. If we assume the molecular weight of the homopolymer formed during the radiation polymerization to be the same as that present in the cotton, the molecular weight at a dose rate of 0.2 Mrads/hr. is about 150,000, and at 10 Mrads/hr. the molecular weight drops to about 25,000, with a total dose of 0.5 Mrads. The molecular weight of the polymer formed at the maximum dose rate of the Van de Graaff generator was about 10,000. The molecular weights were determined from intrinsic viscosity measurements, dimethylformamide being the solvent.[19] These results are in agreement with those of Dainton[20] in work on radiation polymerization of acrylonitrile in which the chain length decreased with increasing intensity.

Effect of Acrylonitrile Concentration on Pickup

The effect of the acrylonitrile concentration in the water phase on pickup by cotton sheeting on irradiation with high-energy electrons is shown in Figure 3. The amount of solution and cotton weight remained constant; only the amount of acrylonitrile in the aqueous phase was changed. The radiation was carried out at a beam current of 250 μamp with a total dose of 1.6 Mrads. The pickup increased with monomer concentration up to about 7%, which is the maximum solubility of this monomer in water at room temperature. Similar effects were also obtained with ^{60}Co radiation. Higher concentrations could be obtained by using an alcohol–water solution; however, a corresponding increase in pickup was not obtained. The use of pure monomer solution did not appear to give the desired pickup in the fabric but resulted in embedded homopolymer with an undesirable appearance. The presence of water appears to be necessary to give a uniform modification of the fabric.

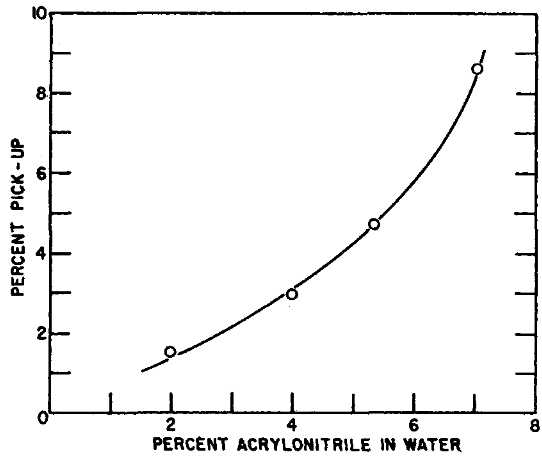

Fig. 3. Effect of acrylonitrile concentration on pickup.

Physical Properties of Cotton Sheeting Modified with Acrylonitrile by Radiation Polymerization

The cotton sheeting that has been modified with acrylonitrile by radiation polymerization with a dose of less than about 2 Mrads has approximately the same strength properties as the original material. The appearance and feel of the material are also not significantly altered with modifications of less than about 15%. Table II lists the breaking strength and elongation of cotton sheeting modified with different per cent pickups of acrylonitrile by radiation polymerization with high-energy electrons at a dose of 1.6 Mrads. The different pickups were obtained by changing the concentration of acrylonitrile in the water phase, as illustrated in Figure 3.

TABLE II
Breaking Strength and Elongation of Modified Cotton Sheeting

Modification[a]	Breaking strength, lbs.	Elong., %
None (control)	38.0	6.8
Irradiated in H_2O	37.4	6.8
Acrylonitrile pickup, %		
2	38.7	6.9
5	37.0	6.5
9	37.3	6.6

[a] Modification with 1.6 Mrads of 2-m.e.v. electrons.

Moisture regain and abrasion resistance were also determined on cotton sheeting at several different levels of acrylonitrile pickup, and were compared with the properties of cyanoethylated cotton. The results given in Table III indicate a moderate increase in abrasion resistance with increasing pickup. A significant improvement is observed at about 17% pickup. Cyanoethylated cotton containing about 11% acrylonitrile, noted for its good abrasion resistance, is considerably better than the radiation-modified material. Moisture regain is decreased by the modification, as one might expect, although still higher than in the cyanoethylated cotton.

