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Physical Properties of Natural and Modified Cotton Cellulose Grafted with Acrylate Monomers

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Synopsis

Natural, cyanoethylated, and formaldehyde-crosslinked cotton cellulose has been grafted with methyl, ethyl, and *n*-butyl acrylate and methyl methacrylate monomers. Various physical properties such as density, moisture regain, birefringence, and mechanical properties were studied. The results indicate that the density and moisture regain of the grafted fibers are less than those of natural cotton. The birefringence of grafted fibers is also less than that of natural cotton. The variation in birefringence with per cent graft-on depends on the monomer. Parameters such as orientation factor, helix angle, and refractive power of fibers were calculated from the birefringence data and the results discussed. It was observed that due to grafting of both natural and crosslinked cotton, there is a decrease in tensile strength, increase in elongation at break, and decrease in the initial modulus. Attempts are made to understand these changes in the properties of cotton in terms of the changes occurring in the fine structure of the fiber.

INTRODUCTION

Grafting of vinyl monomers on natural and modified cotton cellulose may result in improvement of certain physical properties without considerably damaging the basic characteristics of the fiber. Thus, it has been reported that grafting results in a substantial increase in elongation[1,2] and a small decrease in tensile strength of the fiber.[1] Hubert and co-workers,[2] on the other hand, have reported an improvement in tensile strength, no change in wrinkle recovery, and a decrease in flex abrasion due to grafting. Negishi et al.[3] have grafted methyl, ethyl, *n*-propyl, and isobutyl acrylate onto cellulose. They observed that the wet crease and dry crease recovery increase with increasing extent of grafting and with decreasing second-order transition temperature of the grafted polymer. Tear strength of the grafted fabrics decreases for the acrylates giving hard polymers. The stiffness of the grafted cotton increases with increase in the second-order transition temperature of the grafted polymer. Grafting does not have much effect on the flex abrasion strength. Demint and co-workers[4] have observed that grafting of acrylonitrile onto cyanoethylated cotton results in a decrease in permanent set, average stiffness, and solubility and an increase in delayed elastic recovery and elongation at break.

Several workers have studied the properties of cellulose crosslinked with formaldehyde and have reported that crosslinking results in an improvement in the wrinkle recovery. Physical properties of formaldehyde-crosslinked and cyanoethylated cotton grafted with acrylate monomers have been investigated to a lesser extent. In the present paper, we report the study of certain physical properties, namely, density, moisture regain, birefringence, and mechanical properties of natural, cyanoethylated, and formaldehyde-crosslinked cotton grafted with methyl, ethyl, and *n*-butyl acrylate and methyl methacrylate monomers. Birefringence and mechanical properties could not be determined for cyanoethylated and grafted cotton samples, because the yarn becomes very stiff after grafting.

EXPERIMENTAL

Materials and Grafting Method

California cotton yarns (5^{s}, Tpi = 3), Soxhlet extracted with methanol to remove grease and dirt, were used for grafting. BDH reagent-grade chemicals were used. Baker-analyzed ceric ammonium nitrate was used as the initiator. Formaldehyde-crosslinked cotton and cyanoethylated cotton were prepared as reported earlier.[5] Grafting was carried out by a method described elsewhere.[6]

Denier

The deniers of parent and grafted fibers were measured by cutting fixed lengths of fibers and weighing in a bundle on a sensitive microbalance. These denier values were used in finding the tensile properties of the corresponding fibers.

Density and Moisture Regain

Density was determined using a density gradient column containing mixtures of benzene (ρ = 0.879 g/cc) and carbon tetrachloride (ρ = 1.595 g/cc), at different molar ratios.

Moisture regain was determined by vacuum desiccator method using P_2O_5 as dehydrating agent.

Birefringence

The birefringence of the fiber was measured by the Beckline method, using liquid paraffin (n = 1.471) and α-monobromonaphthalene (n = 1.660).

Tensile Properties

Tenacity, elongation at break, and modulus of the fibers were measured from the stress–strain curves obtained on an Instron. The specifications employed were: gauge length = 1 cm; cross-head speed = 0.5 cm/min; chart speed = 100 cm/min; full-scale load calibration = 10 g. All experiments were performed at 65% ± 2% R.H. and 20°C ± 2°C.

RESULTS AND DISCUSSION

Density and Moisture Regain

In Tables I to III, the density and moisture regain values for natural cotton, cotton crosslinked with formaldehyde, and cyanoethylated cotton grafted with various acrylate monomers are given, respectively. As is obvious from the tables, grafting of natural and modified cotton results in a decrease in both moisture regain and density. Further, there is a decrease in these values with increase in the number of moles grafted. Cotton samples grafted with ethyl and *n*-butyl acrylate and methyl methacrylate containing 0.55% moles decrease the density of natural cotton to the same extent, whereas cotton grafted with methyl acrylate does not decrease the density to such an extent.

