A Morphological Examination of Ceric Ion and Preirradiation Acrylic Acid-Grafted Rayon Fibers

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SYNOPSIS

Using the ceric ion and preirradiation methods, acrylic acid was grafted to rayon. The fiber used was large denier (50) continuous filament, particularly suited for examining changes in morphology and properties. The grafted fiber was given decrystallization treatments involving $ZnCl_2$ and NaOH. Optimization studies conducted to seek maximum graft with minimum homopolymer formation has been published elsewhere.[1] Also published earlier were the results of changes in mechanical and physical properties of the fiber resulting from the grafting and decrystallization treatments.[2] Presented in this article are the results on the effects of these treatments on the structure and the morphology of the fiber. The structural features examined were the molecular orientation, crystallinity and crystalline orientation, and the surface morphology. Based on the results of this study and those of the earlier,[2] it was possible to develop and propose a model of fiber structure that fits the present fiber. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Grafting has been known to provide the potential for significantly altering the chemical, physical, or mechanical characteristics of a substrate. In grafting studies the focus generally is on improving selected properties without significantly altering others. However, this is not always the case; the one targeted is achieved, but some others are deteriorated.

The properties that have been the focus of enhancement are high absorbency, ion exchange capabilities, elongation and elasticity, soil conditioning capabilities, dyeability, resistance to microorganisms, light, flame resistance, bactericidal/antimicrobial property, water proofing, and oil-resistance characteristics. Those that have generally not been pursued are the mechanical properties. A study conducted by the authors that involved ceric ion and preirradiation as the grafting methods, acrylic acid as the monomer, and rayon as the substrate, examined in detail the changes that occurred in the tensile properties, namely the tenacity, elongation at break, initial modulus, and the work of rupture.[2] The pretreatments given to the fibers to generate radicals resulted in a drop in the mechanical properties except initial modulus. Ceric ion initiation produced more degradative effects than did the preirradiation procedure. This was attributed to the additional oxidative and acidic effects in the case of the former. Grafting by both methods led to an initial enhancement of properties over the treated controls due apparently to the protective effect imparted by the presence of grafted material. However, as the grafting level increased, the properties degraded, and the rate at which the degradation occurred was greater in the ceric procedure. Decrystallization of grafted fiber with sodium hydroxide caused all properties to be decreased except peak strain, which increased. Reasons for these changes were speculated and are discussed in the article.

A chemical treatment given to a fiber that causes a change in the physical properties must also alter the structure in some respects. The changes in the structure of fibers that result from the grafting procedures are generally not known, although availability of such information is critical if grafting should become a useful tool in engineering products with specific behaviors. The general focus of this study was, thus, to develop an understanding of the structural basis of the changes observed in the prop-

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erties of fibers when they are given grafting and decrystallization treatments.

EXPERIMENTAL

To facilitate the proposed investigation, a large denier (50) continuous filament rayon fiber was used as the substrate. The grafting and decrystallization procedures used and the levels of graft obtained were the same as described in our earlier articles.[1,2] Briefly, for ceric grafting, the Soxhlet extracted and dried rayon samples were soaked for 2 h in 0.1*N* ceric ammonium sulphate solution in 1*N* sulfuric acid. They were rinsed in 10 : 90 methanol : toluene solution to remove excess initiator and dried with an air gun. Grafting was carried out under nitrogen with a 1*N* acrylic acid monomer solution in toluene at 35°C for various lengths of times to obtain different levels of graft. The samples were then washed in methanol, 1*N* H_2SO_4, 1*N* NaOH, and water. For radiation grafting, the purified rayon filaments were preirradiated in a Cobalt 60 chamber at the rate of 0.16 mrad/h under vacuum for 4 mrad at 25°C. An aqueous acrylic acid solution (75% AA, 25% H_2O), degassed, was introduced into the chamber through a break seal. The reaction was allowed to proceed for various lengths of times in a thermostated bath (40°C) to obtain different levels of graft. After grafting, the samples were washed in methanol, Soxhlet extracted, and dried in a vacuum oven. In both methods, percent graft was expressed as the increase in weight after drying over the initial weight (×100). For any given set of conditions, the graft yield found was highly reproducible.[1] From the samples obtained, sets of specimens grafted to three different levels each for the ceric and the radiation-grafted procedures were selected.

One of the important objectives in grafting acrylic acid to fibers has been to greatly enhance absorbency. The studies have shown, however, that such enhancements are generally not obtained by grafting alone; the samples must be postgraft decrystallized using suitable swelling agents.[3-5] For decrystallization in this study, two different agents were used: a 71% $ZnCl_2$ solution at 50°C for 1 h, and a 10% NaOH solution also at 50°C for 1 h. The samples were washed with deionized water and dried.

Characterization of Structural and Morphological Properties

A. Fiber Diameter and Linear Density

All measurements were made after equilibrating the samples with standard atmospheric conditions (21°C, 65% RH). Fiber diameters were measured with an optical microscope under high magnification. Linear density (denier) of fibers was assessed on a Vibroscope™ using ASTM procedure D 1577. The method is based on measuring the velocity of wave propagation under resonance through the fiber held under given tension in an alternating electric field. The decrystallized samples presented somewhat of a problem during this test. They often burnt at the point of contact and broke. Even those fibers

Table I Optical Retardation Values under Various Treatments

Sample Set	Graft Method	Graft Level (%)	Decrystallization Treatment	Optical Retardation (nm)
I	None	0	—	1261
II	Ceric[a]	−2[a]	—	1069[a]
III	Ceric	21	—	945
	Ceric	62		596
IV	Ceric	22	$ZnCl_2$	1202
	Ceric	57	$ZnCl_2$	1156
V	Ceric	23	NaOH	986
	Ceric	63	NaOH	586
VI	Radiation	51	—	1262
	Radiation	135	—	1069
VII	Radiation	44	$ZnCl_2$	1934
	Radiation	135	$ZnCl_2$	841
VIII	Radiation	48	NaOH	767
	Radiation	166	NaOH	202

[a] The fiber given ceric procedure without grafting.

that did not break appeared scorched. Therefore, only a limited number of tests of linear density could be obtained on these samples.

B. Molecular Orientation Under Optical Microscope

The samples were mounted in immersion oil and viewed in polarized light on a Leitz research microscope. A tilting compensator was used to determine the value of optical retardation. The method is based on gradually tilting the compensator until the retardation value of the specimen is exactly matched by that of the compensator. At this point, the birefringent material that was initially in the state of maximum brightness appears dark. From the values of the angle of tilt and the wave length of the light, the magnitude of the optical retardation is determined. The values reported represent the average of several individual measurements. Due to the uncertainties associated with the diameter of the noncircular fiber, the retardation values were used in discussion of results.

C. Crystalline Behavior under X-Ray

Diffraction patterns were obtained with a Siemen's x-ray Spectrophotometer using Cu Kα radiation. Both x-ray diffraction patterns using flat film technique and diffractometer traces were obtained. The fiber bundle was oriented with its axis perpendicular to the direction of the beam. In another experiment, the bundle was oriented with its axis at different angles to the beam, varying from 90° (perpendicular) to 45°, in 9° intervals. This was done because it was felt that a change in crystalline orientation will be more easily detected by a change in specific scattering intensity as the angle is changed. The measurements in this experiment were made at a fixed Bragg angle 2θ of 21.5°. The scattering by the planes oriented at this angle was found to be the most intense when the fiber was positioned in the vertical direction. The ratio of the intensity at an angle to that at 0° (vertical) is reported.

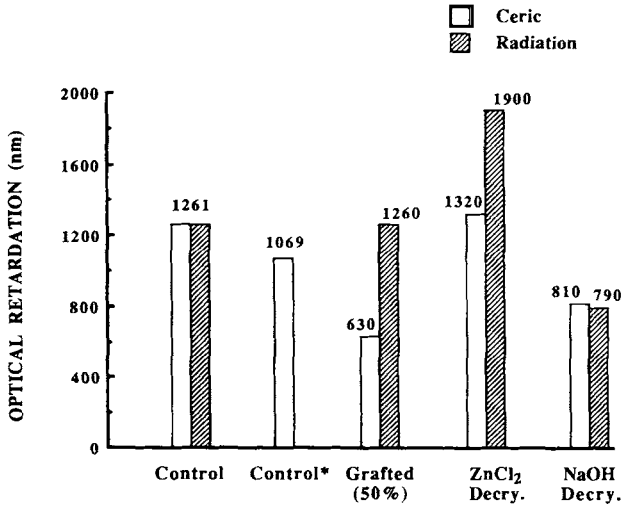


Figure 1 Comparison of optical retardation values obtained from various treatments. (Graft level = 50%).

