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Hans A. Krässig[a]
[a] Research and Development Chemiefaser Lenzing, Lenzing, Austria

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X-Ray Investigations on Celluloses Grafted by the Thiocarbonation Method

HANS A. KRÄSSIG

Research and Development
Chemiefaser Lenzing AG
A-4860 Lenzing, Austria

INTRODUCTION

It is a pleasure for me to contribute to the symposium held in honor of my colleague and old friend Vivian Stannett. The topic of this contribution is results of x-ray investigations on graft modified cellulose fibers.

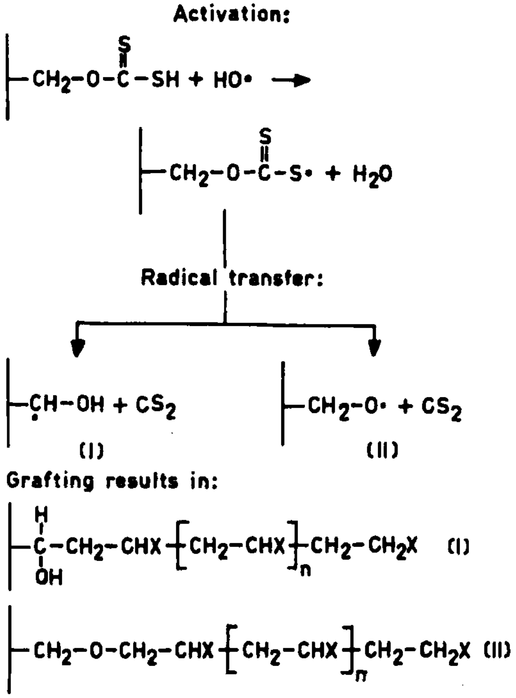
During the last decades the graft modification of cellulose has been of interest to numerous scientists who have studied grafting of cellulose from the scientific as well as from the industrial point of view [1].

Until recently very few industrial applications of grafting of cellulose were known. A new stimulus has been given to the graft modification of cellulose by the finding of the thiocarbonate peroxide grafting method, suggested in the early sixties by Faessinger et al. [2] and later by Dimov [3]. The high rate of radical transfer leading to numerous and short grafted side chains and to a remarkable suppression of homopolymer formation [4] combined with the appropriate technology to graft to relatively high add-ons in very short reaction times have led grafting to technical reality. In principle, it is possible today to perform graft modifications in line during commercial viscose staple fiber production [5].

This new situation has created new and increasing interest for the solution of problems such as the nature of the chemical bonds between the cellulose backbone molecules and the grafted polymer side chains, or for an answer to the question of where in the fiber structure the grafted polymer is attached and deposited. Reports on the mechanism of the grafting reaction and on the nature of the chemical bonds formed between the backbone cellulose molecules and the grafted side chains have been given by Faessinger and his co-workers [6], as well as also by Dimov [3]. It can be considered as proven that most of the side chains formed in this type of grafting are bound by C–C bonds and that a smaller portion of the side chains is linked by C–O bonds (see Scheme 1).

However, the question of where in the fiber structure the polymer side chains are attached still remains unanswered. Two possibilities exist theoretically:

1. The polymer addition occurs statistically on and along all cellulose chains.



SCHEME 1. Mechanism of grafting according to Faessinger and Conté.

2. The polymer addition occurs only topochemically on the surface or in accessible regions of the morphological units, such as the crystallites or fibrils, and in interlinking regions.

X-ray investigation should give an answer to this question. In case the polymer addition occurs statistically on and along all cellulose chains, a lattice widening should be observed at relatively low add-ons. However, in case the polymer addition occurs preferably on the surface of the morphological units building the fiber or in interlinking regions, the crystal structure of the cellulose substrate should stay intact at least for lower degrees of grafting. The first results of such investigations are reported in this paper.

