Grafting of Polyacrylonitrile in Cotton Fabrics*

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INTRODUCTION

The polymerization of vinyl monomers in the presence of textile materials has been studied by several workers.[1-6] Geacintov et al.[7,8] postulated graft formation of polyacrylonitrile (PAN) with cellulose. In the method of polymerization used by them, cellulose treated with acrylonitrile was irradiated with ultraviolet light in the presence of an anthraquinone vat dye sensitizer. They presented evidence in support of their postulate by a study of the solubility of the graft and of a physical mixture of cellulose and polyacrylonitrile, in such solvents as cuprammonium hydroxide (cuoxam) and dimethylformamide (DMF). They also suggested the formation of active centers on the cellulose backbone where the polymer chain would attach itself or grow. Faraone et al.[9] studied the infrared spectra of cellulose acetate derivatives subjected to styrene polymerization and obtained evidence of a graft formation of the two. Das Gupta et al.[10] similarly obtained grafts of polystyrene with nylon fabrics by the use of gamma radiation, and found improvement in certain of the physical properties of the treated fabrics, such as water spray resistance, extensibility, and stretching strength. They also supported the formation of nylon–styrene grafts on the basis of infrared spectroscopic study of the polymerized samples. Demint et al.[11] carried out radiation-induced polymerizations of acrylonitrile with cyanoethylated cotton and found that the extent of interaction between the cotton and acrylonitrile is dependent upon the degree of substitution of the former and upon the dosages of irradiation. They also postulated formation of a graft. Azimov et al.[12] polymerized styrene and acrylonitrile with silk and Kapron by using gamma radiations, and obtained infrared spectra of the irradiated samples which indicated, for treatment with acrylonitrile, the introduction of macromolecules containing —C≡N groups in the silk and Kapron. Usmanov et al.[13]

carried out the polymerization of acrylonitrile and styrene with cotton and viscose cords, employing both physical and chemical methods, viz., (a) initiation through an ozone–oxygen mixture and (b) use of gamma radiations. They found that, in the case of acrylonitrile, graft formation takes place only when the solvent for acrylonitrile is capable of wetting the cellulose well. By hydrolysis of the cellulose–PAN graft in acid media, to break down the cellulose to a mono sugar, they isolated the grafted polymer chains of acrylonitrile and measured their degree of polymerization viscometrically. Kamogawa and Sekiya[14] polymerized acrylamide in cotton fabrics, using cerric ammonium nitrate as catalyst. They obtained graft copolymers which were further treated with crosslinking agents such as formalin in the presence of an acid catalyst; fabrics thus treated showed an improvement in crease recovery. They discussed the ways in which crosslinks would be introduced into the modified cellulose chains, thus supporting the formation of cellulose–PAN grafts.

We have reported earlier[6] a simple method of polymerizing acrylonitrile in cellulosic materials in the presence of potassium persulphate, the polymerization being effected thermally. The present work was conducted mainly (a) to study the effect of such variables as material/liquor ratios and monomer concentrations on the polymer yields on cotton fabrics, with the above method, and (b) to obtain experimental evidence of the formation of cellulose–PAN grafts.

Rot resistance properties of cotton fabrics containing PAN were also studied.

EXPERIMENTAL

Materials

Acrylonitrile monomer (BASF) was used after washing with mild acid and alkali to remove any inhibitors present. Potassium persulphate (Meck), sodium thiosulphate (M & B), copper sulfate (British Drug Houses), and dimethylformamide (Riedel-De-Haen, A.G.) were all B.P.-quality laboratory reagents. Cuoxam solution was in accordance with ASTM specification D539-53 (15 g. of copper and 200 g. of ammonia per liter). Scoured, bleached, and mercerized 38's/38's, cotton fabrics, having 100 ends and 80 picks per inch were used. Unless otherwise specified, all concentrations are expressed as per cent weight per volume.

Effect of Copper Traces on Acrylonitrile Polymerization

For studying the effect of copper traces on acrylonitrile polymerization the following composition was used:

Monomer	5% on $K_2S_2O_8$ (v/v)
$K_2S_2O_8$	0.2%
Material/liquor	1:50
$1N H_2SO_4$	1 ml./100 ml. $K_2S_2O_8$.

Cotton fabrics were first padded with a 2.0% sodium thiosulfate solution at approximately 100% wet pickup and dried. Traces of copper sulfate were added to the reducing solution in one set of experiments, while in the other set no such addition was made. Polymerizations were carried out in stoppered Pyrex conical flasks at 65–70°C. for 20 min. At the end the treated fabrics were given a thorough rinsing followed with soaping

TABLE I

N, %	PAN calcd. from N, %	PAN by wt. increase, %
0.65	2.46	2.40
1.40	5.29	5.40
26.00	98.43	100.00

at boil, to remove loosely held polymer particles, and were finally washed and dried. The polymer in fabrics was determined by weighing the samples conditioned before and after polymerization at 65 ± 2% R.H. and 80°F. That the above-described method gives satisfactory polymer estimates is shown by nitrogen analysis of the fabrics by the Kjeldahl method, results of which are given in Table I.

Effect of Processing Variables on Acrylonitrile Polymerization

For studying the effects of (a) liquor ratios, (b) monomer concentration, and (c) initiator concentration on the polymer yields on fabrics, a small jigger was fabricated to accommodate approximately 0.5 l. of reaction mixture. Cotton fabrics in the form of tapes 3 in. wide were used and the method of polymerization was similar to that described above, in which copper sulfate was added. The fabrics were completely submerged in the reaction mixture. The jigger was closed and transferred to a thermostat maintained at 65°C. The fabric was rolled to and fro on the jigger rollers for about 20 min., when maximum polymer yields were obtained. Details of other experimental conditions are as follows.