TABLE I
Physical Properties of Natural and Grafted Cotton Cellulose

Sample	No. of moles grafted, %	Per cent graft-on	Density, g/cc	Moisture regain, %
Natural cellulose	0	0	1.54	6.2
MA-grafted cotton	0.174	15	1.49	4.7
	0.721	62	1.42	2.8
	0.860	74	1.39	2.7
EA-grafted cotton	0.100	10	1.47	4.5
	0.550	55	1.31	3.1
	0.910	91	1.20	2.7
BA-grafted cotton	0.172	22	1.35	4.1
	0.560	72	1.28	2.4
MMA-grafted cotton	0.135	13.5	1.44	4.6
	0.380	38	1.29	3.6
	0.550	55	1.28	3.3

TABLE II
Physical Properties of Crosslinked Cotton Grafted with Acrylate Monomers

Sample	Bound HCHO, %	No. of moles grafted, %	Per cent graft-on	Density, g/cc	Moisture regain, %
Natural cotton	0.15	0	0	1.52	5.7
	0.42	0	0	1.51	5.6
	1.00	0	0	1.51	5.5
MA-grafted cotton	0.15	1.198	103	1.32	2.2
	0.42	1.162	100	1.34	2.4
	1.00	1.105	95	1.35	2.0
EA-grafted cotton	0.15	0.94	94	1.33	3.1
	0.42	0.86	86	1.35	2.8
	1.00	0.88	88	1.35	2.7
BA-grafted cotton	0.15	1.086	139	1.11	1.6
	0.42	0.8437	108	1.23	2.0
	1.00	0.8594	110	1.28	1.8
MMA-grafted cotton	0.15	0.38	38	1.25	3.5
	0.42	0.23	23	1.28	4.2
	1.00	0.22	22	1.35	4.1

TABLE III
Physical Properties of Cyanoethylated Cotton Grafted with Acrylate Monomers

Sample	Degree of substitution	No. of moles grafted, %	Per cent graft-on	Density, g/cc	Moisture regain, %
Natural cotton	0.12	0	0	1.30	2.8
	0.7	0	0	1.26	4.4
	2.2	0	0	1.23	2.8
MA-grafted cotton	0.12	0.442	38	1.40	1.7
	0.7	0.791	68	1.25	2.5
	2.2	0.360	31	1.23	2.1
EA-grafted cotton	0.12	1.200	120	1.30	1.4
	0.7	1.200	120	1.20	1.5
	2.2	0.470	47	1.15	2.3
BA-grafted cotton	0.12	0.789	101	1.26	1.3
	0.7	0.938	120	1.25	1.6
	2.2	0.953	122	1.22	1.5
MMA-grafted cotton	0.12	0.230	23	1.43	1.9
	0.7	0.650	65	1.22	2.3
	2.2	0.740	74	1.19	1.8

Crosslinking with formaldehyde results in a decrease in both of these properties (Table II). An increase in per cent bound formaldehyde does not influence the behavior of the fiber. Grafting of crosslinked cotton results in a further decrease in moisture regain and density. The effect of crosslinking of cotton with formaldehyde is to increase the per cent graft-on in the case of all the four monomers. If one compares the values of density and moisture regain of cotton samples, natural as well as crosslinked, grafted with methyl, ethyl, and *n*-butyl acrylates, it can be seen that grafting of crosslinked cotton does not reduce the density and moisture regain of the fiber to the same extent as grafting of natural cotton. However, in the case of methyl methacrylate grafted natural and crosslinked cotton, there is practically no difference in the density and moisture regain behavior.

Cyanoethylation of cotton results in greater decrease in density and moisture regain than crosslinking with formaldehyde (Table III). The density decreases with increasing degree of substitution. Moisture regain increases up to a D.S. of 0.7; but at higher D.S., moisture regain drops to a lower value. Grafting of these cyanoethylated cottons further lowers the values of density and moisture regain.

The variations in the densities of grafted cotton, crosslinked and cyanoethylated cotton may be due to swelling which will invariably take place under the reaction conditions.

In cotton cellulose, the free hydroxyl groups in the amorphous region are mainly responsible for the absorption of water since the crystalline regions are inaccessible.[7] It is in these amorphous regions and on the surface of the crystallites that graft copolymerization takes place. Grafting of acrylate polymers which are hydrophobic decreases the moisture regain. Similar results have been obtained by Negishi et al.[3] As a result of crosslinking with formaldehyde, though there is considerable swelling, the hydroxyl groups in the amorphous region are blocked by the crosslinks, thus preventing the absorption of moisture. Similarly, cyanoethylation of cotton utilizes many of the hydroxyl groups in the amorphous region, which explains the decrease in the value of moisture regain. The moisture regain behavior of modified and grafted samples is similar to that of grafted natural cotton.

Optical Properties

The values of $n_{\parallel}$, $n_{\perp}$, and birefringence ($n_{\parallel} - n_{\perp}$) are given in Tables IV and V for natural and formaldehyde-crosslinked cotton grafted with acrylate monomers. The birefringence of the grafted fibers as seen in Table IV is less than that of the natural cotton. The variation of birefringence with extent of grafting depends on the monomer. Crosslinking with formaldehyde results in a decrease in birefringence, the decrease being more at higher degrees of crosslinking. Grafting of crosslinked cotton containing the same per cent graft-on as natural cotton indicates that disorientation is less in crosslinked material than in natural material as a result of grafting. From the birefringence values of the fiber, different parameters such as optical orientation factor f, refractive index of an isotropic fiber, n_{iso}, and spiral angle θ were calculated. Optical orientation factor was calculated using the formula of Hermans[8]:

$$f = \frac{n_{\parallel} - n_{\perp}}{n_{\parallel}' - n_{\perp}'} \cdot \frac{d'}{d}$$