TABLE III
Moisture Regain and Abrasion Resistance of Cotton Sheeting Modified with Acrylonitrile

Modification[a]	Taber flex Abrasion, cycles[b]	Moisture regain, %
None (control)	150	6.2
Irradiated (1.6 Mrads)	130	6.7
Acrylonitrile pickup, %		
6.5	165	5.9
8.5	183	5.2
16.8	310	4.8
Cyanoethylated (11% acrylonitrile)	490	3.5

[a] Modified under 2-m.e.v. electron irradiation.
[b] Cycles for 50% destruction; CS-10 abrasive wheel.

The effect of pickup on the per cent crease recovery of the cotton sheeting is given in Table IV. The crease recovery shows a slight increase with increasing pickup, indicating a gradual stiffening of the material.

TABLE IV
Crease Recovery of Cotton Sheeting Modified with Acrylonitrile

Modification[a]	Crease recovery, %
None (control)	37
Irradiated	36
Acrylonitrile pickup, %	
6	42
10	48
Cyanoethylated cotton (10% acrylonitrile)	50

[a] Modified with gamma-rays from ^{60}Co in 7% acrylonitrile solution.

Rot Resistance of Cotton Sheeting Modified with Acrylonitrile by Radiation Polymerization

As a result of the modification of the cotton fabric with acrylonitrile, the rot and mildew resistance of the material is significantly improved. In

Table V is shown the change in physical properties of several modifications as a result of soil burial. The unmodified cotton was completely consumed in less than 2 weeks of exposure. With as little as 2% pickup of acrylonitrile there was observed a significant decrease in degradation, although some holes were present which made physical testing difficult. With 6% and more of acrylonitrile pickup, the samples were in good condition, and the properties after 3 and 6 weeks' burial are indicated in Table V. With 10–14% pickup, even after 9 weeks of exposure the physical properties were in general not less than half of the original strength properties. All the modifications showed an improvement in resistance to soiling. Similar soil burial exposure of modified canvas duck showed excellent resistance to decomposition after 9 weeks.

Figure 4 is a photograph of samples of cotton fabric modified with acrylonitrile after soil burial exposure. The control and irradiated control were completely decomposed in less than 2 weeks of exposure.

Figure 5 shows a photograph of several cotton samples inoculated with cellulose-degrading fungi. Dish A contains samples of unmodified cotton sheeting, a 10% pickup of acrylonitrile by radiation polymerization, and a sample of cyanoethylated cotton containing 12% acrylonitrile. All samples were inoculated with *Aspergillus terreus* and given the same exposure. In dish B are similar samples of cotton and modified cotton inoculated with *Penicillium Chrysogenum*. Figure 5 illustrates the significant effect of acrylonitrile modifications in retarding the growth of cellulose-degrading fungi. In both samples, the cotton control is completely covered with growth while the radiation-modified cotton is completely free of growth. The cyanoethylated cotton also shows good resistance to *Aspergillus terreus*, and is only slightly affected by *Penicillium chrysogenum*.

The rot resistance of cyanoethylated cotton has been extensively studied in both laboratory and field evaluation.[21]

Solubility and Extraction Properties of Cotton Sheeting Modified with Acrylonitrile by Radiation Polymerization

In an attempt to determine the presence of graft copolymer of the cotton and acrylonitrile, the modified fabric was subjected to extractions with dimethylformamide, a solvent for the polyacrylonitrile, and cupriethylenediamine, a solvent for the cotton. In Table VI are listed the effects of dimethylformamide extraction on the removal of the polyacrylonitrile from the cotton. The per cent acrylonitrile pickup is given for before and after extraction with dimethylformamide for a period of 1 week at 50°C. These results indicate that about 80% of the polyacrylonitrile present in the fabric is unextractable and may be present as a graft copolymer or homopolymer held within the cellulose structure. The latter situation may have arisen as a result of the polymerization of the monomer contained in the swollen cellulose substrate effectively entwining the polyacrylonitrile with the cellulose fibrils.

TABLE V
Effect of Soil Burial on Physical Properties of Cotton Sheeting Modified with Acrylonitrile by Radiation Polymerization

	Initial properties		After 3 weeks		After 6 weeks	
Modification	Breaking strength, lbs.	Elong., %	Breaking strength, lbs.	Elong., %	Breaking strength, lbs.	Elong., %
Control	31.1	5.0	Decom-posed			
Acrylonitrile pickup, %						
6	32.8	4.9	21.5	3.8	[a]	
10	37.6	5.5	26.8	4.5	[a]	
14	36.6	5.5	32.9	5.4	23.3	4.2

[a] Sample intact except for a few small areas of degradation.