1. Liquor ratio varying from 50:1 up to 8:1, and initiator concentration kept at 0.2%; AN monomer varying from 50 ml. for 1:50 material/liquor ratio up to 30 ml. for 1:8 material/liquor ratio.

2. Material/liquor ratio kept at 1:8 and initiator concentration at 1.0%, AN monomer varying from 22 ml. up to 30 ml.

3. Three sets of polymerizations were conducted for studying effect of initiator concentration on polymer yields:

Set 1	Monomer	27 ml.
	Material/liquor	1:8
	$K_2S_2O_8$	0.2–1.0%

Set 2	Monomer	24 ml.
	Material/liquor	1:8
	$K_2S_2O_2$	1.0–2.0%
Set 3	Monomer	22 ml.
	Material/liquor	1:8
	$K_2S_2O_8$	1.0–2.0%

During the polymerizations the air space in the reaction vessel was kept to a minimum and precautions were taken to keep the fabrics well immersed in the liquor.

Testing

Dry crease recoveries were measured on a Monsanto wrinkle recovery tester according to the ASTM D1295-53T method, while wet crease recoveries were measured according to a method described by Lawrence and Phillips.[15] Tensile strength was measured on an Instron tensile tester according to the ASTM D39-59 method. Tear strength was measured on an Elmendorff falling pendulum type of apparatus according to the ASTM D1424-59T method. For testing the resistance to microbial degradation of the treated fabrics, a modified soil burial method described by Lloyd[16] was used. The soiling composition was a mixture of cultivated manure of high bacterial content and black clay 1:1 moistened to a thick slurry. The burial periods ranged from 6 days to 3 weeks. At the end the samples were tested for tensile strength.

RESULTS AND DISCUSSION

Presence of Copper Sulfate

Figure 1 shows the effect of polymerizing acrylonitrile with and without addition of copper sulfate traces in the reaction mixture. Bacon[17a] has reported that traces of certain metal ions, especially copper, greatly accelerate the polymerization of acrylonitrile. He has also mentioned that the time of polymerization can be reduced substantially by using a redox system. We found that in the absence of any reducing agent, the induction periods were 15–20 min. hence the reaction took nearly an hour for completion. Use of sodium thiosulfate as a reducing agent accelerated the reaction rate considerably, so that only 15–20 min. were required for completion. The presence of copper sulfate in the reducing solution (a) yielded higher polymer contents, of the fabrics and (b) reduced the induction period further, from 7 min. to approximately 3 min., confirming Bacon's observations.

In the absence of a reducing agent the formation of homopolymer was visible to a considerable extent. When the fabrics were padded with the reducing solution it was observed that the polymerization was mainly initiated in the fabrics and comparatively lesser quantities of homopolymer
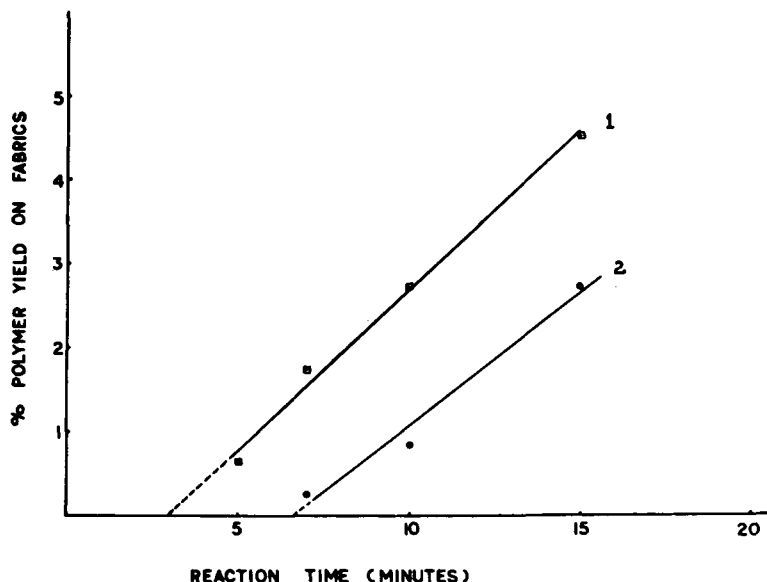
Fig. 1. Effect of copper sulfate traces on AN polymerization. Material/liquor ratio 1:50, $K_2S_2O_8$ 0.2%, AN on $K_2S_2O_8$ 5% (v/v), sodium thiosulfate 2%, temperature 65°C.: (1) with copper sulfate; (2) without copper sulfate.

were visible. Addition of copper sulfate reduced the homopolymer formation still further, yielding fabrics with higher polymer add-ons.

MONOMER CONCENTRATION

In Figures 2 and 3, and in Table II are shown some results of the effect of increasing monomer concentrations, higher initiator concentrations, and lower liquor ratios on the polymer yield on fabrics. These results agree in general with the expected behavior of the polymerization process. In studying the effect of short liquor ratios, it is observed that a reduction in monomer quantity from 50 ml. (1:50 material/liquor) up to 30 ml. (1:8 material/liquor) still gave increased polymer yields in the fabrics.