D. Surface Morphology under SEM

Scanning electron microscopy was performed on a JEOL Model JMS-T300. The samples were first gold and then carbon coated prior to examination.

RESULTS AND DISCUSSION

Molecular Orientation

The values of optical retardation rather than birefringence are reported because the cross-sections of the fibers were noncircular and accurate measures of applicable thicknesses (perpendicular to the field of view, i.e., along the path of light) could not be easily made. The results are given in Table I. Although the behavior is somewhat irregular, general trends are obvious. The retardation value of the control specimen (1261 nm) decreased as it was taken through the ceric procedure without grafting. Grafting with the ceric procedure gave a decrease; generally the greater the graft level, the greater the decrease. With radiation grafting, however, the change was little or none. Decrystallization of the grafted samples with $ZnCl_2$ caused the retardation values to increase except in one case (compare set IV with III and set VII with VI). When decrystallization was carried out with NaOH, however, ceric grafted samples showed little change (compare V with III) although the radiation-grafted samples gave a significant decrease (compare set VIII with VI); the greater the graft level, the greater the decrease. The relative effects of various treatments are more clearly seen in Figure 1 where extrapolated values at comparable graft levels (50%) are illustrated.

Photomicrographs of fiber samples before, during, and after selected treatments are illustrated in Figures 2–4. Figure 2 shows control rayon filament under crossed polars. After soaking the fiber for 1 h in 71% $ZnCl_2$ at 50°C, one obtains a highly swollen sample with greatly reduced birefringence (Fig. 3A). If the rayon sample was grafted (ceric method) with acrylic acid and then treated with $ZnCl_2$ under the

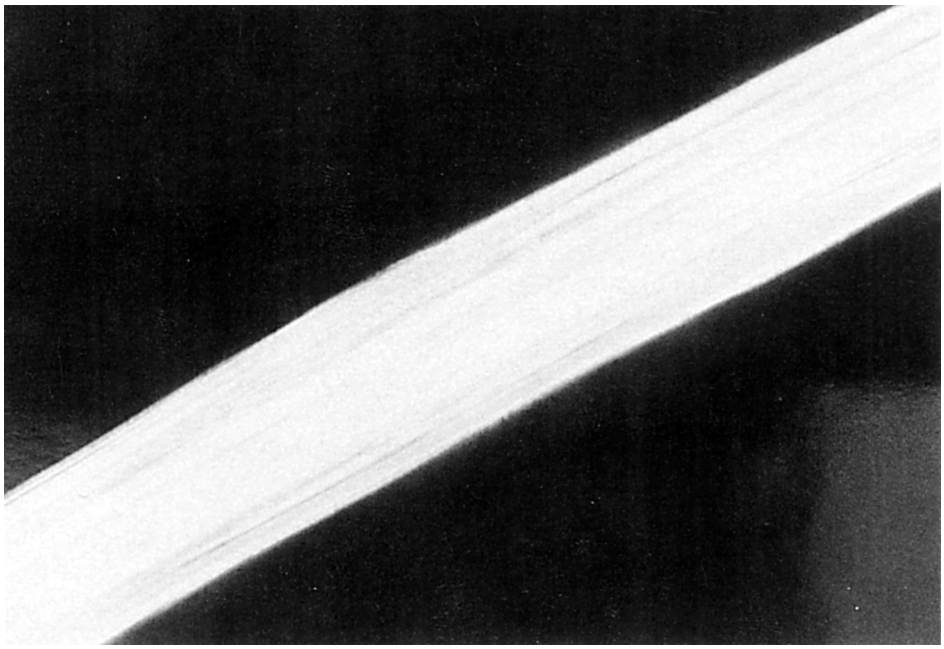


Figure 2 Control rayon under crossed polars.

same conditions as above, little change in dimensions are noted (Fig. 3B). This clearly indicates that the presence of acrylic acid graft has greatly reduced the ability of $ZnCl_2$ to diffuse and interact with the cellulosic material. Figure 4A illustrates an ungrafted rayon fiber given NaOH decrystallization treatment. Some swelling and loss of birefringence are obvious. However, the rayon fiber with 40% acrylic acid graft when subjected to the same decrystallization treatment shows a substantially different structure (Fig. 4B). NaOH greatly interacted with both the cellulose and the acrylic acid graft and caused high swelling and loss of birefringence.

These results, thus, show that treatment with $ZnCl_2$ in the present study did not cause swelling and loss of birefringence; rather, it led to an intensification of structure and, thus, to an increase in retardation and birefringence. In the studies by Zahran et al.[5] and Williams et al.[4] in which $ZnCl_2$ decrystallized acrylic acid-grafted fiber was converted to sodium salt, a very different structure was obtained. The fiber showed great potential for swelling and absorbing large quantities of water. Decrystallization with NaOH, on the other hand, caused significant swelling and loss of birefringence; the greater the grafting, the greater the effect. Because the ceric procedure itself included a NaOH wash, decrystallization with NaOH could not be expected to produce as great a change in the ceric as in the radiation grafted materials.

Wide Angle X-Ray Results

The WAX diffraction pattern shown in Figure 5A is similar to that typically obtained for a rayon fiber. There is a broad peak at $2\theta = 12.5°$ and two broad diffraction rings at 2θ of 21.5° and 20.5°. It is difficult to differentiate between the latter due to line broadening. The ceric grafted specimen showed an interesting behavior. The two diffraction rings that were only slightly distinguishable in the ungrafted rayon became more distinct (Fig. 5B). This tendency was also observed in the rayon control specimen which was taken through the ceric procedure without the monomer. As grafting increased further (60%), however, the two peaks became muted and only a broad peak could be observed. The radiation grafted specimen generally gave a broad peak at all graft levels. Decrystallization with $ZnCl_2$ showed little effect on the WAX patterns, although that with NaOH produced some but definite changes in the patterns (Fig. 6A and B). The latter treatment tended to split the single broad peak into two separate peaks and the spots into rings. These results generally indicate that the sodium hydroxide wash involved in the ceric grafting and decrystallization with NaOH led to some improvement in the perfection of crystallites, especially in samples with low levels of grafts. This was, perhaps, due to swelling and dissolution of small, imperfect, crystallites. The reappearance of broad peak structure in rayon containing