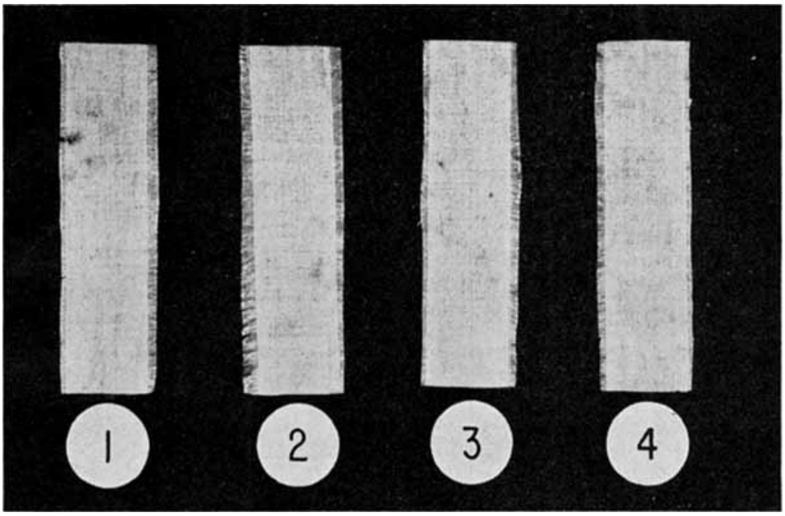

Fig. 4. Samples of acrylonitrile-modified cotton after soil burial: (*1*) 0.5% pickup, 3-week burial; (*2*) 10% pickup, 3-week burial; (*3*) 14% pickup, 3-week burial; (*4*) 14% pickup, 6-week burial.

TABLE VI
Extraction of Acrylonitrile Modified Cotton Sheeting with Dimethylformamide

% Acrylonitrile modification, initial	% Acrylonitrile modification after extraction[a]
10	7.9
12	8.4
16.8	13.9
20.4 (No. 10 canvas duck)	17.8

[a] One week at 50°C.; corrected for weight loss of unmodified sheeting for same extraction conditions (0.7%).

The effect of the acrylonitrile modification on the solubility of the cellulose was carried out according to the method described by Schreiber,[22] except that cupriethylenediamine was the solvent instead of cuprammonium hydroxide. Table VII lists the per cent of the cotton sample soluble in the solvent when modified with different amounts of acrylonitrile. A cyanoethylated cotton sample is also included for comparison. The solubility of the modified cotton decreases as the acrylonitrile content increases. The insoluble matter appears to consist of about 3 to 5 times the weight increase due to the acrylonitrile. The controls and cyanoethylated cotton are considerably more soluble than the radiation-modified material. The comments given concerning the solubility in dimethylformamide are also applicable to the results obtained with cupriethylenediamine, in that

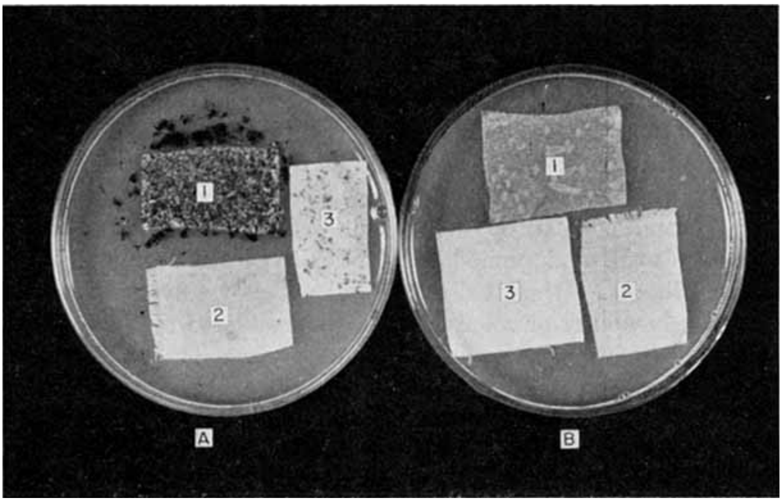

Fig. 5. Cotton samples inoculated with cellulose-degrading fungi: (*1*) cotton control; (*2*) cotton modified with 10% acrylonitrile by radiation polymerization; (*3*) cyanoethylated cotton, 12% acrylonitrile.