TABLE II
Effect of Liquor Ratio on AN Polymerization

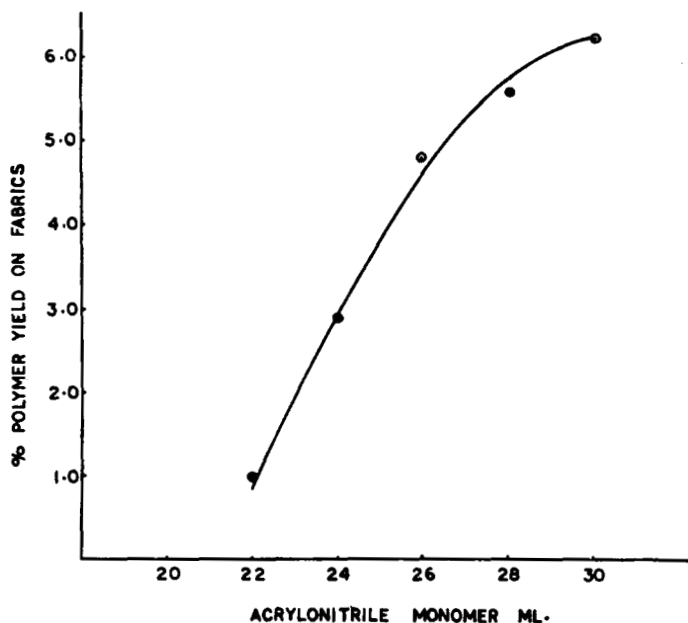| Exptl. cond.	Liquor ratio	AN, ml.	Polymer yield, %
0.2% $K_2S_2O_8$	1:50	50	3.4
2.0% sodium			
thiosulfate + copper sulfate	1:35	40	4.0
65–70°C.			
20 min.	1:15	30	5.4
	1:10	30	5.9
	1:8	30	6.0

Fig. 2. Effect of monomer concentration on AN polymerization.   Material/liquor ratio 1:8, $K_2S_2O_8$, 1.0%, sodium thiosulfate 2.0%, + copper sulfate.   Reaction time 20 min., at 65°C.
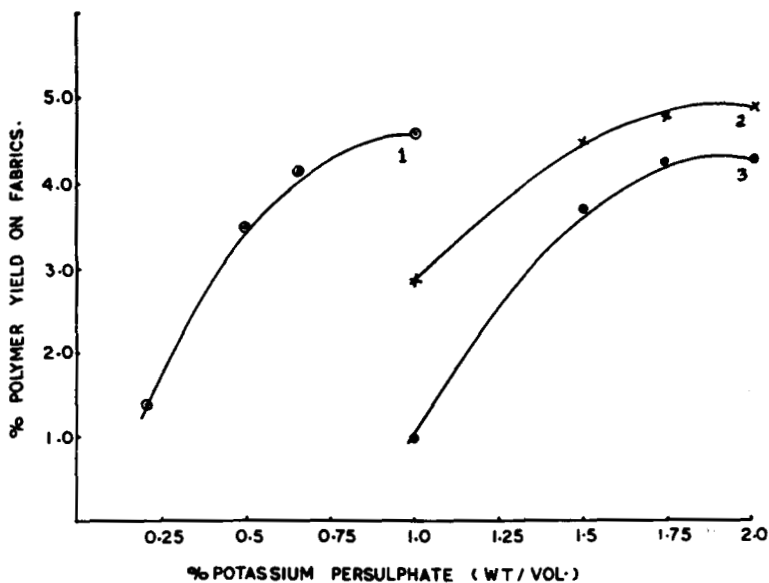

Fig. 3. Effect of initiator concentration on AN polymerization.   Material/liquor ratio 1:8, sodium thiosulfate 2.0%, + copper sulphate.   Reaction time 20 min., at 65°C. AN monomer, ml.: (*1*) 27; (*2*) 24; (*3*) 22.

Resistance of Fabrics Containing PAN to Microbial Degradation

Figure 4 shows the per cent loss in tensile strength of the samples after soil burial. Data for three sets of samples are shown: (1) samples containing 5–8% PAN obtained with 0.2% $K_2S_2O_8$ and, (2) and (3), samples containing 2–3% PAN obtained with 2.0% $K_2S_2O_8$. All the treated samples show considerable resistance to microbial degradation. Using higher initiator concentrations, one would expect more polymer chains to be formed, but of shorter length. Thus, as against treatments involving low initiator concentrations, protection against microbial degradation should be obtained at lower levels of polymer add-ons. This, in fact, is observed experimentally.
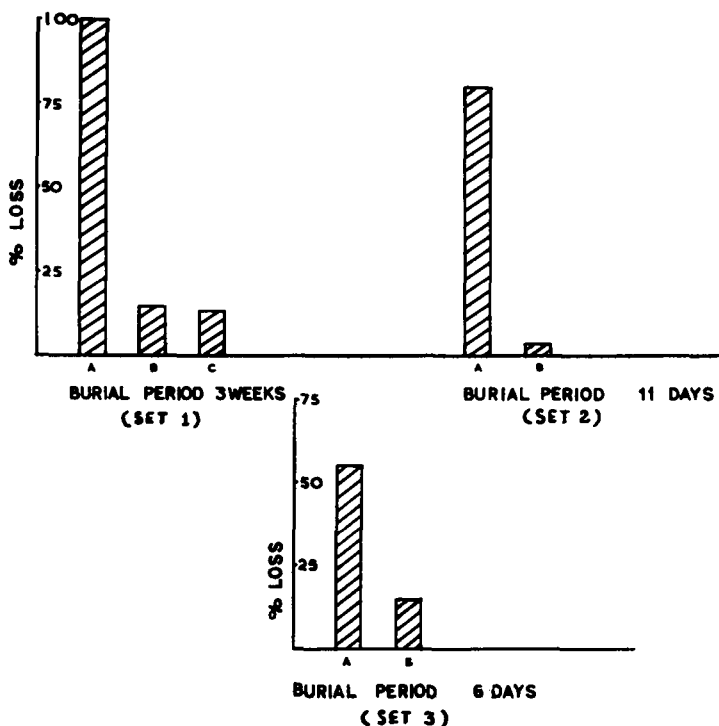

Fig. 4. Resistance of fabrics containing PAN to microbial degradation. Set 1, $K_2S_2O_8$ 0.2%: (A) blank; (B) 5.4% PAN; (C) 8.0% PAN. Set 2, $K_2S_2O_8$ 2.0%: (A) blank; (B) 3.0% PAN. Set 3, $K_2S_2O_8$ 2.0%: (A) blank; (B) 2.0% PAN.