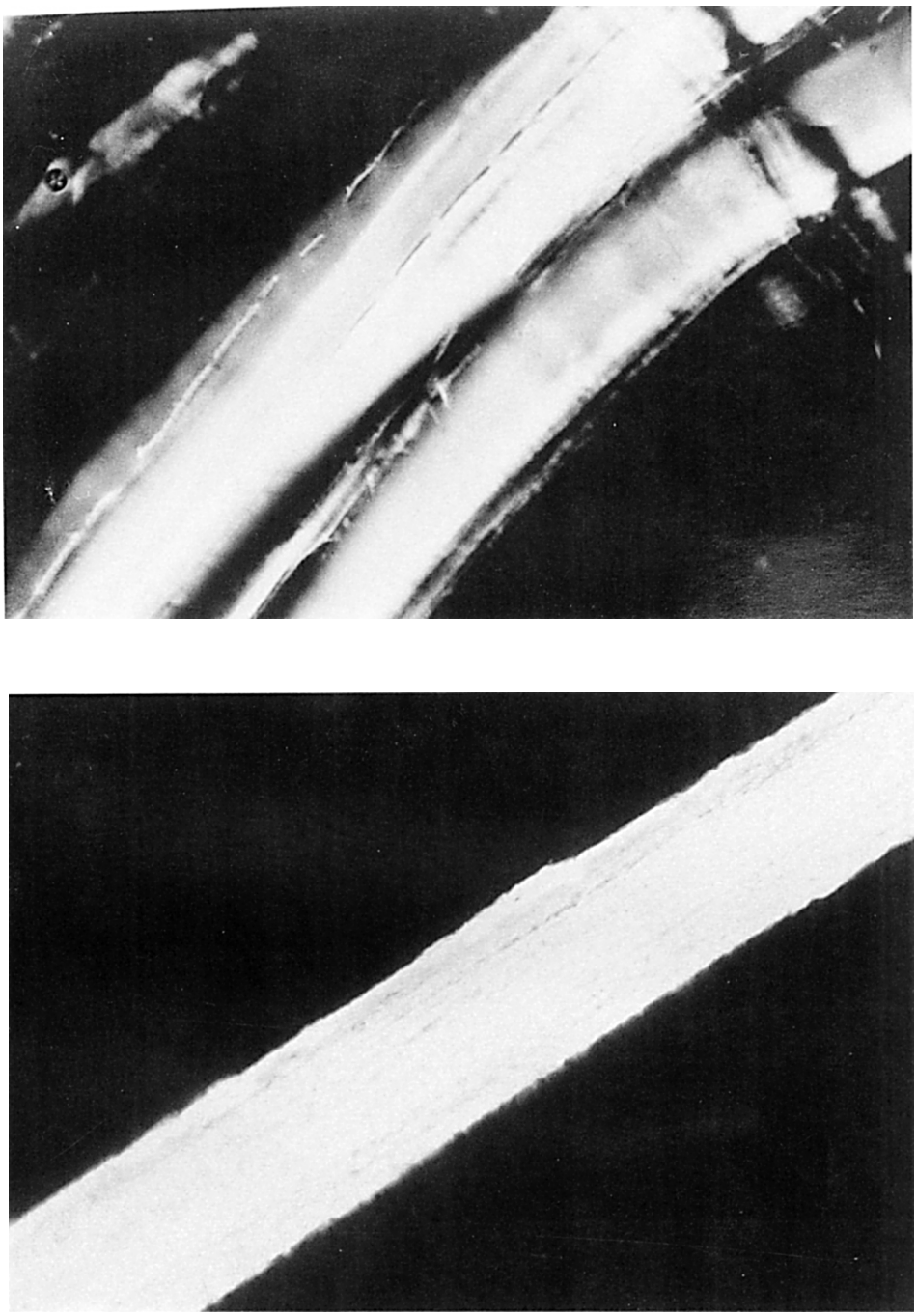
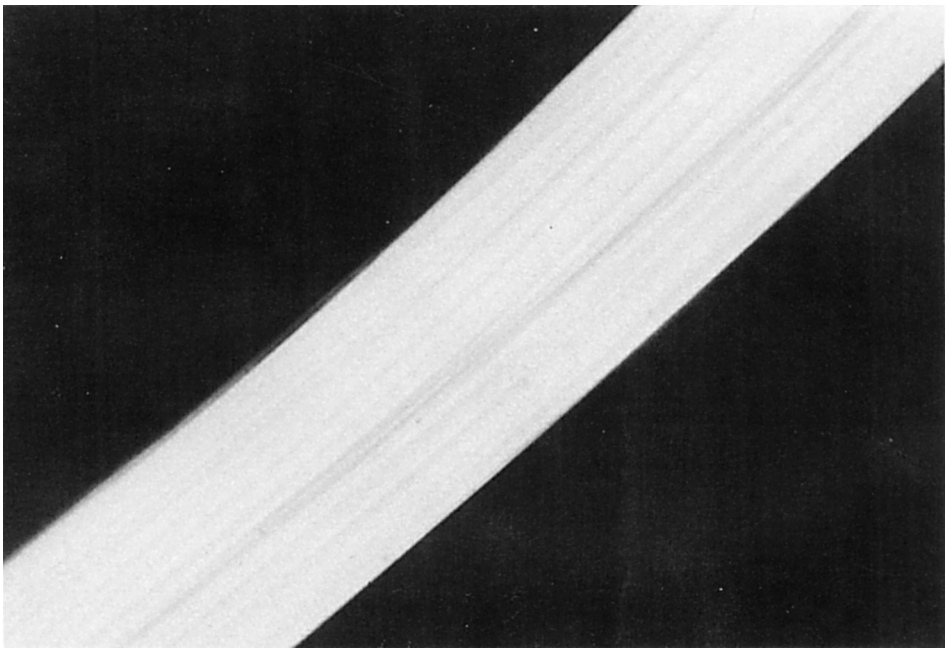


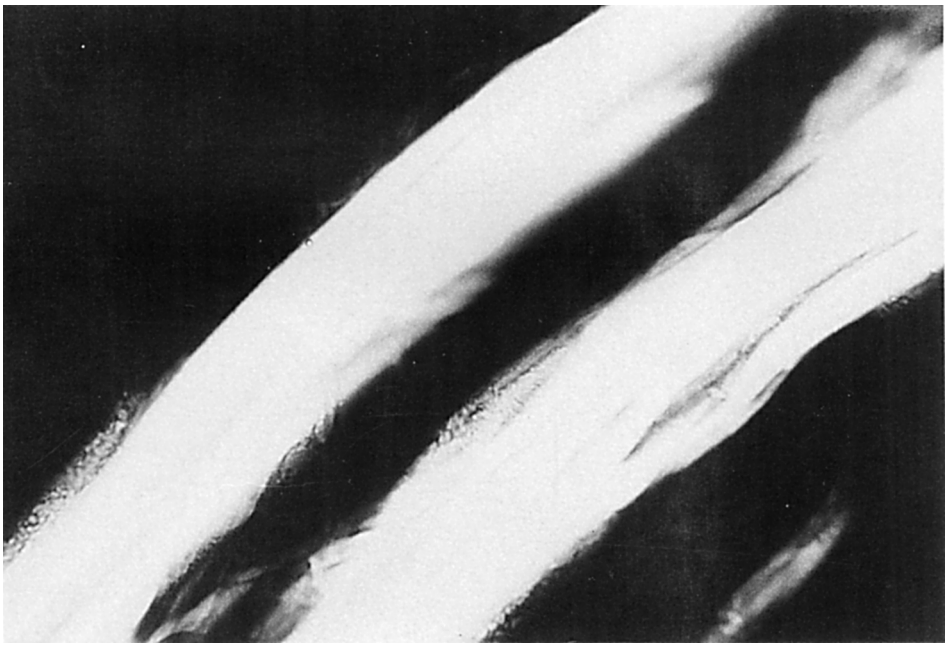
Figure 3 Rayon given $ZnCl_2$ treatment: (A) ungrafted; (B) grafted.

high levels of grafts was no doubt due to the hinderance presented by the grafted chains to the rearrangement of the molecules in crystalline order upon drying. Changing of the spots (Fig. 5A) into rings (Figs. 5B, 6A, and 6B) indicates that the crystallites became increasingly disoriented with the NaOH treatment. A support for these observations is obtained from the results found in diffractometer traces reported below.