TABLE IV
Optical Data on Natural Cotton Grafted with Acrylate Monomers

Sample	$n_{\parallel}$	$n_{\perp}$	Birefringence ($n_{\parallel} - n_{\perp}$)	n_{iso}	$\frac{n_{iso} - 1}{d}$	Optical orientation factor f	Spiral angle θ
Natural cotton	1.56490	1.52300	0.04131	1.53696	0.3487	0.6509	42°25′
MA-grafted cotton							
15%	1.55074	1.52687	0.02387	1.53482	0.3588	0.3887	55°32′
74%	1.55063	1.54234	0.00929	1.54444	0.3906	0.1621	55°43′
EA-grafted cotton							
10%	1.55154	1.54548	0.00608	1.54750	0.2725	0.1000	55°46′
55%	1.55074	1.54219	0.00755	1.54504	0.4160	0.1582	55°32′
91%	1.54313	1.54017	0.00226	1.54116	0.4506	0.0457	63°34′
BA-grafted cotton							
22%	1.55230	1.54731	0.00499	1.54897	0.4066	0.0649	53°58′
72%	1.55578	1.54731	0.00847	1.55013	0.4298	0.1456	50°39′
MMA-grafted cotton							
13.5%	1.55846	1.54856	0.00990	1.55186	0.3832	0.1516	48°11′
38%	1.55811	1.54644	0.01167	1.55033	0.4266	0.1990	48°17′
55%	1.55832	1.55074	0.00758	1.55326	0.4322	0.1308	48°06′

TABLE V
Optical Data on Formaldehyde-Crosslinked and Acrylate-Grafted Cotton

Sample	$n_{\parallel}$	$n_{\perp}$	Birefringence $(n_{\parallel} - n_{\perp})$	n_{iso}	$\frac{n_{iso} - 1}{d}$	Optical orientation factor f	Spiral angle θ
Formaldehyde-crosslinked cotton with % bound HCHO							
0.15%	1.56394	1.52231	0.04103	1.53618	0.3513	0.595	46°18′
0.42%	1.56394	1.52346	0.04048	1.53695	0.3552	0.587	46°18′
1.00%	1.55984	1.52131	0.03853	1.53415	0.3538	0.559	46°45′
MA-grafted cotton							
0.15%	1.55728	1.54844	0.00844	1.55138	0.4178	0.1551	49°29′
0.42%	1.55498	1.54455	0.01143	1.54836	0.4092	0.1644	50°20′
1.00%	1.55628	1.54873	0.00755	1.55124	0.4082	0.1351	50°13′
EA-grafted cotton							
0.15%	1.55701	1.54996	0.00705	1.55231	0.4088	0.1315	49°46′
0.42%	1.55645	1.54826	0.00818	1.55099	0.4081	0.1472	50° 7′
1.00%	1.54806	1.54033	0.00754	1.54209	0.4013	0.1380	58°11′
BA-grafted cotton							
0.15%	1.55598	1.54030	0.01568	1.54552	0.4909	0.3432	50°20′
0.42%	1.55834	1.54425	0.01411	1.54894	0.4463	0.2771	48°05′
1.00%	1.55430	1.52419	0.03011	1.53752	0.4200	0.5662	52°08′
MMA-grafted cotton							
0.15%	1.55207	1.53608	0.01599	1.54141	0.4340	0.3105	55°34′
0.42%	1.55207	1.52246	0.03004	1.53244	0.4159	0.566	53°50′
1.00%	1.55404	1.53548	0.01853	1.54166	0.4013	0.334	55°05′

where f is the orientation factor; $n_{||}'$ and $n_{\perp}'$ and $n_{||}$ and $n_{\perp}$ are the refractive indices of an ideal fiber and the fiber under consideration in the parallel and perpendicular directions, respectively; d' = density of the crystalline fiber; and d = density of the fiber under consideration.

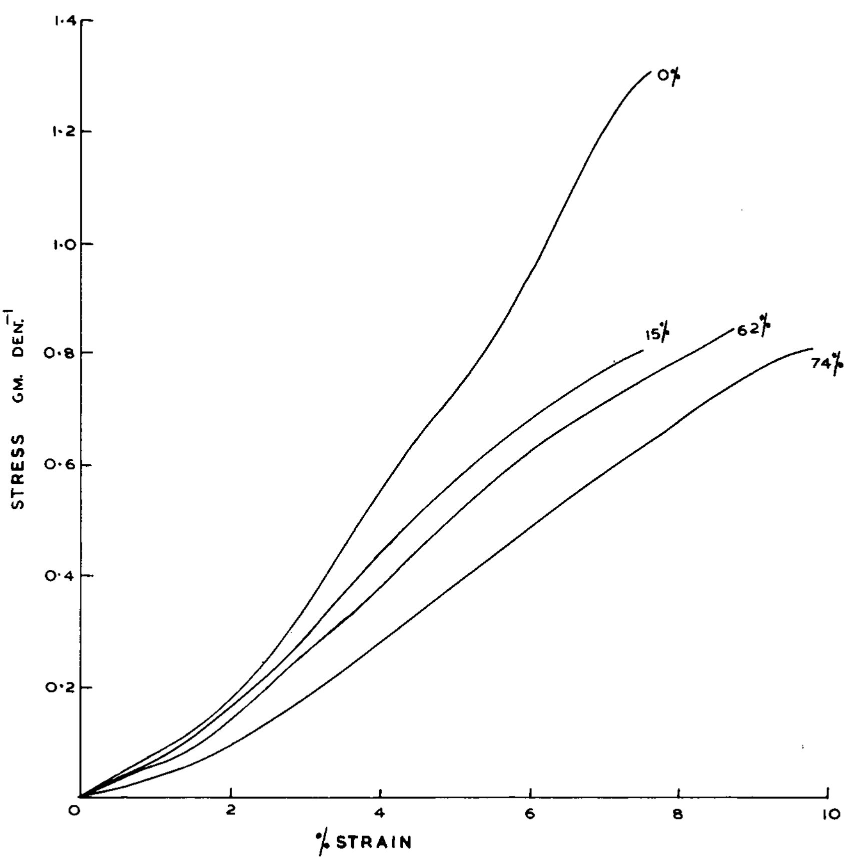
Since the x-ray diffraction patterns do not show any appreciable shift in the spacings of (101), (10$\bar{1}$), and (002) lattices in all the samples, one can justifiably assume that d' remains constant and is 1.553 g/cc, that of ramie fiber. At $f = 0$, one can obtain the polarizability of the isotropic fiber.[8]