EXPERIMENTAL PROCEDURES

For our investigations, a series of graft modified regenerated cellulose fibers was produced. The grafting was performed by reacting aftertreated but unfinished viscose staple fibers first with alkali and carbon disulfide to introduce a small number of thiocarbonate groups and to bring the thus activated cellulose fibers in contact with hydrogen peroxide and a monomer during a reaction time of about 45 min at 85°C. As monomers, acrylonitrile, styrene, and a phosphorous-containing vinyl monomer were used. Thus graft-modified fibers having polymer contents of 30 to 40% were synthesized for the x-ray investigations. The composition of these graft copolymers is listed in Table 1.

It should be mentioned that we have recently also synthesized corresponding graft copolymers having polymer contents of 50 to 70%. However, the x-ray investigations on these samples have not yet been completed.

The x-ray investigations were performed using a wide-angle fiber diffraction camera, developed by Kratky and co-workers at the University of Graz in Austria. The x-ray generator uses a Philips x-ray tube of high intensity giving copper (α) rays. The portion of copper (β) was eliminated by the use of a nickel filter. The operation conditions of the x-ray unit were 50 kV and 28 mA.

The primary intensity was adjusted before the start of each measurement with the use of a polyethylene tablet for a standard diffraction intensity, e.g., a fixed number of impulses per time unit, at a Bragg angle of $2\vartheta = 20°$. The fiber samples were parallel, gathered at both ends to form a bundle, and introduced into a quarz capillary of standard size. The bundle was then stretched to remove the natural crimp of the fibers and glued into position. The weight of the fiber bundles was approximately 0.11 g/5 cm. The exact amount was adjusted in such a way that the attenuation factor (A_s) for all fiber samples was approximately of the same order of magnitude.

TABLE 1

Sample	% Add-on	Composition of Graft	
		%Cellulose	% Polymer
Unmodified Viscose Staple Fibers	–	100.0	–
–Grafted with Styrene	72.4	58.0	42.0 1)
–Grafted with Acrylonitrile	52.4	65.6	34.4 2)
–Grafted with P-containing Vinyl Monomers	41.8	70.5	29.5 3)

1) From gravimetric determination of polymer portion after hydrolysis of cellulose back-bone.

2) From nitrogen content of graft.

3) From phosphorus content of graft.

For the determination of the equatorial diffractions used to estimate the degree of order, a quarz capillary with parallel fiber bundles was positioned horizontally into the x-ray beam and the diffracted intensities were measured by moving a counter along the equator, measuring the diffracted intensity in the range of the Bragg angle $2\vartheta = 3°$ to $42°$ as impulses per time intervals of 4 min.

The measurements along the azimuth for the determination of the degree of orientation were performed by turning the capillary with the fiber bundle stepwise from the horizontal position to the vertical position and back to the horizontal position. The turning was performed near the horizontal position in steps of 1°, and for greater deviations than 10° in steps of 5°. The counter was thereby put in fixed positions corresponding to the 2ϑ values of the A_0 and the A_3 reflections. The diffraction values obtained were corrected for Compton scattering and for the scattering of the empty capillary.

The corresponding powdered polymers were prepared from acrylonitrile, styrene, and the phosphorous-containing vinyl monomer by polymerization in suitable solvents, using hydrogen peroxide as polymerization catalyst. When the polymer formed was soluble in the solvent used, it was precipitated by addition of a polymer nonsolvent. X-ray investigations on these polymers to determine their wide-angle scattering were performed by placing the powdered polymers into quartz capillaries. Here, too, the attenuation factor (A_s) was determined in each case.

RESULTS AND DISCUSSION

Microscopical investigations on the cross sections of cellulose fibers grafted to various add-ons have indicated that in the course of the grafting reaction an increase in cross-sectional area occurs which is directly proportional to the relative amount of added polymer, as illustrated in Fig. 1. Since polyacrylonitrile and polystyrene both have densities appreciably lower than cellulose, this increase in cross-sectional area is approximately 15 to 20% lower than what is theoretically expected. The polymer incorporation apparently is accompanied by some densification of the fiber structure.