The ratio of the intensities due to crystal scatters at $2\theta = 21.5°$, $20.5°$, and $12.5°$ to that due to amorphous scatter at $2\theta = 30°$ are given in Table II. All three intensity ratios show approximately similar trends with treatments. A change in these ratios give a rough idea about the change in the sample crystallinity with grafting and decrystallization. A decrease in the value with grafting should be expected, due to the addition of largely amorphous graft ma-



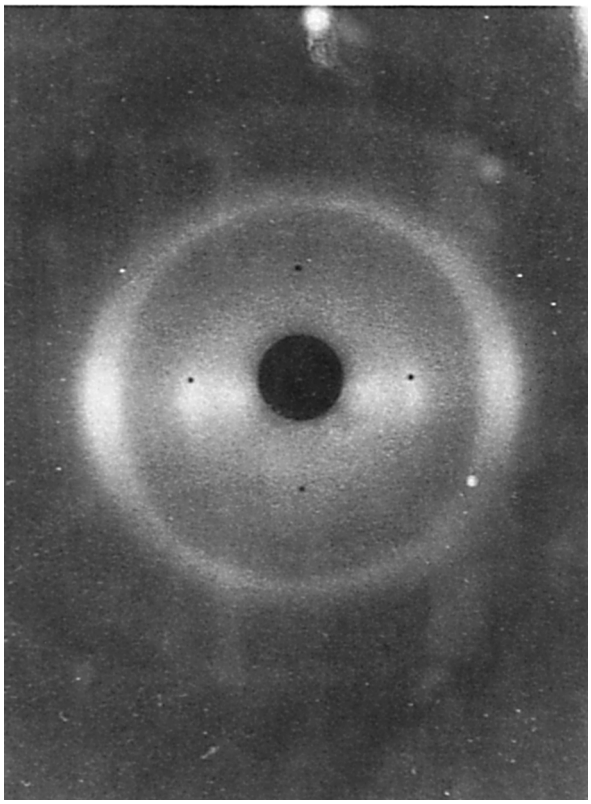
(A)



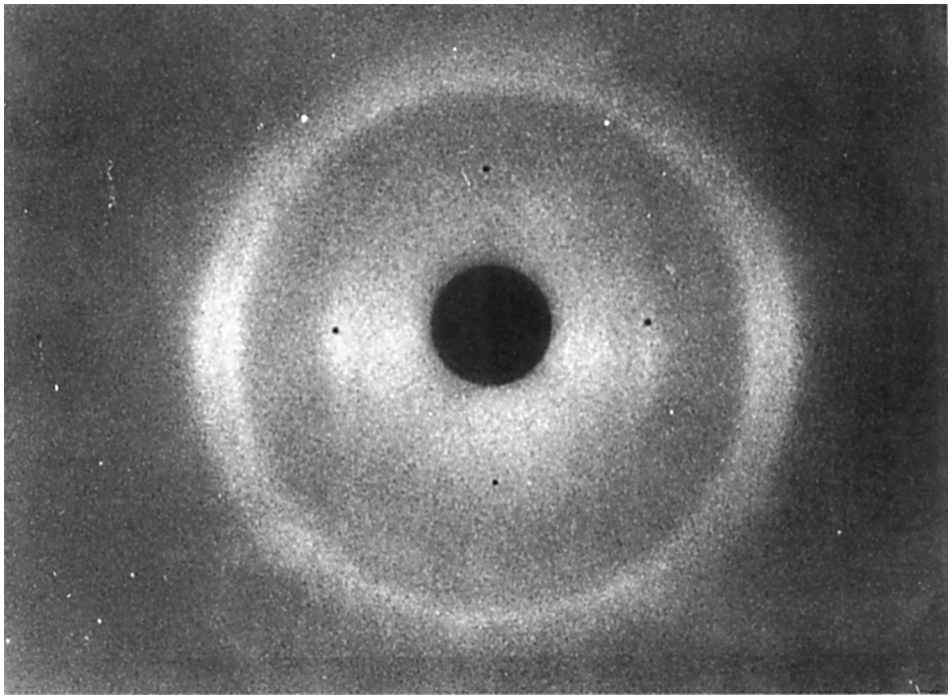
(B)

terial to the semicrystalline substrate, and this is generally the result obtained in all treatments except one (21% graft with ceric ion). Decrystallization with $ZnCl_2$ produced little effect on the ratios, indicating that the crystalline structure was not further affected by this treatment. In contrast, decrystallization with NaOH gave reduced intensities (over value of grafted materials). This indicates that the decrystallization treatment with NaOH gave a decrease in crystallinity, due, perhaps, to its causing small, imperfect, crystallites to dissolve and convert into amorphous regions.

Table III lists the values of the ratio of the intensities at different angles α to that at $\alpha = 0°$ for selected samples. It is seen that the ratio for the ungrafted rayon decreased as the angle with the ver-



(A)



(B)

Figure 5 X-Ray diffraction patterns of rayon filaments: (A) untreated rayon; (B) 20% ceric grafted rayon.

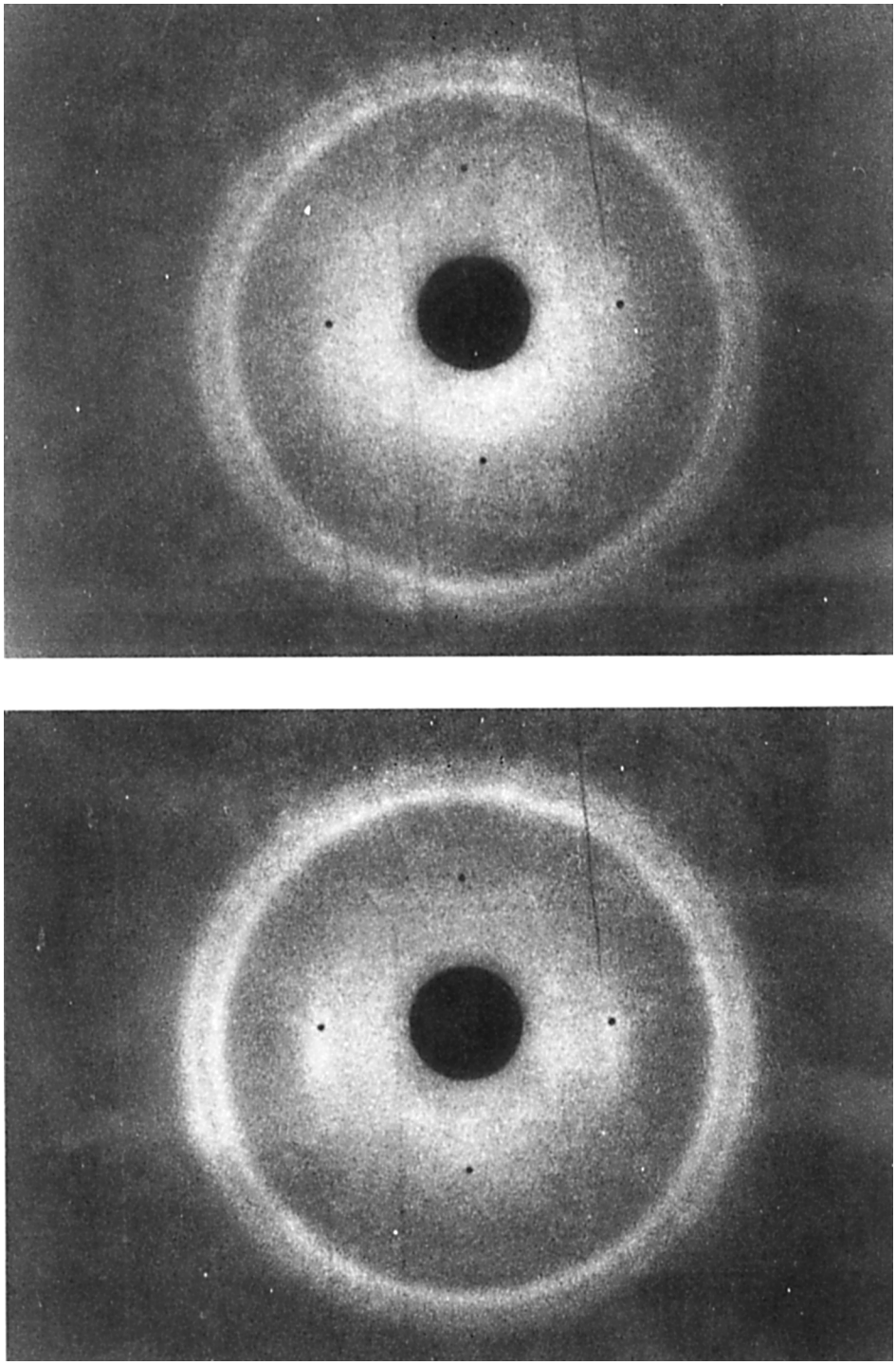


Figure 6 X-Ray diffraction patterns of NaOH decrystallized rayon filaments: (A) 60% ceric grafted; (B) 50% radiation grafted.

tical increased. This indicates that the structure is anisotropic with the crystallites oriented preferentially parallel to the axis of the fiber.