Mechanism of Grafting

Solubility in Acetone and DMF

With a view to examining the presence of a PAN–cellulose graft, the solubility behavior of a cellulose acetate–PAN system in acetone and DMF was studied.

Secondary cellulose acetate in the form of filament yarn was used. It was found that polymerization from aqueous solutions gave poor yield of the polymer on cellulose acetate, probably because of the lack of swelling of the latter. However, when a mixture (1:1) of DMF and 0.2% persulfate solution was used, good yields of polymer on cellulose acetate could be obtained. The resulting material was shaken with a mixture of acetone and DMF (3:2) and the soluble fraction recovered by precipitation with water. It was dried, redissolved in a small quantity of DMF, and precipitated by addition of an excess of acetone, to remove any cellulose acetate still present, and dried. This fraction gave an acetyl content of 3.2, corresponding to about 7% cellulose acetate. Since the polymerization was effected with a DMF–aqueous $K_2S_2O_8$ mixture, the cellulose acetate was swollen considerably, giving very high polymer yields. The isolated graft thus contained a large excess of PAN. Also, since the exact degree of substitution of cellulose acetate was unknown, no quantitative significance was attached to this value of acetyl content. However, the presence of cellulose acetate in this fraction strongly supports the postulate of its existence as a graft with PAN. This is further confirmed by nitrogen estimation of this fraction which gave a lower value, viz., 23.6% N (that for PAN by the same method being 26.0%), corresponding to about 92% PAN in the isolated fraction.

Insolubility in Cuoxam

Another important property of cellulose subjected to acrylonitrile polymerization is its insolubility in cuoxam solution. If, as is postulated by Geacintov et al.,[7,8] polymer chains are grafted to cellulose chains at the active sites, the resultant graft would exhibit insolubility in solvents for both cellulose and PAN. This, in fact, has been observed to be true, since the polymer in the cellulose samples cannot be fully extracted with DMF even on repeated extractions. However, the fact that cellulose and PAN in the treated samples cannot be separated by physical means such as solution is not conclusive evidence of grafting, since insolubility can be attributed to a mechanical hindrance of swelling. It is, however, possible to isolate the cuoxam-insoluble fraction and study the ratio of cellulose to PAN in it. Assuming graft formation between the two, it could be argued that under identical conditions of the polymerization reaction (i.e., where temperature, initiator concentration, etc., remain unaltered) the ratio of the number of PAN chains grafted to cellulose chains would remain more or less constant even at different polymer add-ons. As the polymer content of the sample increased, the number of cellulose chains forming a graft would also proportionately increase.

Mercerized cotton yarn and cellophane were polymerized with acrylonitrile and fully extracted with DMF overnight at room temperature; the polymer still remaining in the samples was estimated by weighing. The samples were then shaken overnight with cuoxam solution with exclusion of air, filtered through a No. 3 sintered-glass crucible, washed successively

with fresh cuoxam, ammonia, acetic acid, water, and acetone, and dried and weighed. The known amount of polymer was subtracted from the weight of the residue, and the ratio of cellulose to polymer determined. These results are presented in Table III.

TABLE III
Cuprammonium Insolubility of PAN–Cellulose System

PAN on cell. wt., %	PAN on tot. wt. %	Insol. on tot. wt., %	Cell PAN ratio
Set 1, Cellophane, Initiator Concn. 0.2%			
28	21.8	33.0	0.51
36	26.5	40.0	0.51
45	31.0	46.5	0.50
58	36.7	56.0	0.52
122	55.0	82.5	0.50
Set 2, Mercerized Cotton, Initiator Concn. 0.2%			
10	9.1	38.5	3.2
13.5	12.0	48.0	3.0
18	15.2	62.5	3.1
22	18.0	72.0	3.0
26.5	21.0	84.0	3.0
29.5	22.8	89.0	2.9
Set 3, Mercerized Cotton, Initiator Concn. 0.05%			
15	13.0	34.0	1.6
27	21.2	57.0	1.7
54	35.0	87.5	1.5

It is seen clearly that a change in the initiator concentration affects the ratio. This is quite reasonable since the average molecular weight of the polymer chains would vary inversely with the initiator concentration. The substrates used in the three sets (viz., mercerized cotton and cellophane) would also change this ratio on account of their having different molecular weights.

From these results, graft formation between PAN and cellulose is favored for two reasons: (a) the cuoxam-insoluble fraction in all the cases contains a certain proportion of undissolved cellulose, and (b) a constant relation exists between the PAN and the cellulose in this fraction over a wide range of polymer add-ons.

Introducing Crosslinks in the Cellulose–PAN System

It is known that the —C≡N group in the PAN would undergo modification with various chemical treatments. Of these, the saponification reaction with alkali was of special interest to us, since it was thought that the —CONH$_2$ groups formed after saponification could be further modified to the —CO—NH—CH$_2$OH groups by an alkaline formaldehyde treatment. These groups are known to react with cellulose in the presence of an acid catalyst. Assuming, therefore, that a polymer chain is grafted at one end

to a cellulose chain, it should be possible to introduce crosslinks by making some of the —CO—NH—CH$_2$OH groups react with adjoining cellulose chains, by means of an acid curing treatment.   Such a treatment would be expected to produce profound changes in the wrinkle recovery properties of the fabric and provide experimental evidence of grafting.

