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X-Ray Diffraction Studies of Graft Copolymers of Natural and Modified Cotton Cellulose and Acrylate Monomers

D. S. VARMA & VEENA NARASIMHAN
Fibre Science Laboratories, Indian Institute of Technology, New Delhi 110029

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X-ray diffraction patterns of natural, formaldehyde crosslinked and cyanoethylated cotton samples graft copolymerized with methyl, ethyl, *n*-butyl acrylate and methyl methacrylate monomers have been studied. The prominent equatorial and meridional reflection arcs of native cotton remained unaffected as a result of modification by cyanoethylation, crosslinking and grafting, but the intensity of the diffuse background scattering was increased slightly. The Bragg angles and the corresponding interplanar spacings, d_{101} and d_{002}, for natural cotton cellulose also did not change, indicating that no transformation of unit cell has taken place. The crystallite size was not affected, whereas crystallite orientation was decreased due to chemical modification and grafting.

X-RAY diffraction has been used for evaluating the changes in the structure of cellulose fibre modified by various chemical treatments. Thus, the fine structure of cyanoethylated cellulose and its reactivity with melamine resins have been investigated[1]. Stanonis and coworkers[2] studied the fine structure of benzhydrylated cotton cellulose. Very little information is available regarding X-ray studies on graft copolymers of cotton. Imamura *et al.*[3] studied the graft copolymers of acrylonitrile and viscose rayon and showed by the X-ray diffraction method that grafting takes place in the amorphous regions of the fibre. Hori and coworkers[4] studied the effect of crystallinity and the ratio of the intensity of cellulose on reactivity during grafting of acrylonitrile onto gel cellophane. Graft yield decreased as crystallinity increased and the intensity ratio increased, indicating that grafting takes place in the amorphous regions of cellulose. Mercea[5] investigated the structure of grafted cotton fabrics dyed with Ramazol brilliant orange RR and confirmed that the acrylonitrile grafted cotton fibres show a decrease in the orientation index and lateral order; the degree of crystallinity remained unchanged. Investigations of the fine structure of cellulose in the methyl methacrylate graft copolymer have indicated that crystallinity bears no clear quantitative relationship with the graft ratio, except at low monomer concentration[6]. Chou *et al.*[7] obtained a new X-ray diffraction pattern, different from that of natural cellulose due to grafting of acrylonitrile. The degree of orientation was also lowered due to grafting.

In this paper, the results of X-ray diffraction studies on natural, cyanoethylated and formaldehyde (HCHO) crosslinked cotton samples grafted with methylacrylate (MA), ethylacrylate (EA) *n*-butylacrylate (BA), and methyl methacrylate (MMA) are reported. The lattice spacings, the crystallite sizes and crystallite orientation were determined.

Experimental Procedure

Preparation of samples — California cotton yarn was bleached and solvent extracted with methanol before use. Formaldehyde crosslinked cotton and cyanoethylated cotton samples were prepared as reported earlier[8]. Grafting of the natural cotton and modified cottons was carried out by the method described elsewhere[9].

X-ray diffraction patterns — The X-ray diffraction patterns were recorded with the Philips Norelco generator utilizing the flat film technique. A bundle of parallel fibres was fixed near the collimator. The