$$n_{\text{iso}} = {}^1/_3\,(n_{||} + 2n_{\perp}).$$

This simple equation enables to predict from the two principal refractive indices of an anisotropic fiber what would be its refractive index in the isotropic state, and thus to express its refractive power.

Meredith[9] has derived an equation for the calculation of helix angle, θ according to which

$$\cos^2\theta = \frac{n_r^2(n_r' + n_\alpha)(n_r' - n_\alpha)}{(n_r')^2\,(n_r + n_\alpha)\,(n_r - n_\alpha)}$$



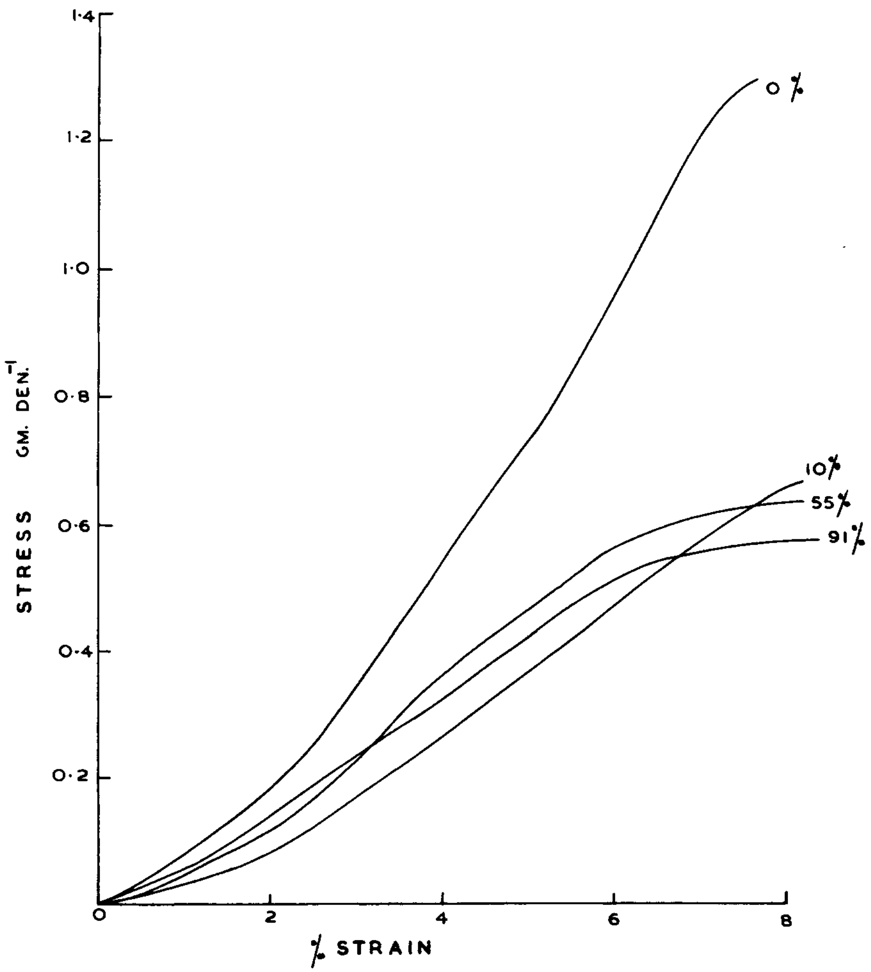
(a)

Fig. 1 (*continued*)

where n_r' = refractive index of the fiber under consideration in the parallel direction; n_r = refractive index of the crystallite formed by the closely packed molecular chains; $n_\alpha \approx n_\alpha'$ is the refractive index of the crystallite which in unaffected by orientation, because the crystallites are oriented in layers parallel to the surface of the fiber. After substituting the values of n_r and n_α for that of ramie, which is considered an ideal fiber, the equation becomes

$$\cos^2 \theta = \frac{12.72(n_r' + 1.531)(n_r' - 1.531)}{(n_r')^2}.$$

The values of f, n_{iso}, θ, and k are given in Tables IV and V; k was calculated from the equation $(n_{\text{iso}} - 1)/d$, where d is the density of the fiber at 65%