Fabrics containing from 1.5% to 7.3% PAN obtained with different initiator concentrations were refluxed for approximately $^1/_2$ hr. with sodium hydroxide of various concentrations.   The samples turned brick red, indicating saponification of the —C≡N groups to —CONH$_2$ groups.
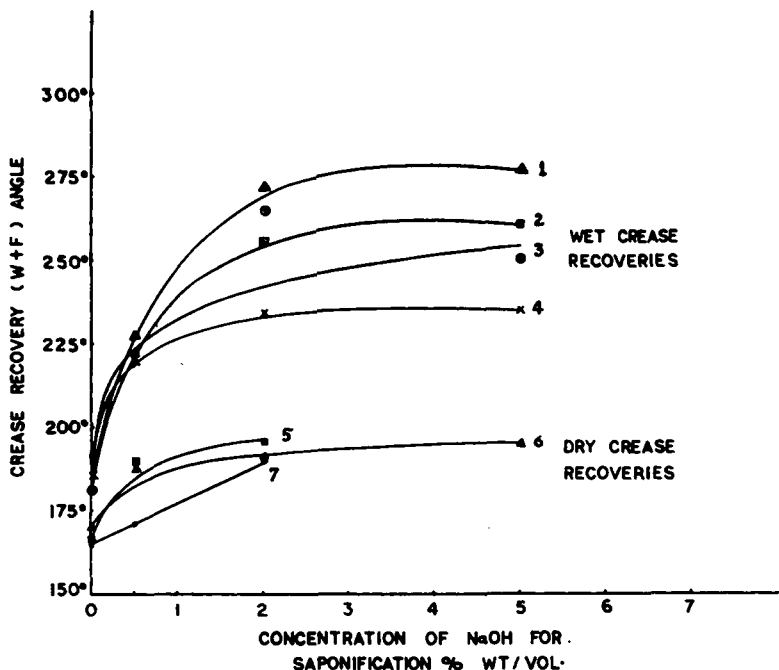

Fig. 5. Effect of alkali concentration, for saponification of PAN, on crease recoveries of treated fabrics after modification of the nitrile groups.   PAN, %: (1) 7.3%; (2) 5.6%; (3) 2.9%; (4) 1.4%; (5) 7.3%; (6) 2.9%; (7) 1.4%.

Kern and Fernow[17b] have reported similar changes in coloration of PAN powder with 40% NaOH solutions, until finally a colorless water-soluble product was obtained, indicating the completion of reaction with the formation of —COONa groups.

The saponified fabrics were given a formaldehyde treatment at 60–70°C. (30% formaldehyde solution) at pH 9.5 for nearly 24 hrs.   It was observed that when the formaldehyde treatment was carried out at room temperature (30°C.) the fabrics, on acid curing, did not exhibit noticeable changes in the wrinkle recovery, but a similar treatment at slightly higher temperatures (60–70°C.) ultimately produced considerable improvement in
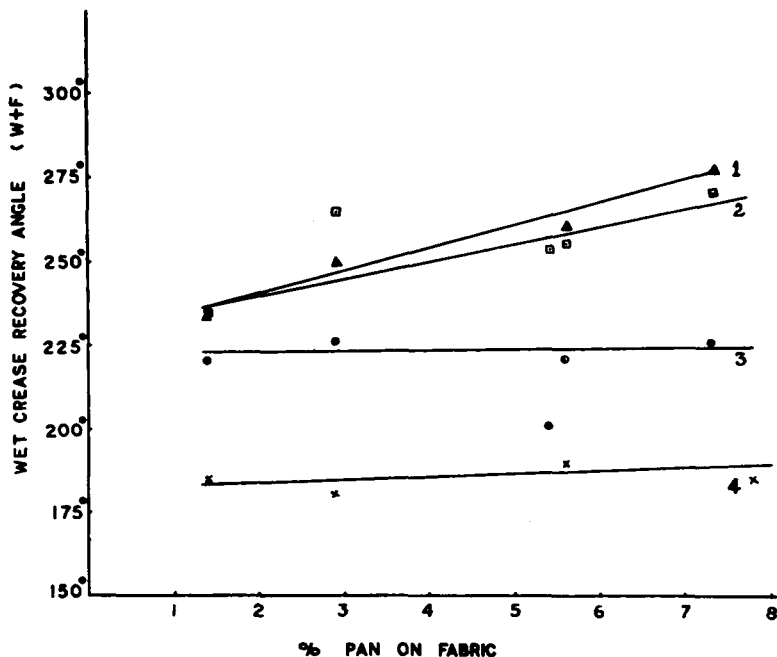
Fig. 6. Effect of polymer add-on on wet crease recoveries of treated fabrics after modification of the nitrile groups. Saponified with (1) 0.5% NaOH; (2) 2.0% NaOH; (3) 0.5% NaOH; (4) unsaponified.

wrinkle recovery. The fabrics were next washed, neutralized for any residual alkali, padded with a 10% $MgCl_2$ solution, dried at 110°F. for 8 min., and baked at 150°C. for 5 min. Results for the dry and wet crease recoveries and the loss in tensile and tear strength after acid curing are presented in Figures 5 and 6 and Tables IV and V.

TABLE IV
Elmendorf Tear Strength of Fabrics Containing PAN after
Saponification, Alkaline Formaldehyde Treatment, and Acid Cure

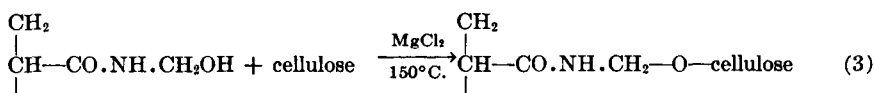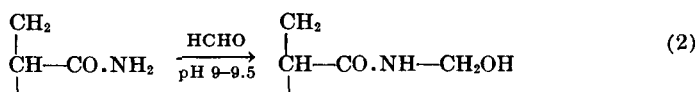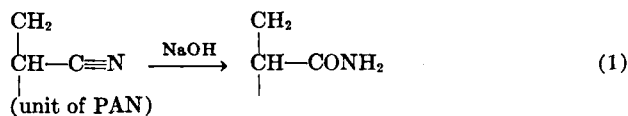| No.	PAN in fabric, %	$K_2S_2O_8$, %	% NaOH for sapon., %	Av. tear strength, g.
1	7.0	0.2	—	749[a]
2	1.4	0.2	0.5	501
3	5.4	0.2	2.0	336
4	7.0	0.2	5.0	336
5	2.9	1.0	5.0	384
6	5.6	1.0	2.0	432
7	7.3	1.0	0.5	464

[a] Blanks (without formaldehyde treatment and acid cure).