The change in the intensity ratio with the angle can be characterized by the magnitude of the slope which is given in the last column. A decrease in the slope with a treatment should indicate that the latter is causing a disorientation among the crystallites, and a slope of zero should be obtained if the crystallites are wholly randomly arranged. It is seen that

Table II Ratios of Crystal to Amorphous Scatter

Graft Method	Graft Level (%)	Decrystallization Treatment	Intensity Ratios, I_x/I_{30}		
			x = 21.5	20.5	12.5
None	0	None	5.25	4.96	2.67
Ceric	21	None	5.35	5.49	3.42
Ceric	62	None	3.20	3.19	2.14
Ceric	22	$ZnCl_2$	3.65	3.72	1.98
Ceric	57	$ZnCl_2$	3.55	3.48	2.16
Ceric	23	NaOH	3.45	3.54	2.10
Ceric	63	NaOH	2.75	2.91	1.69
Radiation	51	None	3.90	3.85	2.22
Radiation	135	None	3.15	3.25	2.01
Radiation	44	$ZnCl_2$	4.19	4.15	2.27
Radiation	135	$ZnCl_2$	3.12	3.16	1.94
Radiation	48	NaOH	3.33	3.35	1.91
Radiation	135	NaOH[a]			

[a] Values corresponding to graft level of 135% were not available in this case.

with grafting the slope decreased. While decrystallization with $ZnCl_2$ did not greatly affect it that with NaOH significantly decreased it.

Scanning Electron Microscopy Results

Changes in surface morphology of rayon fiber with various treatments were examined under SEM. The filament (Fig. 7) has striations on the surface parallel to the axis that are typical of the crenulated rayon fiber. The fiber shows a large lobed structure overlaid with smaller striation texture. Grafting via ceric initiation yielded a surface that has the graft bridging from one striation to another as seen in the 20% grafted fiber shown in Figures 8A and B. This feature involving surface graft became more pronounced as the grafting level increased to 60% (Fig. 8C). The fibers grafted via this method apparently also suffered damage on the surface in the form of longitudinal cracks, a tendency that was more pronounced at the higher graft levels. This damage most likely occurred due to the grafting procedure itself as the rayon control sample, exposed to the ceric procedure, also exhibited such damage (Fig. 9).

The surface morphology of the ceric grafted fibers was only slightly altered when the fiber was decrystallized with $ZnCl_2$. Decrystallization with NaOH, however, produced somewhat greater effect. The striations appeared to have twisted about each other (Fig. 10), a result noted at all graft levels.

The radiation-grafted samples showed greatly dif-

Table III Values of Relative Scatter Intensities at Different Angles

Method of Graft	% Graft	Postgraft Treatment	Relative Intensities at γ of						Slope ($Deg^{-1} \times 10^3$)
			0°	9°	18°	27°	36°	45°	
None	0	None	1.0	0.884	0.658	0.530	0.471	0.428	−13.5
Ceric	20.5	None	1.0	0.846	0.684	0.585	0.514	0.506	−11.3
Ceric	42.9	None	1.0	0.995	0.912	0.802	0.705	0.653	−8.6
Ceric	22.4	$ZnCl_2$	1.0	0.943	0.824	0.729	0.647	0.603	−9.4
Ceric	38.7	$ZnCl_2$	1.0	0.926	0.834	0.744	0.652	0.625	−8.9
Ceric	23.0	NaOH	1.0	1.030	0.961	0.860	0.810	0.810	−5.5
Ceric	39.1	NaOH	1.0	0.993	0.983	0.993	1.000	1.000	−0.1
Radiation	71.1	None	1.0	0.911	0.804	0.698	0.601	0.575	−10.0
Radiation	134.8	None	1.0	0.924	0.844	0.773	0.763	0.734	−6.0
Radiation	74.4	$ZnCl_2$	1.0	0.961	0.872	0.780	0.700	0.653	−8.3
Radiation	74.4	NaOH	1.0	0.969	0.942	0.932	0.918	0.907	−2.0

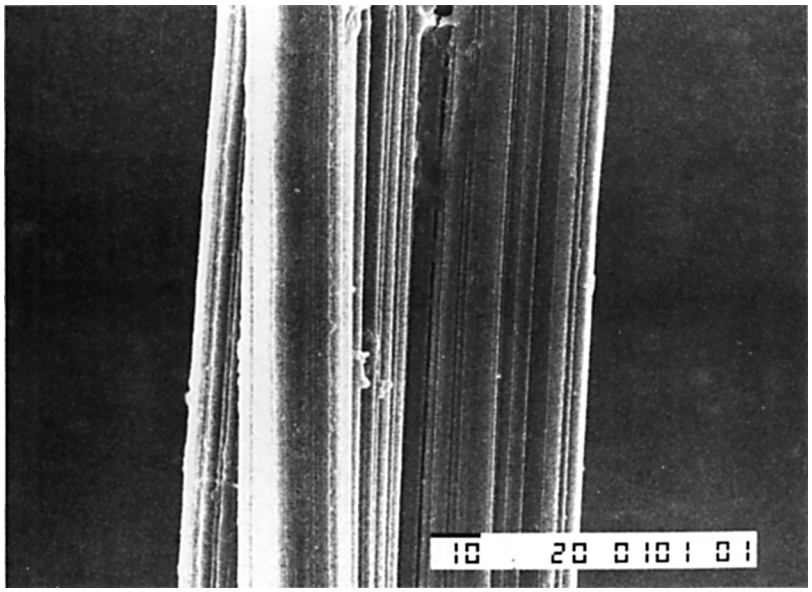
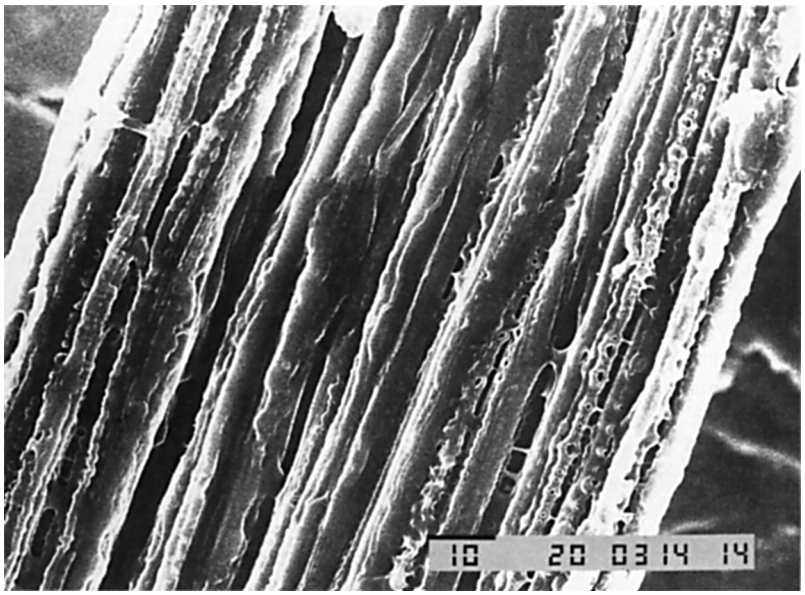


Figure 7 Rayon control after methanol extraction (750×).

ferent results. The grafted fibers showed little surface deposition (Fig. 11). The striations and the general morphology of the grafted fiber were very similar to those of the ungrafted specimen. Even at 166% graft, the fiber showed little evidence of surface graft. Occasionally, one could observe acrylic acid polymer bridging the gap from one striation to another or appearing in the form of small particulate matter on the surface (Fig. 11C).