TABLE VII
Solubility of Acrylonitrile-Modified Cotton Sheeting in Cupriethylenediamine

Modification	% Soluble [b]
Control	92.4
Control (Irradiated)	95
Acrylonitrile pickup, %	
6	69
11	62
16	49
10 [a]	45
Cyanoethylated cotton (11% acrylonitrile)	97

[a] Polymerization under high-energy electrons; others were carried out under gamma-rays (^{60}Co).
[b] Cupriethylenediamine (0.5*M* in copper) procedure.[22]

either a graft copolymer or entrapping of homopolymer would give the result noted in Table VII.

An attempt was made to carry out acetylation of the modified cotton to determine whether the hydroxyl groups were affected by the radiation polymerization process. The degree of substitution was, in general, reduced as a result of the modification to values of 2.3–2.5, with a value of about 3 for the unmodified material. Radiation alone reduced the degree of substitution to 2.8 at 0.5 Mrads. Since the modified cotton is considerably less soluble in the acetylation medium, the availability of the hydroxyl groups to the acetylating agent may be considerably reduced and result in a lower degree of acetylation.

Dyeability of Acrylonitrile-Modified Cotton

Dyeing of the modified fabric was carried out to determine the homogeneity of the modification and to determine in qualitative manner any large effects the modification may have on the dyeability of the fabric.

The modified fabric was treated with: a direct dye, Calcomine Blue R; a basic dye, Calcozine Violet; an acid dye, Orange II and Calcosyn Brilliant Scarlet. Visual comparisons were made between the modified fabric, irradiated controls, and unmodified fabric, dyed with these dyes under similar conditions. Irradiated cotton did not show any significant difference in the dyeability or color from the nonirradiated material. In some cases a very slight reduction in color intensity was observed with the irradiated fabric. At a 10% acrylonitrile pickup, the color intensity was greater than that of the control for the various dyes considered. The greatest effects were observed with acid and basic dyes. The modified fabric dyed uniformly, indicating that the fabric was very uniformly modified with the polyacrylonitrile. Several samples of modified sheeting containing imbedded homopolymer on the surface gave spotted nonuniform dyeing. These samples were obtained from modifications using pure monomer resulting in considerable homopolymer formation on the surface of the fabric.

Modification of Cotton Yarn and Other Fabrics with Acrylonitrile by Radiation Polymerization

The majority of the work reported here was concerned with the modification of cotton sheeting, although other types of cotton fabric, yarn, and blends can also be modified with acrylonitrile by a similar technique and many synthetic fabrics also appear to be easily modified under the same conditions. To illustrate the extent of modification produced on other types of fabric, the pickup obtained under similar conditions with the use of 7% acrylonitrile–water solutions is given in Table VIII; all modifications were carried out under electron irradiation from the Van de Graaff gener-

TABLE VIII
Pickup of Acrylonitrile by Various Fabrics Under Ionizing Radiation
Radiation of fabric carried out in 7% acrylonitrile solution

Fabric	Dose, Mrads	Beam current, μamp	Pickup, %
10-oz. cotton duck	3.0	246	10
Cheesecloth	1.5	200	10
Rayon	1.6	246	9
Wool	1.6	246	6
Cotton/Saran	1.6	246	12
Dynel	1.6	246	5
Nylon	1.6	246	10

ator at the dose and beam current given. The cotton duck requires a higher dose for pickups comparable to those of the cotton fabric, while cheesecloth is modified to about the same extent as cotton sheeting under similar conditions.

Cotton yarn also has been modified with acrylonitrile by a similar radiation polymerization. In general, the conditions and technique described for the cotton fabric are applicable to the modification of yarn. Skeins or holders containing the yarn were irradiated in the monomer solution. Typical results of the modification of cotton yarn No. 8.5/1 by radiation in 7% acrylonitrile–water solution with high-energy electrons is given in Table IX. The effect of dose on pickup of acrylonitrile and the resulting physical properties are given. The breaking strength and elongation are not greatly affected until a dose of more than about 2 Mrads has been reached. The effect of radiation and solution parameters on the modification of the yarn are similar to that found with sheeting.