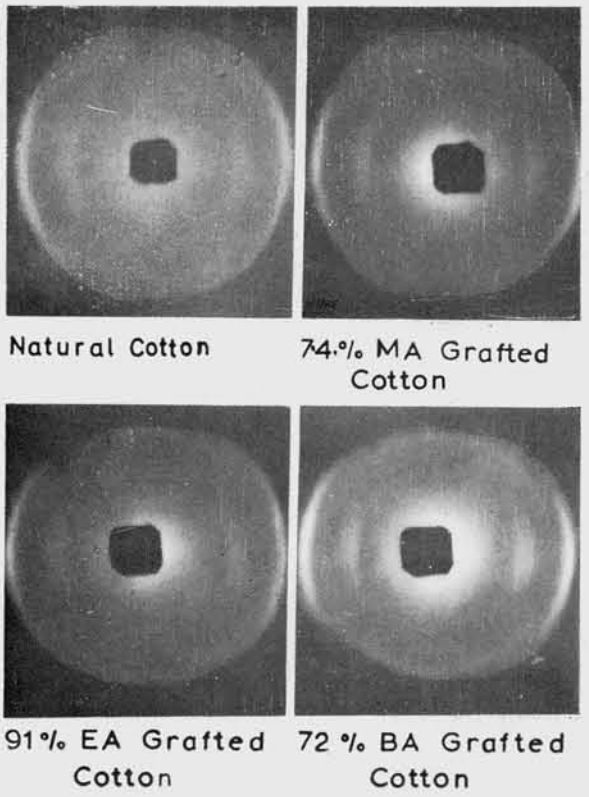

Fig. 1(a) — X-ray diffraction photographs of natural and grafted cotton

specimen to film distance of 5 cm was maintained. The X-ray beam was so adjusted as to completely bathe the fibre bundle. The undiffracted beam was so aligned as to fall at the centre of the photographic plate. The generator was operated at 30 kV and 30 mA. Filtered CuKα radiation was employed. The exposure period was 3 hr and the specimen size and film processing technique were standardized as far as possible.

The Joyce-Loebel microdensitometer Mark II with linear and polar tables was used for scanning the films. The Bragg angles for (101), (10$\bar{1}$) and (002) reflections, the intensity of these reflections at the equatorial and the azimuthal intensity distribution of (002) were determined. The angles were obtained from the linear scan and the corresponding d spacings were calculated for first order reflections using Bragg's equation : $n\lambda = 2\,d \sin\theta$.

Measurement of crystallite size and crystallite orientation — The crystallite size was determined using the Scherrer equation :

$$D_{hkl} = \frac{k\lambda}{\beta \cos\theta} \quad .. \quad (1)$$

The crystallite sizes perpendicular to (002) planes were calculated taking k as unity and β as the angular width at half maximum intensity.

The X-ray orientation factor was calculated using the equation :

$$f_x = 1 - 3\,\overline{\sin^2\alpha_0} \quad .. \quad (2)$$

The average value of $\sin^2\alpha_0$ was determined from the equation

$$\overline{\sin^2\alpha_0} = \frac{\Sigma I \sin^2\alpha_0 \cos\alpha_0}{\Sigma I \cos\alpha_0} \quad .. \quad (3)$$

Eq. (2) applies to natural cellulose and modified fibres in which there is no lattice conversion.

Results and Discussion

The X-ray photographs of natural, crosslinked cyanoethylated and grafted cotton cellulose fibre