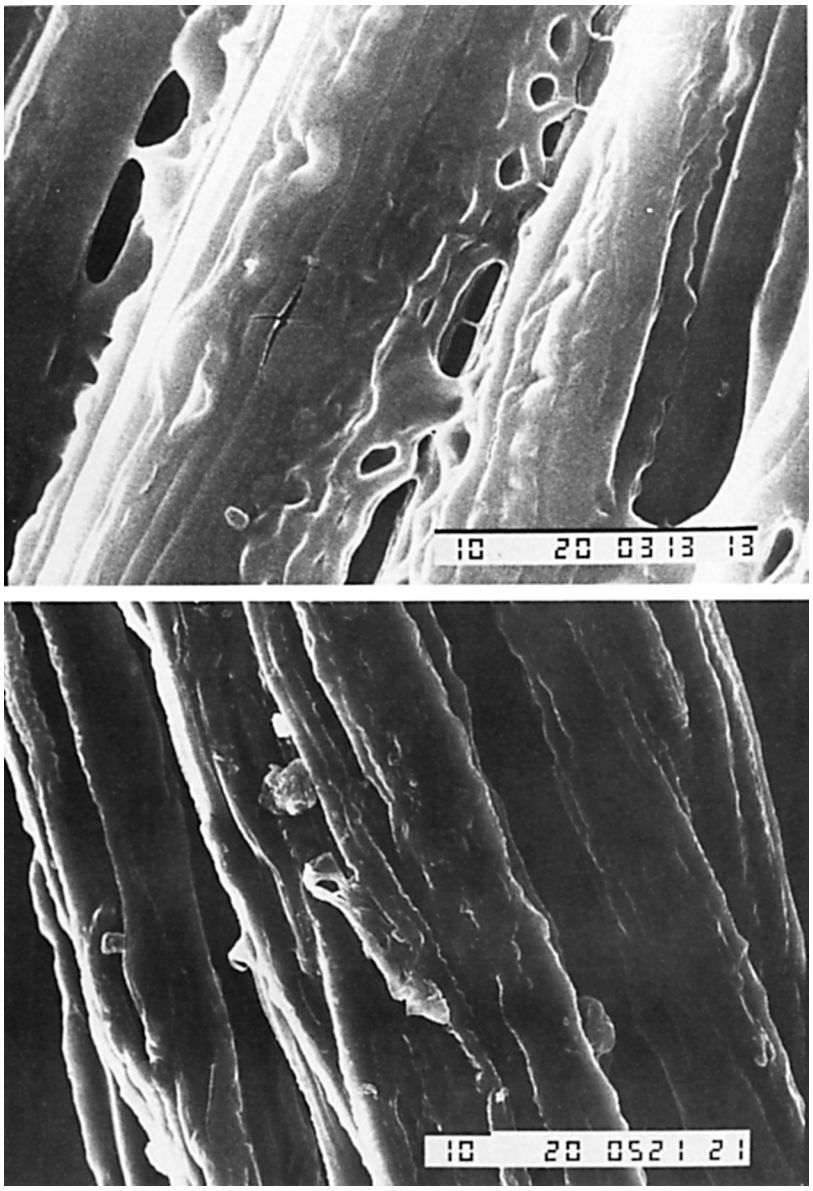
Decrystallization with $ZnCl_2$ produced little change in the morphology of the fiber for most part; however, in selected regions, the fiber topological structure had disappeared (Fig. 12). The effects observed in these areas could be due to selective decrystallization, possibly initiated by some fiber damage at these points.

The sodium hydroxide decrystallization, however, produced markedly different results. The striations on the surface became less distinct; at places, they even seemed to have disappeared. Those still present



(A)

Figure 8 Ceric ion grafted rayon: (A) 20% graft, 1000×; (B) 20% graft, 5000×; (C) 60% graft, 1000×.



(B)

(C)

Figure 8 (*Continued from the previous page*)

appeared twisted onto each other (Fig. 13), as was also observed with the ceric grafted samples. This phenomenon became more pronounced as grafting level increased. Indeed, at 166% graft the NaOH decrystallized samples had few fibrous-like structures remaining on the surface. The cracks apparent in the SEM photomicrographs were caused by the electron beam that easily damaged the structure.

SUMMARY

Effect of Grafting

Based on the results of structure and morphology obtained in this study, and of the tensile and physical properties published earlier,[2] one can put together a reasonably accurate hypothesis of the changes that took place in the fiber when it was grafted with acrylic acid.

Grafting via ceric ion initiation produced substantial changes. The diameter and the denier of the yarn increased with grafting.[2] It caused rearrangement in structure as well as some degradation. The latter should be obvious from the fact that the fiber taken through the ceric procedure without the graft had shown a significant decrease in tensile properties.[2,3] The former observation is supported by the results of optical and x-ray diffraction studies which showed a decrease in amorphous and crystalline ori-

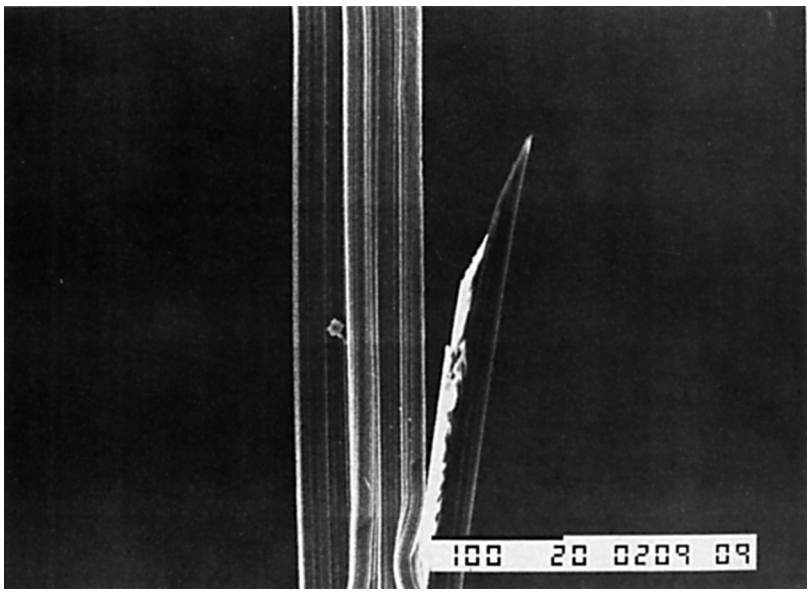


Figure 9 Rayon control exposed to the ceric ion procedure (200×).

entations as well as a decrease in crystallinity with grafting. These changes could be expected to occur due to the addition of acrylic acid mass, essentially amorphous, and the selected dissolutions and swellings in the structure caused by 1*N* NaOH used during the postgraft wash. The separation of the broad peak into somewhat more distinct arcs at low level graft indicates that the treatment caused dissolution of some small imperfect crystallites.

In spite of the care taken in minimizing surface deposition and formation of homopolymers by removal of excess initiator solution from the fiber prior to grafting, a large amount of graft was still found to lie at or near the fiber surface. This graft, noted only in ceric grafted samples, is surface graft (not homopolymer),[1] and resulted from the initiator solution diffusing out of the fiber interior when the monomer solution was added and reacting with the latter on or closer to the surface.

The radiation-grafted samples exhibited changes in tensile properties that were similar to those of the ceric-grafted samples. However, the changes

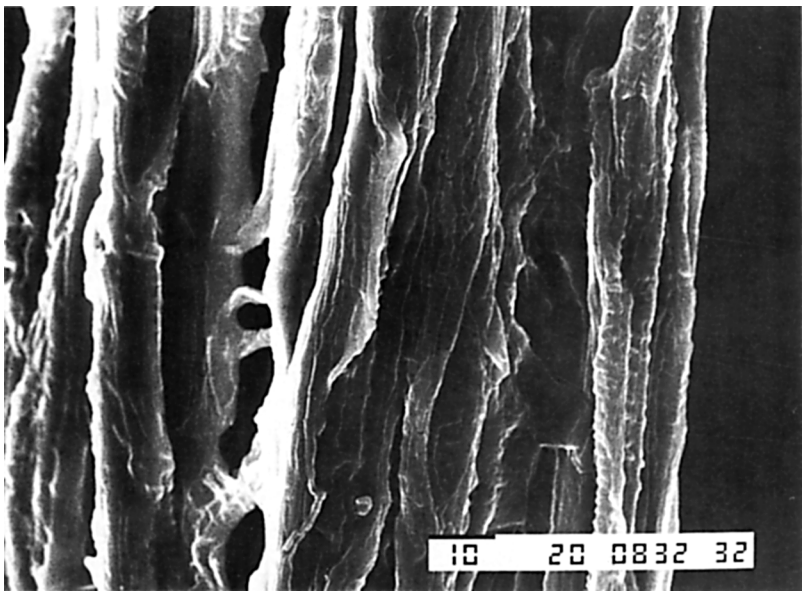


Figure 10 Ceric ion grafted rayon (20%) given NaOH decrystallization (1000×).