TABLE V
Instron Tensile Strength of Fabrics Containing PAN after
Saponification, Alkaline Formaldehyde Treatment, and Acid Cure

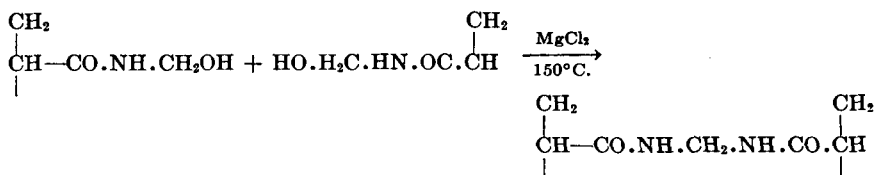| No.	PAN in fabric, %	$K_2S_2O_8$, %	NaOH for sapon., %	Av. tensile strength, kg.
1	7.0	1.0	—	24.0[a]
2	1.4	0.2	0.5	16.8
3	1.4	0.2	2.0	13.0
4	1.4	0.2	5.0	12.5
5	5.6	1.0	2.0	14.9
6	5.6	1.0	5.0	10.8
7	7.3	1.0	0.5	15.7

[a] Blanks (without formaldehyde treatment and acid cure).

The modification of the —C≡N groups of PAN to form crosslinks with cellulose is shown below:

$$
\begin{array}{ccc}
CH_2 & & CH_2 \\
| & & | \\
CH-C\equiv N & \xrightarrow{NaOH} & CH-CONH_2 \\
| & & | \\
(unit\ of\ PAN) & &
\end{array}
\qquad (1)
$$

$$
\begin{array}{ccc}
CH_2 & & CH_2 \\
| & & | \\
CH-CO.NH_2 & \xrightarrow[pH\ 9-9.5]{HCHO} & CH-CO.NH-CH_2OH \\
| & & |
\end{array}
\qquad (2)
$$

$$
\begin{array}{ccc}
CH_2 & & CH_2 \\
| & & | \\
CH-CO.NH.CH_2OH + cellulose & \xrightarrow[150°C.]{MgCl_2} & CH-CO.NH.CH_2-O-cellulose \\
| & & |
\end{array}
\qquad (3)
$$

Thus, if the PAN chain is grafted originally to a cellulose chain, subsequent modification as shown in reactions (1), (2), and (3) would produce crosslinks.

There is also a possibility that the polymer can form crosslinks within itself, if two or more —CO—NH—CH$_2$OH groups of two PAN chains interact as shown below:

$$
\begin{array}{cc}
CH_2 & CH_2 \\
| & | \\
CH-CO.NH.CH_2OH + HO.H_2C.HN.OC.CH & \xrightarrow[150°C.]{MgCl_2}
\end{array}
$$

$$
\begin{array}{cc}
CH_2 & CH_2 \\
| & | \\
CH-CO.NH.CH_2.NH.CO.CH \\
|
\end{array}
$$

The presence of highly crosslinked polymer could affect the crease recovery of the treated fabric, although it is not reacted covalently with cellulose. To examine this possibility, polymerizations were carried out as described in the first section under Results and Discussion, in the presence of a polyfunctional monomer such as divinyl benzene (1% v/v on acrylonitrile monomer). The polymer so formed did not improve the

wrinkle recovery of the treated fabric. Thus it may be argued that in the case of PAN, too, crosslinking within the polymer structure itself would not improve the wrinkle recovery of the fabrics unless a PAN–cellulose graft were formed during polymerization.

Figure 7 shows schematically some possible formations of cellulose–PAN crosslinks after modification with formaldehyde and acid cure.

Kamogawa and Sekiya[14] similarly crosslinked cellulose grafted with polyacrylamide. They polymerized acrylamide in cotton fabrics, using cerric ammonium nitrate as catalyst. The grafted polyacrylamide was then methylolated by an alkaline formaldehyde treatment (10% HCHO at 25°C. for 1 hr.) and the methylolated fabrics were subsequently neutralized with acetic acid, scoured with water to remove free HCHO, and dried.
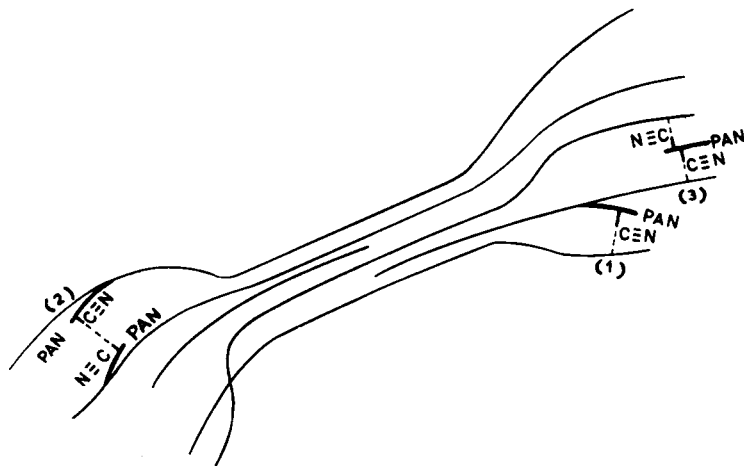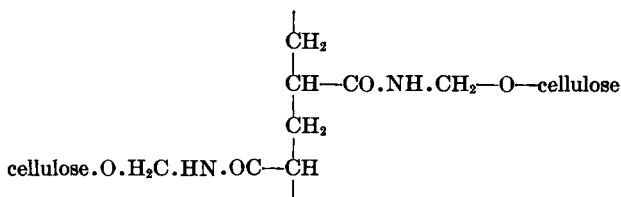

Fig. 7. Schematic representation of the possibilities of introducing crosslinks in fabrics containing PAN, after modification of the nitrile groups: (1) Grafted PAN crosslinking with cellulose; (2) Two grafted PAN chains interacting to produce a cross link; (3) A PAN chain bridging adjoining cellulose chains.