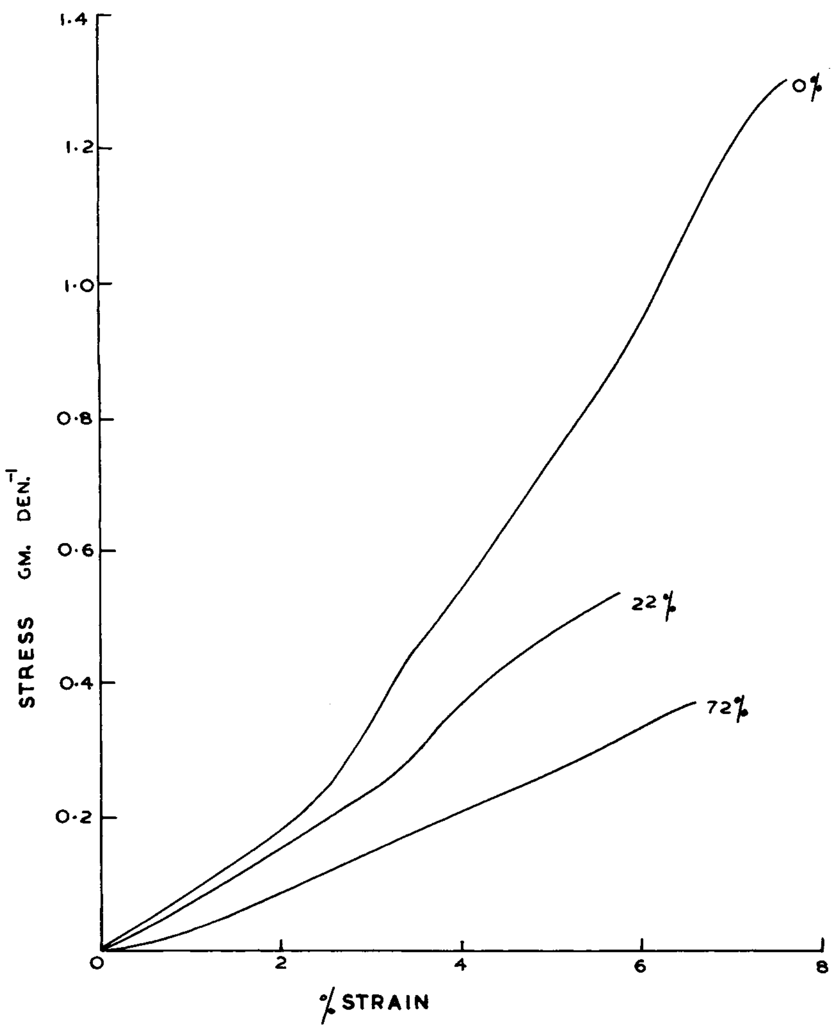


(b)

Fig. 1 (*continued*)

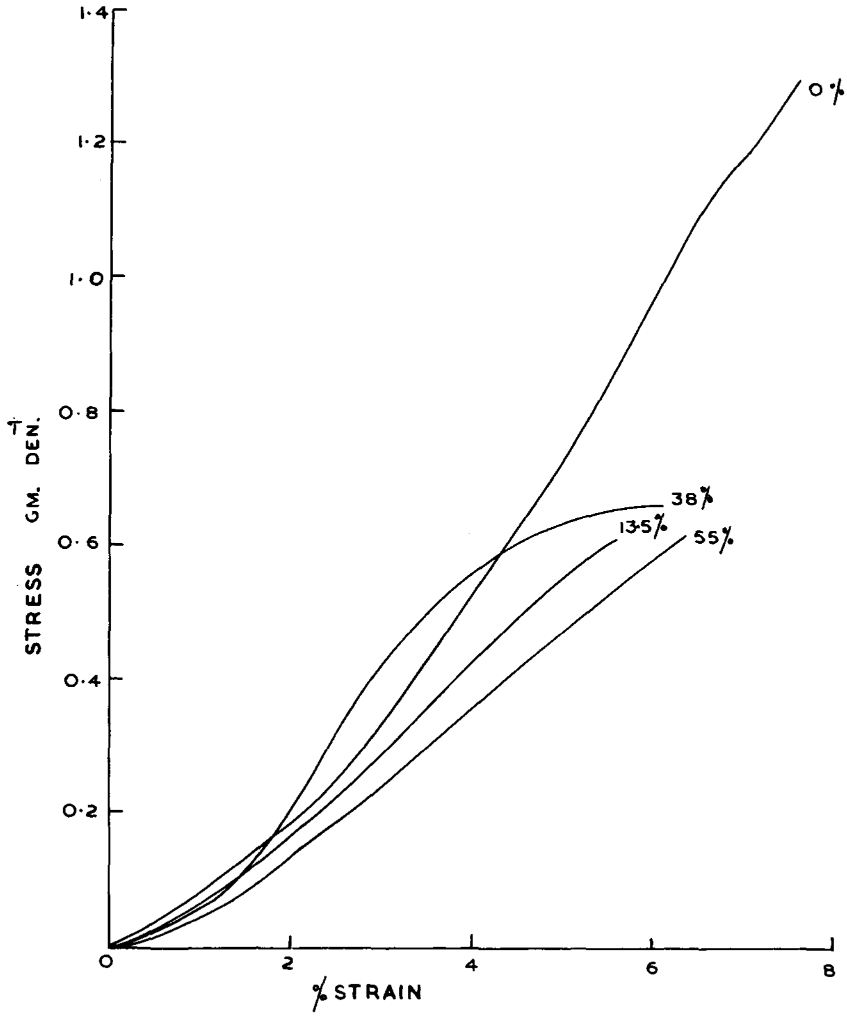
R.H. and 20°C. It is obvious from the results that the helix angle and n_{iso} do not vary with the per cent graft-on for all monomers. The helix angle θ and n_{iso}, nevertheless, are larger for all grafted fibers as compared to natural cotton. Comparing the n_{iso} values for different monomers investigated, it can be seen from the results that the values gradually increase as the size of the monomer increases.