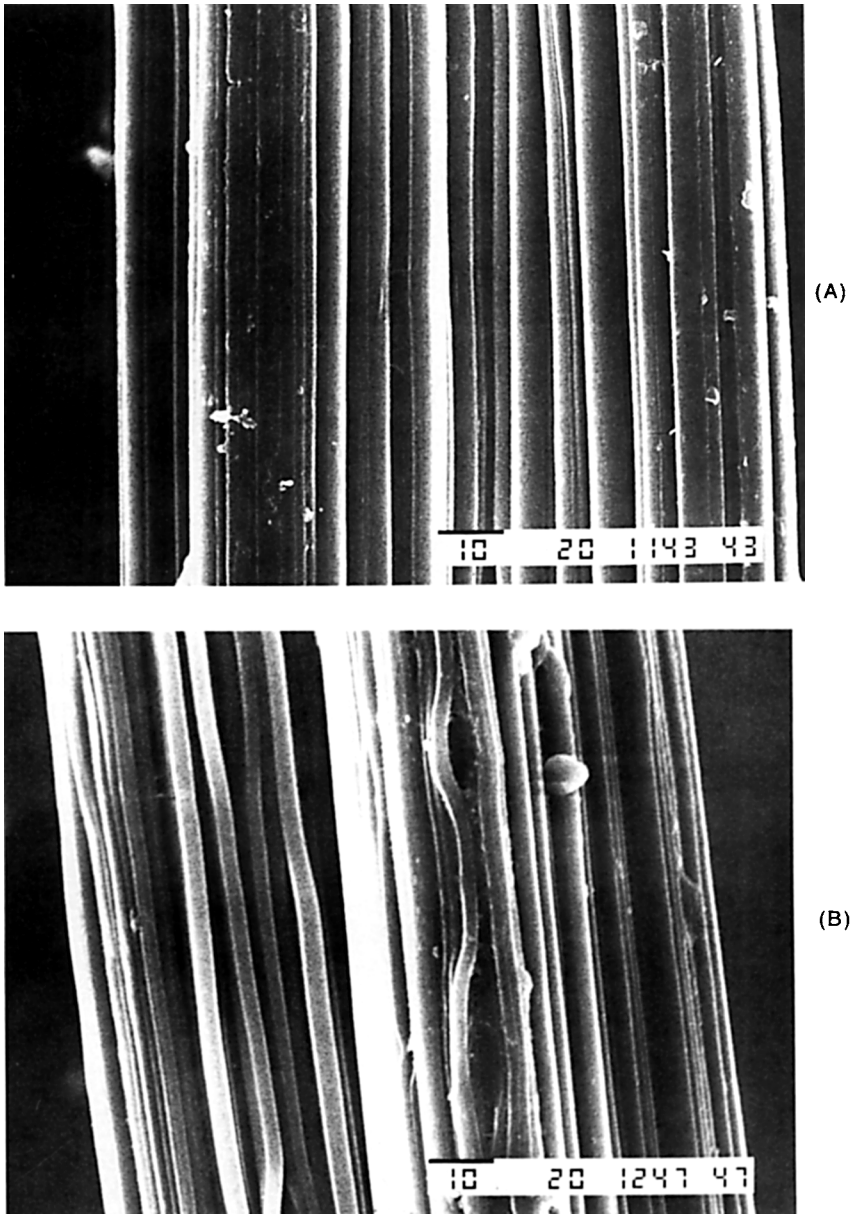
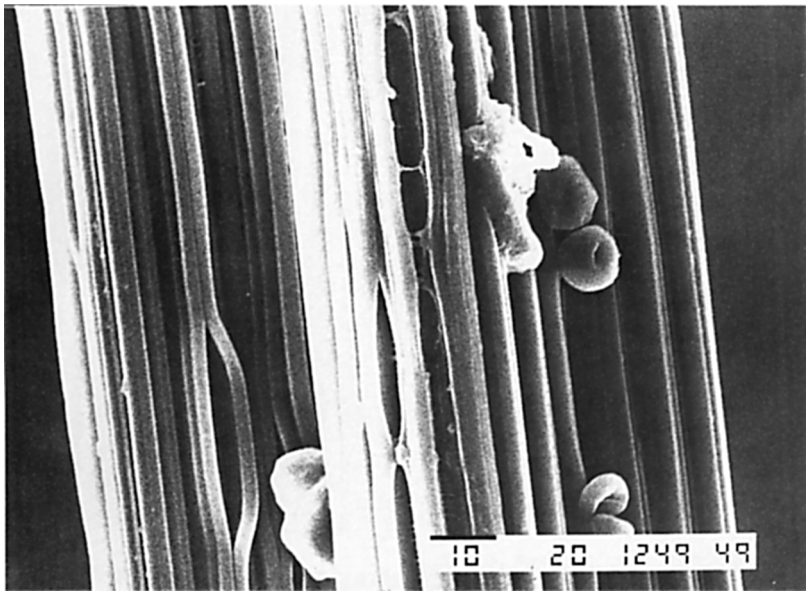


Figure 11 Radiation grafted rayon (1000×): (A) 50% graft, (B) 70% graft, (C) 70% graft showing some surface deposition.

were not as severe as they were with the ceric method. Because no postgraft washing procedure comparable to ceric method was involved, the changes noted could more or less be attributed to some degradation and disruption caused by irradiation of the fiber and to the addition of essentially amorphous polyacrylic acid mass to the fiber. The most outstanding difference between the two methods was in the surface morphology they led to. Although in ceric grafting most of the graft was found at or near the surface, in radiation grafting most of the graft was contained within the structure. The monomer diffused into the internal structure of the fiber and grafted at the free radical sites generated by the gamma radiation. Because there was no initiator in the form of solution involved, grafting could only take place by the diffusion of monomer into the interior.

Effect of Decrystallization

The grafted fibers exposed to the $ZnCl_2$ decrystallization treatment exhibited only slight changes in structural and morphological properties over those given by the grafted fibers. Consequently, the



(C)

Figure 11 (*Continued from the previous page*)

changes in the physical and tensile properties (not reported) were also relatively small. One possible reason for this is that although $ZnCl_2$ is a solvent for cellulose (Fig. 3A), it does not effectively interact and swell polyacrylic acid (Fig. 3B). The presence of grafted chains on and/or inside the surface, thus, restricts diffusion as well as lateral swelling. In view of the present results and those by the others who used $ZnCl_2$ as the decrystallizing agent[4,5], it appears clear that for $ZnCl_2$ to act as an effective decrystallizing agent for acrylic acid-grafted cellulose the conversion of the acid graft to alkali was necessary. This could be achieved by the conversion of the polyacrylic acid to the sodium salt form by reaction with NaOH in one of the last steps of the process.

Decrystallization of the grafted fiber with NaOH, however, led to marked changes in properties. In general, there was an increase in fiber diameter[2] that indicated that swelling had occurred and that the structure remained in the swollen state upon drying. Because the ceric procedure itself includes NaOH wash, one can expect that the changes in properties with decrystallization with this agent will not be as dramatic in the ceric-grafted samples as would be in the radiation-grafted ones. In general, retardation decreased which, when combined with increase in

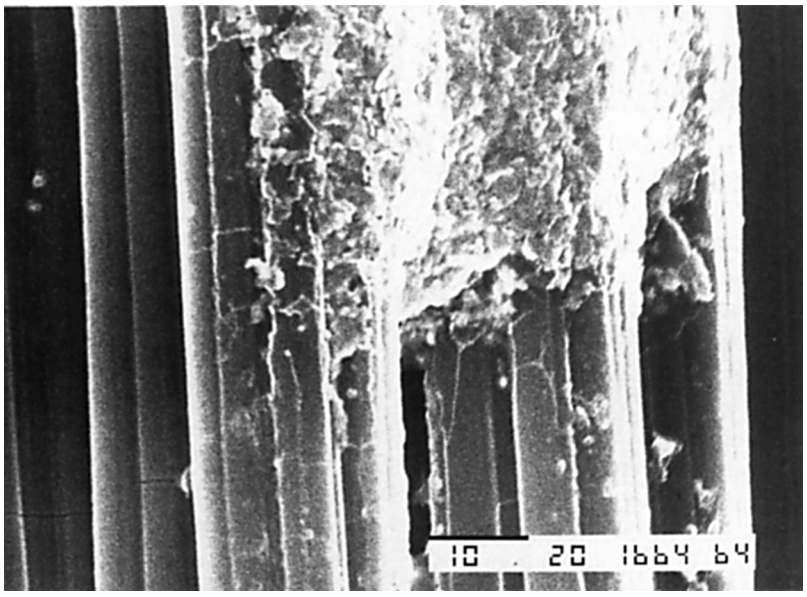


Figure 12 Radiation grafted fiber (70%) given $ZnCl_2$ decrystallization (1500×).