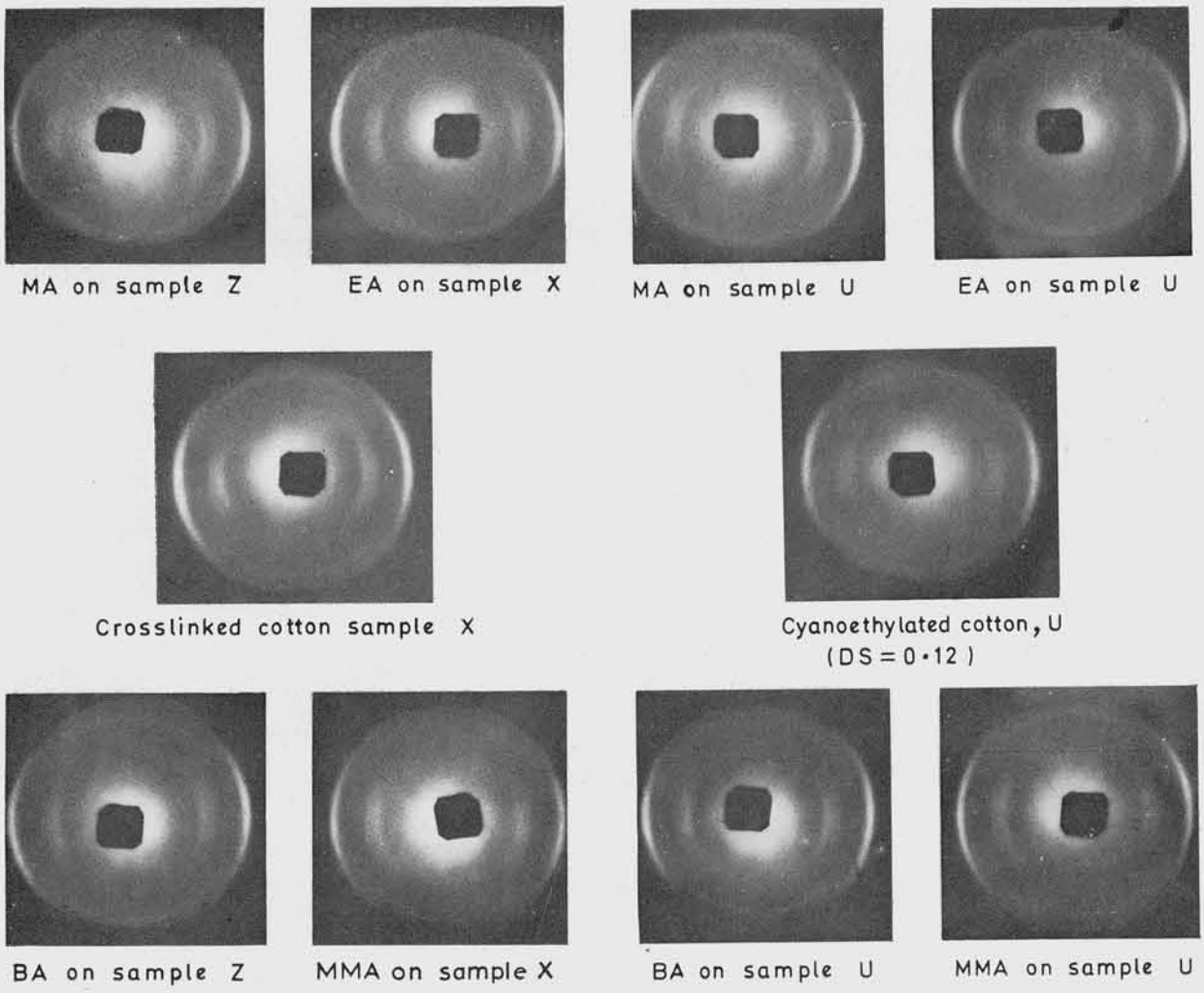

Fig. 1(b) — X-ray diffraction photographs of HCHO crosslinked and grafted cotton

Fig. 1(c) — X-ray diffraction photographs of cyanoethylated and grafted cotton

samples are shown in Figs. 1(a)-(c). It is seen that the prominent reflections of cellulose structure, viz. those due to (002), (101) and ($10\bar{1}$) planes along the equator and that due to (040) plane on the meridian are retained in the case of all modified and grafted samples. In addition to these sickle shaped reflections, some increase in diffuse background scattering is noticed. The intensity of diffuse scattering does not differ appreciably either with increase in graft-on percentage with a given monomer or with different monomers on natural cellulose. However, crosslinking with formaldehyde (0.15-1.0%) and cyanoethylation (0.12%) increases appreciably the intensity of diffuse scattering as compared to that in natural cellulose fibre. Further increase in the degree of crosslinking or degree of substitution affects the diffuse scattering intensity to a negligible extent.

The values of Bragg angle and interplanar spacings d_{101} and d_{002} for natural cotton, formaldehyde crosslinked cotton, cyanoethylated cotton and these cottons grafted with acrylate monomers are given in Table 1. It is seen that Bragg angles and the corresponding spacing values are constant, implying that no transformation of unit cell cellulose I takes place as a result of grafting. However, it is realized that these paratropic reflections do not throw any light on the possible changes in the dimensions along the fibre axis, which is the b-axis. Therefore, three conclusions emerge : (i) the grafted chains align parallel