It has been reported that double refraction of a fiber is inversely proportional to its degree of swelling.[10] This means that, as the fiber swells, the birefringence decreases and the helix angle increases. The density values (Tables I, II, and III) show that as a result of grafting the density decreases, thereby implying that there is considerable swelling.



(c)

Fig. 1 (*continued*)



(d)

Fig. 1. Stress–strain curves for cotton grafted with acrylate monomers: (a) methyl acrylate on cotton; (b) ethyl acrylate on cotton; (c) butyl acrylate on cotton; (d) methyl methacrylate on cotton.

It is well known that refractive power increases as density increases for an isotropic material, that is,

$$\frac{n_{\text{iso}} - 1}{d} = k \text{ (constant)}.$$

The results in Tables IV and V do not, however, conform to this theory. In order to maintain k constant, the density and refractive power must increase or decrease. The result indicates that the value of k increases with per cent graft-on because the density decreases due to grafting for all the monomers (Tables I, II, and III). It has been reported[11] that the density varies directly with moisture up to a $\approx 5\%$ regain; and for almost all the grafted fiber samples, regain values lie in this range. Thus, the $(n_{iso} - 1)/d$ increases and does not remain constant for the natural as well as crosslinked cotton cellulose grafted with acrylate monomers.

Tensile Properties and Orientation

The stress–strain curves for natural and crosslinked cottons grafted with acrylates are given in Figures 1a to 1d and Figures 2a to 2e. Tables VI and VII give the values of initial modulus, breaking stress, and breaking elongation for these cottons.

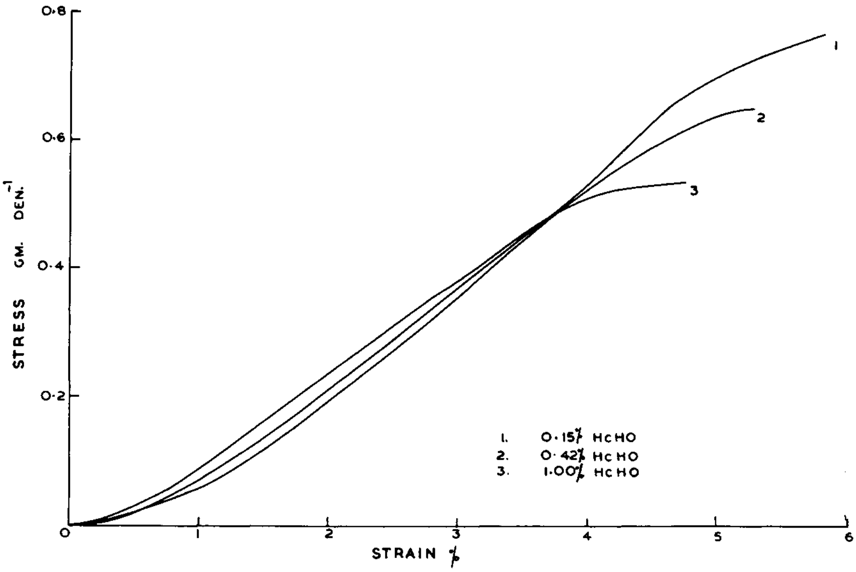
TABLE VI
Mechanical Properties of Grafted Cotton Cellulose

Sample	Per cent graft-on	Initial modulus, g/den	Breaking stress, g/den	Breaking elongation, %
Natural cellulose	0	0	11.5	7.6
MA-grafted cotton	15	6.6	8.0	7.6
	62	5.3	8.4	8.7
	74	3.3	8.0	9.7
EA-grafted cotton	10	4.0	6.7	8.25
	55	4.6	6.4	8.2
	91	6.0	5.8	8.4
BA-grafted cotton	22	7.3	5.3	5.7
	72	4.0	3.8	6.6
MMA-grafted cotton	13.5	5.0	6.1	5.6
	38.0	5.0	6.6	6.1
	55.0	4.6	6.2	6.4

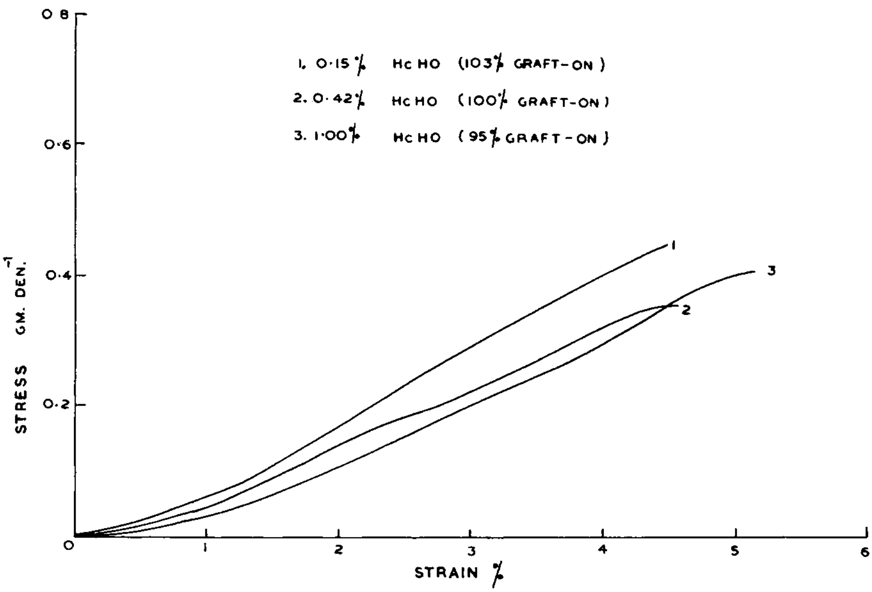
TABLE VII
Mechanical Properties of Formaldehyde-Crosslinked Cotton Grafted with Acrylate Monomers