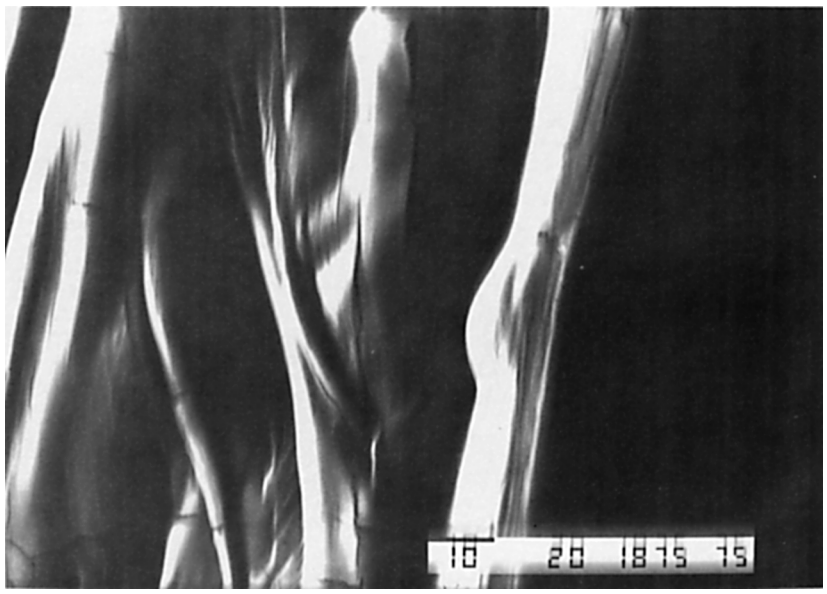


Figure 13 Radiation grafted fiber (50%) given NaOH decrystallization (1000×).

diameter, should give a decrease in birefringence. Also, both the crystal orientation and the degree of crystallinity decreased with NaOH treatment. A decrease in tenacity, initial modulus, and work of rupture and an increase in elongation at break[2] took place as expected due to the above changes in the structure and the plasticizing effect of sodium salt in the cellulosic and acrylic acid domains. The hydration capacity of sodium ions could also be expected to lead to large increases in moisture regain and water retention values as observed and reported earlier.[2,4,5] However, the dissolution of small and imperfect crystallites that took place led to some rearrangement and improvement in crystalline structure.

The apparent separation of some striations or fibrils and their twisting about each other could be expected to be the result of the NaOH reagent penetrating in areas between these structures, dissolving the molecules, and releasing stresses introduced during the fiber formation process.

Proposed Models of Fiber Structure

Based upon the observations made in this and the earlier articles, one can put together a reasonable model of fiber structure that applies to the rayon material used in this study. The major features of this model are: (a) Two-phase (or multiphase) structure having both amorphous and crystalline

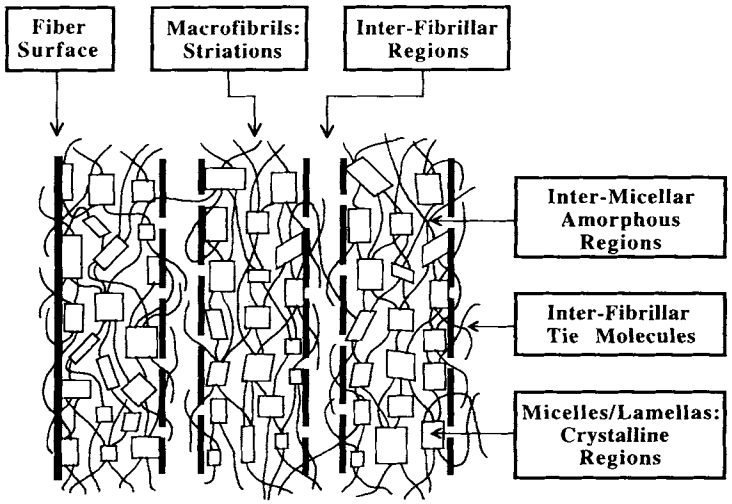


Figure 14 Proposed model of rayon fiber structure.

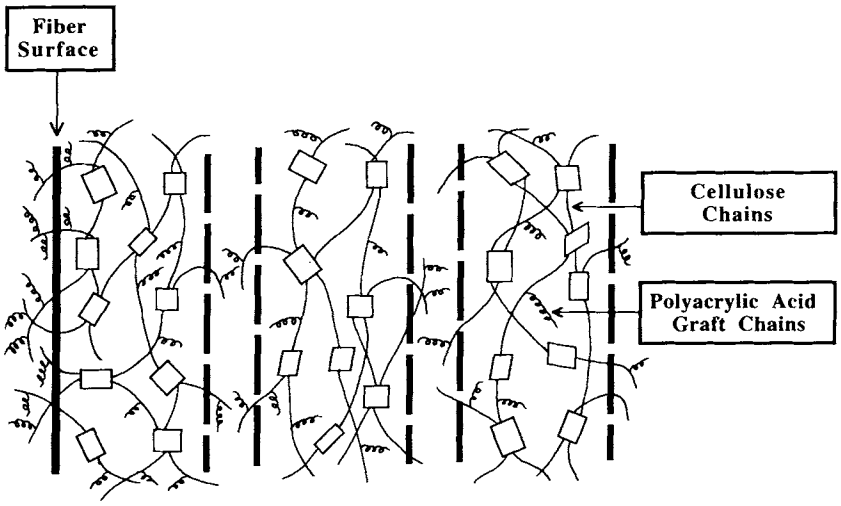


Figure 15 Proposed model of grafted and decrystallized rayon fiber.

regions of varying degrees of order and perfection; (b) fibrils of relatively large lateral dimensions, easily observable under SEM; (c) weak connections between the fibrils, easily disrupted by a swelling agent; and (d) regions of order and disorder of varying degrees distributed within the fibrils. These regions are of microscopic dimensions, but are detectable by x-ray diffraction.

Figure 14 shows the schematic of a model that incorporates these features and supports the data. Because the rayon fiber used in this study was manufactured by a conventional wet spinning process, although modified somewhat to allow for the extrusion and regeneration of a large denier fiber, the proposed model may well represent the macromolecular structure of conventional rayon fiber in general.

There have been many discussions of cellulose structure starting with that by Wooding[6] and more recently by Blackwell, Sarko, and Japanese workers. These have been covered by Hayashi[7] and Hatakeyama[8] and the references contained therein. Although there is no direct discussion of the morphology of rayon fiber in these articles, the proposed model is consistent with the observations contained. The effects of grafting and decrystallization on morphology of cellulose have not been discussed in detail. The model of Williams and Stannett[4] appears reasonable. The grafted side chains are presumably mainly in the intermicellar amorphous regions and only affect the properties, therefore, to a limited degree. This is clearly illustrated in the water sorption isotherms of refs. 4 and 2. The side chains do, however, enable the cellulose graft copolymers to be treated with a solvent for the cellulose component without completely dissolving. Upon removal of the solvent, the cellulose recrystallizes but only to a much lower extent as the copolymers properties restraint the process. The results of the present study show that not only the amount of crystallinity is reduced but also the structure became less oriented. These features make the material highly suitable for absorbing large amounts of fluid. The schematic of a model of grafted and decrystallized rayon fiber consistent with the present work is illustrated in Figure 15. This model, in particular, shows large surface graft as noted in ceric grafted samples. The structure of the radiation grafted sample will be slightly different in that most of the graft will be contained within the interior of the fiber.

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