TABLE 1 — X-RAY DIFFRACTION DATA

Sl No.	Sample	$\theta_{(002)}$	$\theta_{(101)}$	$d_{(002)}$ Å	$d_{(101)}$ Å
1	Natural cellulose	11°38′	7°43′	3.828	5.749
2	MA grafted 63.5%	11°33′	8°15′	3.856	5.381
3	do 74%	11°38′	7°43′	3.828	5.749
4	EA grafted 10%	11°32′	7°36′	3.858	5.837
5	do 91%	11°34′	7°38′	3.856	5.79
6	BA grafted 20.5%	11°25′	7°36′	3.89	5.79
7	do 72%	11°27′	7°31′	3.89	5.88
8	MMA grafted 13.5%	11°34′	7°36′	3.856	5.837
9	do 55%	11°23′	7°31′	3.91	5.88
10	FCC X	11°27′	7°31′	3.89	5.88
11	FCC Z	11°27′	7°36′	3.89	5.837
12	MA on FCC X	11°26′	7°24′	3.89	5.98
13	do Z	11°26′	7°36′	3.89	5.837
14	EA on FCC X	11°23′	7°24′	3.91	5.98
15	do Z	11°32′	7°34′	3.858	5.861
16	BA on FCC X	11°20′	7°24′	3.93	5.98
17	do Z	11°28′	7°36′	3.89	5.837
18	MMA on FCC X	11°26′	7°36′	3.89	5.837
19	do Z	11°26′	7°36′	3.89	5.837
20	CEC U	11°26′	7°34′	3.89	5.861
21	MA on CEC U	11°23′	7°36′	3.91	5.837
22	EA on CEC U	11°23′	7°24′	3.91	5.98
23	BA on CEC U	11°21′	7°18′	3.929	6.06
24	MMA on CEC U	11°21′	7°18′	3.929	6.06

FCC : formaldehyde crosslinked cotton; X : 0.15% bound formaldehyde; Z : 1.0% bound formaldehyde.
CEC : cyanoethylated cotton; U : DS of 0.12.

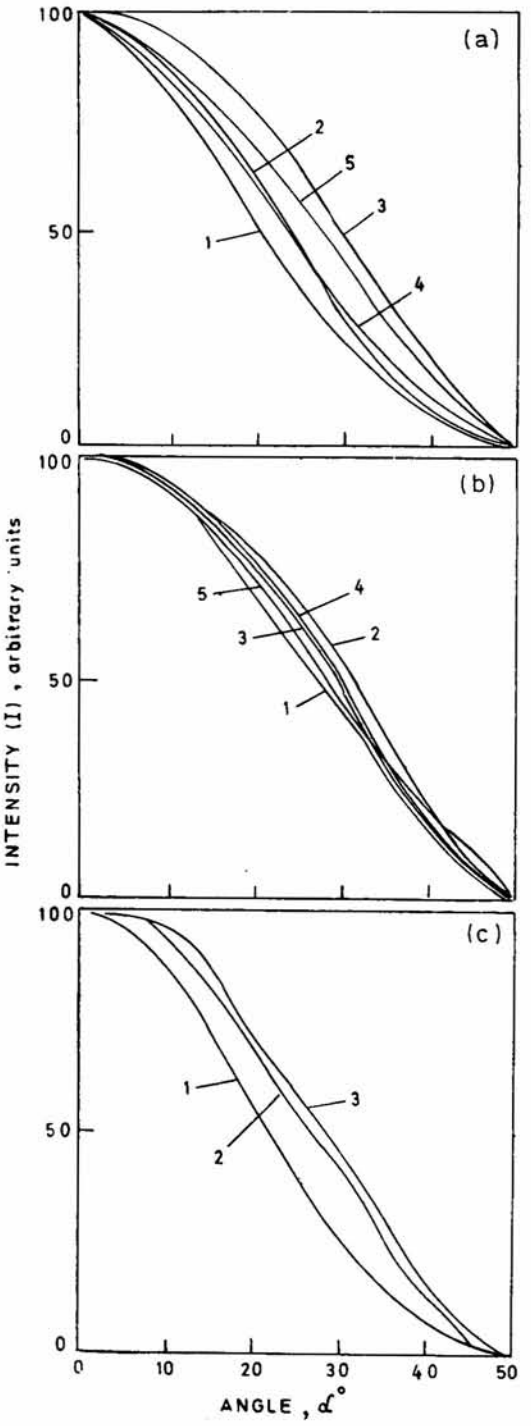

Fig. 2(a) — Intensity profiles of natural and grafted cottons [(1) natural cotton; (2) 74% MA grafted cotton; (3) 10% EA grafted cotton; (4) 72% BA grafted cotton; (5) 55% MMA grafted cotton]. Fig. 2 (b) — Intensity profiles of crosslinked and grafted cotton [(1) 1% HCHO crosslinked cotton; (2) MA on crosslinked cotton; (3) EA on crosslinked cotton; (4), BA on crosslinked cotton; and (5) MMA on cross linked cotton]. Fig. 2(c) — Intensity profiles of cyanoethylated and grafted cottons [(1) DS = 0.12, cyanoethylated cotton; (2) MA, EA and MMA grafted cyanoethylated cottons; and (3) BA grafted cyanoethylated cotton]