The fabrics (the grafted only, as well as the grafted and subsequently methylolated) were then given various crosslinking treatments by being padded with a latent acid catalyst such as ammonium chloride and with crosslinking materials such as formalin, dimethylol ethylene urea.

These authors have shown that, in addition to crosslinks of the types 1 and 2 in Figure 7, the hydroxyl groups of cellulose would form methylene ether crosslinks by reacting with formaldehyde, since it was used as a crosslinking agent. In the case of cellulose–PAN grafts, saponified and methylolated as described above, some formaldehyde may be liberated during the curing stage, owing to the dissociation of a few methylol groups, and form methylene ether crosslinks. However, no significant improvement in the wrinkle recovery of the blanks (original fabrics and unsaponified fabrics containing PAN) was obtained after the formaldehyde and acid

cure treatment. The effect of methylene ether crosslinks is therefore probably negligible.

However, the possibility that a physically deposited (ungrafted) PAN chain producing crosslinks of the type 3 in Figure 7 cannot be altogether ruled out:

$$
\begin{array}{l}
\quad\quad\quad\quad\overset{|}{CH_2} \\
\quad\quad\quad\quad\overset{|}{CH}-CO.NH.CH_2-O-cellulose \\
\quad\quad\quad\quad\overset{|}{CH_2} \\
cellulose.O.H_2C.HN.OC-\overset{|}{CH}
\end{array}
$$

Kamogawa and Sekiya[14] found that the nitrogen content of the treated cellulose fractions, precipitated out from cuoxam by acidification of the latter, was almost four times higher than that of the initial polyacrylamide-treated samples, indicating strongly the formation of polyacrylamide–cellulose grafts. These samples were earlier extracted with hot water to remove the ungrafted polyacrylamide. Hence, the possibility that ungrafted polyacrylamide crosslinks cellulose in the manner mentioned above has not been considered by them.

Recently, Gardon[18] followed a reverse sequence, that of crosslinking N-methylol acrylamide with cellulose. In this the methylolated acrylamide first reacted with cellulose at 150°C. with a mild acid catalyst. This was then crosslinked with cellulose by means of ammonium persulfate or potassium hydroxide, to bring about the reaction of the vinyl double bonds with cellulose hydroxyls. During this treatment, the polymerization of some vinyl double bonds also took place.

Gardon observed improved dry and wet crease recovery in the fabrics after this treatment, and has postulated crosslinking due chiefly to two types of mechanisms: (a) a methylolated acrylamide monomer unit reacting with cellulose chains at both ends, and (b) the methylolated acrylamide monomers, having previously reacted with cellulose chains at the methylol ends, polymerizing with each other through the vinyl double bonds. Crosslinks of the first type are similar to those shown as type 3 in Figure 7.

The data presented in this paper offer considerable evidence in support of the grafting mechanism, but do not constitute a direct and positive proof of it. It is hoped that further work planned in this study will contribute such a proof.

References

1. Landells, G., and C. S. Whewell, *J. Soc. Dyers Colourists*, **67**, 338 (1951); *ibid.*, **71**, 171 (1955).

2. Landells, G., J. A. Leathley, and C. S. Whewell, *J. Soc. Dyers Colourists*, **73**, 496 (1957).

3. Nowakowski, A., *Textile Res. J.*, **21**, 740 (1951).

4. Haydel, C. H., H. J. Janssen, H. L. E. Vix, and E. Gastrock, *Textile Res. J.*, **27**, 975 (1957).

5. Arthur, Jr., J. C., R. J. Demint, W. F. McSherry, and J. F. Jurgens, *Textile Res. J.*, **29**, 759 (1959).

6. Chitale, A. G., and A. Y. Kulkarni, *J. Sci. Ind. Res. (India)*, **20D**, 223 (1961).

7. Geacintov, N., V. Stennet, and E. W. Abrahamson, *Macromol. Chem.*, **36**, 52 (1960).

8. Geacintov, N., V. Stennet, E. W. Abrahamson, and J. J. Hermans, *J. Appl. Polymer Sci.*, **3**, 54 (1960).

9. Faraone, G., G. Parasacco, and C. Cogrossi, *J. Appl. Polymer Sci.*, **5**, 16 (1961).

10. Das Gupta, S., J. T. Slobodian, and D. L. Rawat. *Can. Textile J.*, **78**, No. 22, 41 (1961).

11. Demint, R. J., J. C. Arthur, Jr., and W. F. McSherry, *Textile Res. J.*, **31**, 821 (1961).

12. Azimov, S. A., Kh. U. Usmanov, N. V. Kordub, and S. I. Slepakova; through *B.C.I.R.A. Abstr.*, **41**, No. 1, 23 (1961).