TABLE IX
Modification of Cotton Yarn[a] with Acrylonitrile under Ionizing Radiation

Dose, Mrads[b]	Pickup, %	Breaking strength, g.	Elong., %
0.0	0	1130	6.2
0.4	1.2	1140	4.9
0.8	4.0	1155	4.7
1.2	6.1	1000	4.2
2.0	12	980	4.0
2.8	16	625	4.0

[a] Cotton yarn No. 8.5/1 in 7% aqueous acrylonitrile.
[b] Beam current, 246 μamp.

Modification of Cotton with Monomers Other than Acrylonitrile

It is possible to modify cotton with other radiation-polymerizable monomers by techniques similar to those used for the acrylonitrile modifications. For water-insoluble monomers, alcohol–water mixtures are effective in giving sufficient solubility for uniform modification. In Table X is listed a number of monomers and the resulting pickup by cotton sheeting. No complete evaluation has been made of these modifications; however, the relative reactivity of the various monomers in the modification of cotton was thought to be of sufficient interest to be included here.

The modification of cotton by acrylic acid resulted in an interesting material. When dry, the modified fabric shrinks but when wet with water it stretches and is somewhat elastic. The modified fabric also has a high affinity for copper ions and can be used to separate them from solution. The copper can subsequently be recovered from the cotton by an acid wash.

TABLE X
Modification of Cotton with Monomers Other than Acrylonitrile

Monomer	Concn., %	Radiation,[a] Mrads	Pickup, %
Styrene	10 in H_2O/MeOH	V.G., 1.5	1
Styrene	5 in H_2O/MeOH	^{60}Co, 0.5	24
Vinyl acetate	10 in H_2O	V.G., 1.5	3
Acrylic acid	20 in H_2O	V.G., 1.5	33
Acrylic acid	5 in H_2O	V.G., 1.5	8
Methyl isopropenyl ketone	10 in H_2O	V.G., 1.5	3
Methyl isopropenyl ketone	5 in H_2O	^{60}Co, 0.5	30
Ethyl acrylate	5 in H_2O/MeOH	^{60}Co, 0.5	9
Methyl methacrylate	5 in H_2O/MeOH	^{60}Co, 0.5	10

[a] V.G. = Van de Graaff radiation.

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Synopsis

The modification of cellulose (cotton fabric or yarn) has been carried out with acrylonitrile under ionizing radiation. Irradiation of the cotton in aqueous acrylonitrile solutions with gamma- or electron radiation produces a modified cotton with improved rot and mildew resistance similar to that of cyanoethylated cotton. Strength properties are not significantly affected, provided the radiation dose is less than 5 Mrads. The pickup of acrylonitrile by cotton depends on monomer concentration, dose, and dose rate. It was also observed that water was necessary to give the desired uniform modification. Doses of 0.5–1.5 Mrads produced modifications in the range of 8–15%. Dose rate effects are present at low doses, where pickup decreases with increasing dose rate. Above 5 Mrads, dose rate effects are minimized. Although the data do not show whether actual grafting is occurring with the cellulose, either directly from radiation or through oxidative products formed in the water, or whether the cellulose is being swollen with the aqueous monomer solution which is then intimately polymerized by radiation fragments resulting from the radiation, it is apparent that polymer is formed uniformly upon or within the cellulose structure and that it cannot be removed by solvent extraction. As a result of the modification, the solubility of the cellulose in its usual solvents is decreased and other properties are modified, especially rot resistance, which is improved. Modification of cotton with monomers other than acrylonitrile has also been considered. Pickups of styrene, acrylic acid, methyl isopropenyl ketone, ethyl acrylate, and methyl methacrylate have been obtained from methanol–water solutions.