Sample	HCHO, %	Per cent graft-on	Initial modulus, g/den	Breaking stress, g/den	Breaking elongation, %
Natural cotton	0.15	0	12.5	7.7	5.82
	0.42	0	13.6	6.5	5.3
	1.00	0	13.5	5.4	4.75
MA-grafted cotton	0.15	103	6.0	4.5	4.5
	0.42	100	4.5	3.6	4.5
	1.00	95	3.5	4.1	5.1
EA-grafted cotton	0.15	94	8.4	5.1	4.4
	0.42	86	5.6	4.6	4.6
	1.00	88	4.0	4.6	4.6
BA-grafted cotton	0.15	139	7.00	6.4	6.0
	0.42	108	6.0	4.3	5.0
	1.00	110	4.0	6.1	5.5
MMA-grafted cotton	0.15	38	8.6	4.7	4.8
	0.42	23	5.0	4.6	4.4
	1.00	22	5.0	4.9	4.5

Grafting with acrylate monomers results in a decrease in initial modulus and tensile strength. There is a decrease in initial modulus with increase in per cent graft-on in MA, MMA, and BA grafted samples, while an increase is observed in EA. The tensile strength decreases with an increase



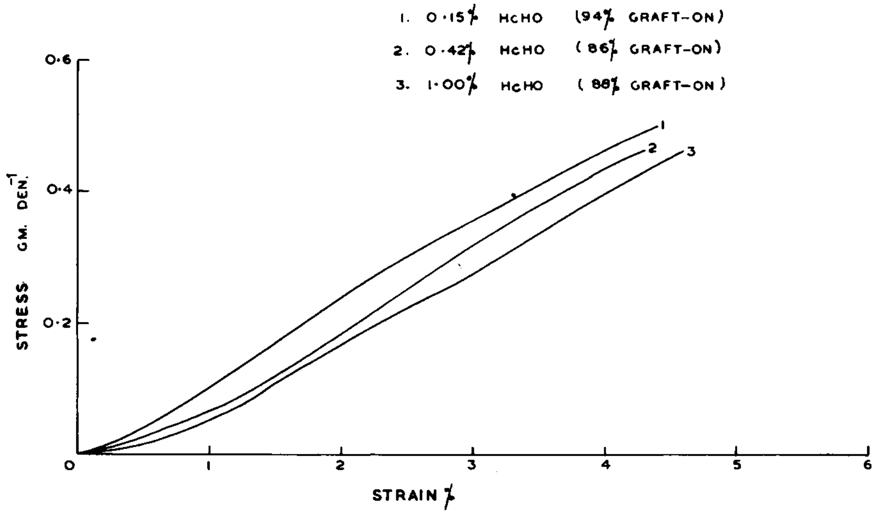
(a)



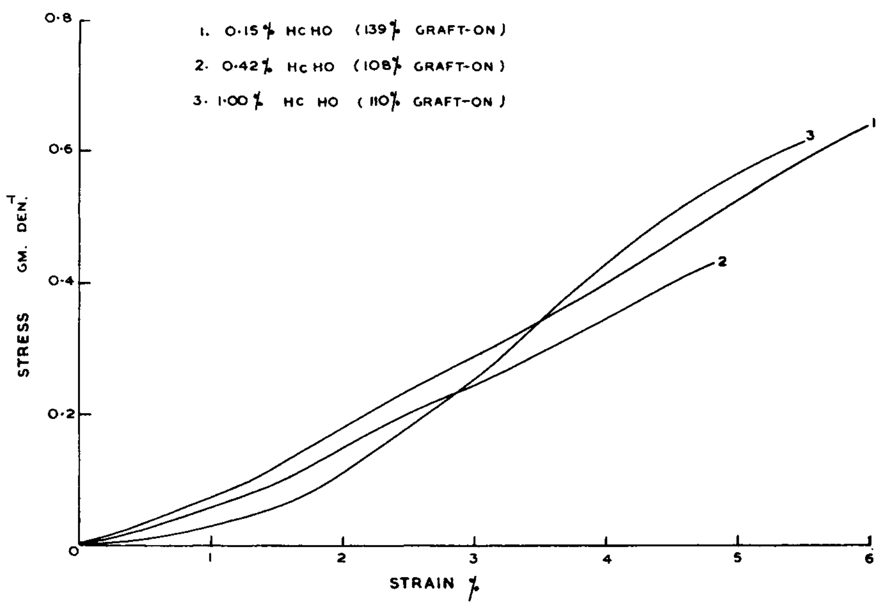
(b)

Fig. 2 (*continued*)

in per cent graft-on in all monomers, except in MMA where the change is not significant. This decrease in initial modulus and tensile strength may be due to a decrease in density and orientation of the fiber. The spiral angle θ is larger for grafted fibers than for natural cotton. Since the initial modulus is inversely proportional to the area of the fiber cross section, increase in spiral angle may also be a contributory factor to a decrease in