13. Usmanov, Kh. U., B. I. Aikhodzhaev, and U. Azizov, *J. Polymer Sci.*, **53**, 87 (1961).

14. Kamogawa, H., and T. Sekiya, *Textile Res. J.*, **31**, 585 (1961).

15. Lawrence, E. W., and R. H. Phillips, *Am. Dyestuffs Reptr.*, **45**, 550 (1956).

16. Lloyd, A. O., *J. Textile Inst.*, **46T**, 653 (1955).

17. Schildknecht, C. E., Ed., *Vinyl and Related Polymers*, Wiley, New York, 1952; (a) pp. 265–66; (b) p. 272.

18. Gardon, J. L., *J. Appl. Polymer Sci.*, **5**, 734 (1961).

Synopsis

With a sodium thiosulfate–potassium persulfate redox system, *in situ* polymerization of acrylonitrile was studied in cellulosic materials. Traces of copper are found to accelerate the rate of polymerization, giving higher yields on the treated materials. Other variables studied were (a) material/liquor ratios, (b) monomer concentrations, and (c) initiator concentrations. It is found that high material/liquor ratios and higher initiator concentrations cause increased polymer yields on cotton fabrics. Fabrics containing polyacrylonitrile (PAN) are resistant to microbial degradation. Acrylonitrile was polymerized in secondary cellulose acetate, mercerized cotton, and cellophane. Studies of the insolubility behavior of the treated cellulose acetate samples in acetone and dimethylformamide, and of mercerized cotton and cellophane in cuprammonium hydroxide, were carried out for the purpose of examining the presence of cellulose–PAN grafts. In the latter case, a constant ratio of cellulose to PAN was obtained in the cuprammonium hydroxide-insoluble fraction over a wide range of polymer add-ons. Alkaline saponification of the nitrile groups in the treated cotton fabrics, followed by a treatment with formaldehyde at pH 9–9.5 and subsequent curing in the presence of an acid catalyst, yield highly crosslinked fabrics which exhibit a considerable improvement in the wet crease recovery with slight loss in tensile and tear strengths. It is believed that these changes are brought about by the formation of a —CO.NH.CH$_2$.O—cellulose type of crosslink. These results strongly support the presence of a cellulose–PAN graft.

Résumé

On a étudié la polymérisation *in-situ* de l'acrylonitrile dans des matériaux en cellulose en utilisant un système redox thiosulfate de sodium-persulfate de potassium. On a trouvé que des traces de cuivre augmentent la vitesse de polymérisation et donnent des rendements supérieurs pour les matériaux ainsi traités. Les autres variables étudiées sont: (*1*) le rapport des phases, (*2*) les concentrations en monomère et (*3*) les concentrations en initiateur. Un pourcentage élevé de matériaux et de fortes concentrations en initiateur donnent des rendements supérieurs en polymère pour les matériaux en coton. Les produits contenant du polyacrylonitrile (PAN) résistant à la dégradation microbienne. L'acrylonitrile a été polymérisé dans le diacétate de cellulose, dans du coton mercérisé et dans la cellophane. La présence de greffages cellulose–PAN a été examinée en étudiant l'insolubilité dans l'acétone et le diméthyl-formamide des échantillons traités d'acétate de cellulose, et l'insolubilité dans l'hydroxyde de cuproammonium du coton mercérisé et de la cellophane. Dans le dernier cas, on a obtenu un rapport cellulose–PAN constant dans la fraction insoluble dans l'hydroxyde de cuproammonium et ce dans un large domaine de polymère additionné. La saponification alcaline des groupes nitriles dans le coton traité suivant la méthode avec le formaldéhyde à pH 9–9.5 et la vulcanisation ultérieure en présence d'un catalyseur acide, donnent des produits fortement pontés et considérablement améliorés pour le retour dimensionnel à l'état humide avec une faible diminution des forces de tension et de rupture. On croit que ces changements sont dus à la formation de ponts du type —CO—NH—CH$_2$—O—cellulose. Ces résultats confirment très bien la présence d'un greffage cellulose–PAN.

Zusammenfassung

Mit einem Natriumthiosulfat-Kaliumpersulfat-Redoxsystem wird die in situ Polymerisation von Acrylnitril in Cellulose untersucht. Spuren von Kupfer beschleunigen die Polymerisation und liefern höhere Ausbeuten. Als weitere Variable wurden untersucht (*1*) das Verhältnis Cellulose zu Flüssigkeit, (*2*) die Monomerkonzentration und (*3*) die Starterkonzentration. Ein hohes Verhältnis Cellulose zu Flüssigkeit und höhere Starterkonzentration liefert an Baumwollgeweben eine erhöhte Polymerausbeute. PAN-enthaltende Gewebe sind gegen mikrobiellen Abbau beständig. Acrylnitril wurde in sekundärem Celluloseacetat, mercerisierter Baumwolle und Cellophan polymerisiert. Eine Untersuchung des Löslichkeitsverhaltens der behandelten Celluloseacetatproben in Aceton und Dimethylformamid und von mercerisierter Baumwolle und Cellophan in Cuprammoniumhydroxyd wurde zur Prüfung auf Vorhandensein von Cellulose-PAN-Aufpfropfungen durchgeführt. Im letzteren Falle wurde bei der Cuprammoniumhydroxyd-(Cu, Am)-unlöslichen Fraktion über einen weiten Bereich von Polymerzusätzen ein konstantes Verhältnis Cellulose zu PAN erhalten. Alkalische Verseifung der Nitrilgruppen in den behandelten Baumwollgeweben, darauffolgende Behandlung mit Formaldehyd bei pH 9–9,5 und schliessliche Einwirkung eines sauren Katalysators liefert stark vernetzte Gewebe, die eine beträchtliche Verbesserung der Nassknitterfestigkeit bei schwachem Rückgang der Zug- und Reissfestigkeit zeigen. Es wird angenommen, dass diese Veränderungen durch die Bildung von Vernetzungen vom Typus —CO—NH.CH$_2$.O—Cellulose erzeugt werden. Die Ergebnisse sprechen für die Gegenwart von Cellulose-PAN-Aufpfropfungen.