Résumé

La transformation de la cellulose en tissu ou fil de coton a été effectuée au moyen de l'acrylonitrile avec rayonnement ionisant. L'irradiation du coton dans des solutions aqueuses d'acrylonitrile au moyen d'un rayonnement gamma ou électronique produit un coton modifié possédant une resistance accrue à la pourriture et à l'humidité semblable à celle du coton cyanoéthylé. Les propriétés de résistance ne sont pas affectées de façon significative pourvu que la dose de radiation soit inférieure à 5 Mrads. La fixation d'acrylonitrile par le coton dépend de la concentration en monomère, de la dose de radiation et de la vitesse d'application de cette dose. On a aussi observé que l'eau était nécessaire pour donner la transformation uniforme désirée. Des doses de 0.5 à 1,5 Mrads produisent des transformation de l'ordre de 8 à 15%. Les effets de la vitesse d'application de la dose se manifestent à de faibles doses, où la fixation décroît avec une vitesse d'application croissante. Au-dessus de 5 Mrads, les effets de vitesse de dose sont réduits. Bien que les résultats ne montrent pas si le greffage actual a lieu avec la cellulose, produit soit directement par radiation ou par l'intermédiaire des produits d'oxydation formés dans l'eau, ou si la cellulose a été gonflée par la solution aqueuse de monomère qui est alors polymérisée par des fragments résultant de la radiation, il est apparent que le polymere se forme uniformément sur ou à l'intérieur de la structure cellulosique, polymère qui ne peut être enlevé par extraction par solvant. Il résulte de cette modification que la solubilité de la cellulose dans ses solvents usuels décroît et que d'autres propriétés sont modifiées, spécialement une amélioration dans la résistance à la pourriture. La transformation du coton avec des monomères autres que l'acrylonitrile a aussi été considérée. Les fixations de styrène, d'acide acrylique, de méthyle isopropényle-cétone, d'acrylate d'éthyle et de méthacrylate de méthyle ont été obtenues à partir de solutions eau–méthanol.

Zusammenfassung

Die Modifizierung von Cellulose in Form von Baumwollgewebe oder Garn wurde mit Acrylnitril unter ionisierender Bestrahlung durchgeführt. Bestrahlung der Baumwolle in wässriger Acrylnitrillösung mit γ- oder Elektronenstrahlung liefert eine modifizierte Baumwolle mit verbesserter Verrottungs- und Stockfleckenbeständigkeit, ähnlich wie cyanäthylierte Baumwolle. Die Festigkeitseigenschaften werden bei Strahlungsdosen kleiner als 5 Mrad nicht wesentlich beeinflusst. Die Acrylnitrilaufnahme durch Baumwolle hängt von Monomerkonzentration, Dosis und Dosisgeschwindigkeit ab. Weiters wurde beobachtet, dass die Gegenwart von Wasser zur Erreichung der erwünschten, einheitlichen Modifizierung notwendig ist. Dosen von 0,5–1,5 Mrad ergaben eine Modifizierung im Betrag von 8–15%. Ein Einfluss der Dosisgeschwindigkeit ist bei niedrigen Dosen vorhanden, wo die Aufnahme mit steigender Dosisgeschwindigkeit abnimmt. Oberhalb 5 Mrad bestehen nur minimale Einflüsse der Dosisgeschwindigkeit. Obwohl die Ergebnisse nicht erkennen lassen, ob tatsächlich eine Aufpfropfung auf Cellulose, entweder direkt durch die Strahlung oder durch im Wasser gebildete Oxydationsprodukte, auftritt oder ob die Cellulose in der wässrigen Monomerlösung quillt und diese dann durch strahlungserzeugte Bruchstücke im Innern zur Polymerisation angeregt wird, zeigt es sich, dass das Polymere einheitlich auf oder innerhalb der Cellulosestruktur gebildet wird und durch Lösungsmittelextraktion nicht entfernt werden kann. Als Folge der Modifizierung wird die Löslinchkeit der Cellulose in den üblichen Lösungsmitteln herabgesetzt und andere Eigenschaften werden verändert, besonders tritt eine Verbesserung der Verrottungsbeständigkeit ein. Auch die Modifizierung von Baumwolle mit anderen Monomeren als Acrylnitril wurde in Betracht gezogen. Eine Aufnahme von Styrol, Acrylsäure, Methylisopropenylketon, Äthylacrylat und Methylmethacrylat aus Methanol–Wasserlösungen konnte nachgewiesen werden.

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