TABLE 2 — CRYSTALLITE SIZES AND X-RAY ORIENTATION FACTORS OF NATURAL, MODIFIED AND GRAFTED SAMPLES

Sl No.	Sample		Angular width at I max/2 radians	Crystallite size D_{002} Å	X-ray orientation factor (fx)
1	Natural cellulose		0.0338	46.6	0.795
2	MA grafted	63.5%	0.0380	41.4	0.692
3	do	74%	0.0372	42.4	0.740
4	EA grafted	10%	0.0355	44.4	0.7000
5	do	91%	0.0321	49.1	0.7340
6	BA grafted	20.5%	0.0388	40.5	0.7877
7	do	72%	0.0338	46.6	0.7600
8	MMA grafted	13.5%	0.0330	47.7	0.7720
9	do	55%	0.0313	50.4	0.7005
10	FCC	X	0.0338	46.6	0.7100
11	FCC	Z	0.0355	44.4	0.7607
12	MA on FCC	X	0.0270	58.3	0.7600
13	do	Z	0.0313	50.4	0.7300
14	EA on FCC	X	0.0338	46.6	0.7006
15	do	Z	0.0363	43.3	0.7270
16	BA on FCC	X	0.0338	46.6	0.7210
17	do	Z	0.0355	44.4	0.7210
18	MMA on FCC	X	0.0296	53.2	0.7457
19	do	Z	0.0346	45.5	0.7480
20	CEC	U	0.0338	46.6	0.7882
21	MA on CEC	U	0.0321	49.1	0.7700
22	EA on CEC	U	0.0346	45.5	0.7762
23	BA on CEC	U	0.0321	49.1	0.7540
24	MMA on CEC	U	0.0304	51.8	0.7700

FCC : formaldehyde crosslinked cotton; X : 0.15% bound formaldehyde; Z : 1.0% bound formaldehyde. CEC: cyanoethylated cotton; U : DS of 0.12.

to the b-axis in which case measurable changes should be observed in the diatropic reflections, (ii) the grafted chains may be parallel to either the a- or the b-axis with the same periodicity as those of the axes; and (iii) grafting may take place only in the space between the crystallites as a result of which only reorientation of crystallites may be possible, leaving the unit cell unchanged. Any of these three factors or all of them may be responsible for the observed situation. A stronger possibility, however, is that the grafting takes place in the less ordered regions of the fibre. If it is so, the unit cell dimensions should remain unchanged. Similar results were obtained by Imamura and coworkers[3] and Hori *et al.*[4] in the case of grafted fibres.

The half intensity width and the crystallite size for (002) reflection for all the samples are given in Table 2. The results indicate that the crystallite sizes of all cotton fibre samples are constant within the limits of experimental error. The independence of crystallite size D_{002} (which is a paratropic direction) with the modification and grafting on the cotton suggests that the chemical treatments will probably affect the crystal perfection, but not the size.

The values of orientation factor for natural and modified cellulose and these celluloses grafted with the acrylate monomers are also given in Table 2. Figs. 2 (a)-(c) show the intensity profiles of these samples. In the case of all the monomers, the X-ray orientation factor decreases due to grafting. The effect of nature of the monomer and extent of graft-on on the orientation factor is not clear from the results, because f_x does not follow any particular trend. As pointed out earlier, grafting takes place in the disorderd regions of the cellulose fibre in the neighbourhood of crystallites, and the dimensions of the unit cell are not affected. But the grafted chains tend to disorient the cellulose molecule chains, thus decreasing the crystallite orientation. Micrea[5] reported a similar result in the case of acrylonitrile grafting onto cotton.

It is obvious from the results presented in Table 2 that due to crosslinking with formaldehyde and cyanoethylation, crystallite orientation is decreased. During crosslinking and cyanoethylation reactions, considerable slack swelling takes place. This should result in decreased orientation. Grafting of these crosslinked and cyanoethylated cotton fibres with acrylate monomers does not decrease the orientation factor much.

Conclusion

The X-ray diffraction patterns of natural, modified and grafted cotton fibre samples do not show any change in the prominent equatorial and meridional reflection arcs. But due to modification and grafting, the intensity of the diffuse background scattering is increased slightly. Crystallite size is not affected as a result of modification and grafting, whereas crystallite orientation is decreased.

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