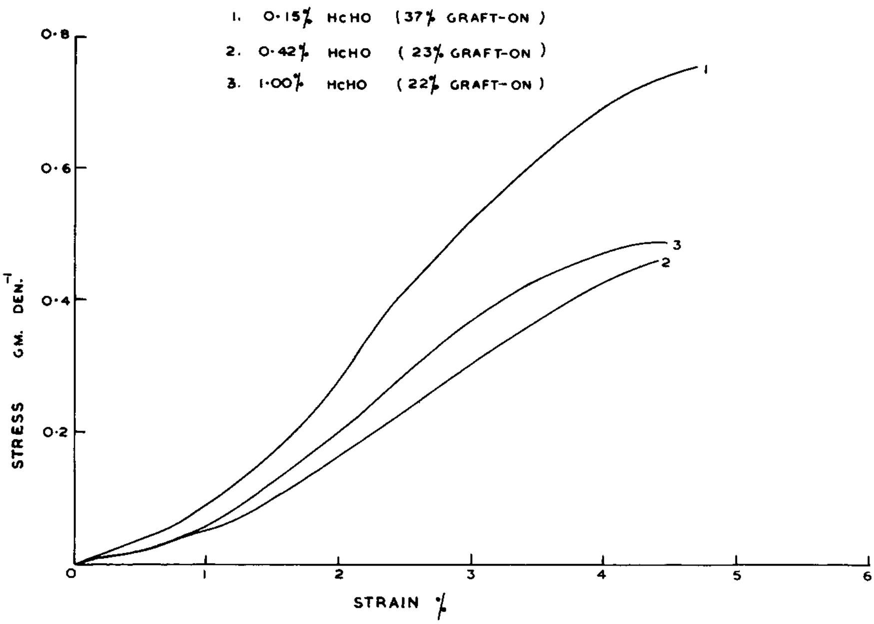


(c)



(d)

Fig. 2 (*continued*)



(e)

Fig. 2. Stress–strain curves for formaldehyde-crosslinked cotton grafted with acrylate monomers: (a) formaldehyde crosslinked cotton; (b) methyl acrylate on formaldehyde-crosslinked cotton; (c) ethyl acrylate on formaldehyde-crosslinked cotton; (d) butyl acrylate on formaldehyde-crosslinked cotton; (e) methyl methacrylate on formaldehyde-crosslinked cotton.

initial modulus. Owing to the treatment of cotton with formaldehyde, the breaking strength is reduced and initial modulus is increased. The crosslink renders the fibers more rigid, and thus the initial modulus and tensile strength are affected. Grafting of crosslinked cotton reduces the tensile strength and initial modulus. Since very high graft yields are obtained due to the opened-up structure of the fiber after the HCHO crosslinking reaction, the per cent graft-on plays a predominant part in bringing down the value of the initial modulus. Comparison of samples with approximately the same per cent graft-on reveals that the initial modulus is higher in grafted fibers which are crosslinked by HCHO than in natural cotton.

Breaking elongation increases as a result of grafting in MA and EA and decreases in BA and MMA grafted samples as compared to natural cotton. In the case of MMA grafted samples, decrease in breaking elongation is expected since it is a very rigid polymer at room temperature. But the behavior of BA is rather peculiar, since it forms a rubbery polymer at room temperature. However, higher add-on renders a rise in elongation nearer to the natural cotton. This increase in breaking elongation is natural, since there is a decrease in orientation factor which indicates that due to grafting many of the intermolecular forces holding the chains together are broken, facilitating the slippage of molecules. Also, since these acrylate polymers, except MMA, have their glass transition temperature values below room temperature, they are rubbery at room temperature, rendering the grafted polymer more easily extendable.

But as a result of crosslinking with formaldehyde, the breaking elongation is reduced considerably. Breaking elongation decreases with increase in bound formaldehyde content. Grafting the crosslinked cotton with acrylate monomers does not improve the elongation properties. This may be due to the rigidity of the structure caused by crosslinking with formaldehyde.

References

1. F. A. Blouin and J. C. Arthur, Jr., *Text. Res. J.*, **33**, 727 (1963).

2. H. H.ST. Mard, C. Hamalainen, and A. S. Cooper, Jr., *Amer. Dyestuff Rep.*, **56**, 136 (1967).

3. M. Negishi, Y. Nakamura, T. Kakinuma, and Y. IIzuka, *J. Appl. Polym. Sci.*, **9**, 2227 (1965).

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

5. D. S. Varma and V. Narasimhan, *J. Appl. Polym. Sci.*, submitted for publication.

6. D. S. Varma and V. Narasimhan, *J. Appl. Polym. Sci.*, **16**, 3225 (1972).

7. J. Mann, Proceedings of the Wood Chemistry Symposium, Montreal, Canada, 1961, Butterworths, London, 1962, p. 91.

8. P. H. Hermans, *Physics and Chemistry of Cellulose Fibers*, Elsevier, Amsterdam, 1949, p. 230.

9. R. Meredith, *J. Text. Inst.*, **37**, T205 (1946).

10. O. Krathy and P. Platzek, *Kolloid.-Z.* **84**, 268 (1938).

11. W. E. Morton and J. W. S. Hearle, *Physical Properties of Textile Filones*, Butterworths, London, 1962, p. 152.

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