In addition, microscope studies on cross sections of acrylic acid graft-modified cellulose fibers, which were dyed with Victoria Blue, have indicated that the side chain polymer is distributed relatively uniformly throughout the whole cross section.

For the evaluation of the equatorial wide-angle diffraction patterns of the graft copolymers, the assumption was made that the added copolymer was mainly attached to the surface of the fibrillar aggregates forming the fiber or was incorporated in the interstices between these fibrillar aggregates. Should this assumption be correct, the diffraction behavior of the graft-modified fibers would be the sum of the diffraction of the cellulose portion and of the polymer fraction in the grafted samples.

In order to prove the validity of this concept, a computer program for curve fitting was designed by which the best fitting constants K_1 and K_2 in the formula

$$I_{\text{graft}} = K_1 I_{\text{cellulose}} + K_2 I_{\text{polymer}}$$

were derived.

In Table 2 the result of each curve fitting is shown for the fiber graft modified with styrene. The standard deviation of the calculated diffraction pattern from the experimentally observed pattern was found to be only ±4.73% in this case. Also, in the two other cases these differences of the calculated diffractograms were well below 5% of the total observed diffraction intensities over the whole range of Bragg angles.

The fractional factors K_1 and K_2 for the contribution of the cellulose and of the polymer to the diffracted intensities are composed of the weight fraction of each of the components in the x-ray beam and the ratio of the attenuation factors:

$$K_1 = \frac{A_s\,(\text{graft})}{A_s\,(\text{cellulose})}\;\frac{m(\text{graft}) \times \%\ \text{cellulose in graft}}{m(\text{cellulose})}\;K_1'$$

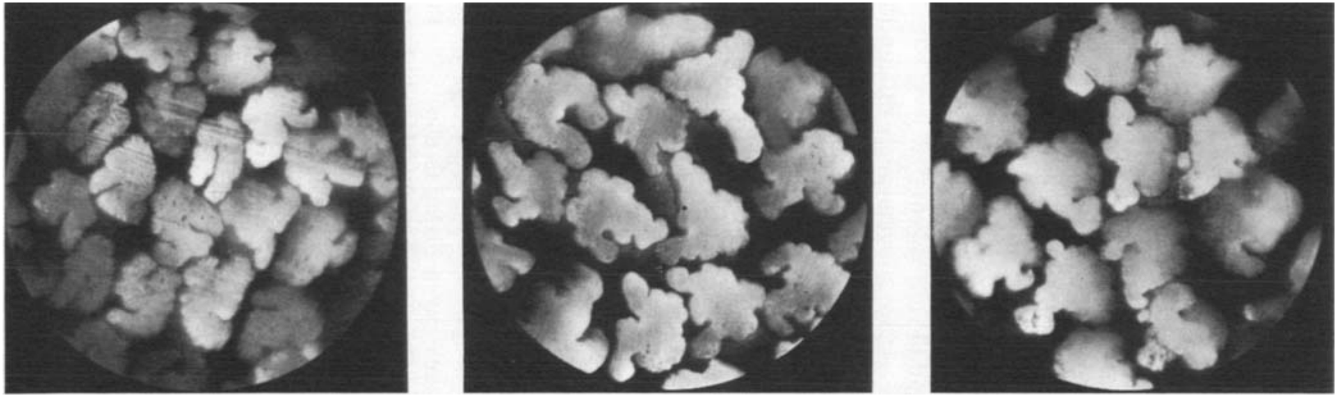


FIG. 1. The effect of graft modification of viscose fibers on cross-sectional area. Left: Crimped rayon staple, with a denier of 8.74 and a ratio of 1; and with a relative cross-sectional area of 143 and a ratio of 1. Center: Grafted with a phosphorous-containing polyvinyl compound (46%), with a denier of 12.9 and a ratio of 1.47; and with a relative cross-sectional area of 204 and a ratio of 1.43. Right: Grafted with acrylonitrile (45%), with a denier of 12.7 and a ratio of 1.45; and with a relative cross-sectional area of 212 and a ratio of 1.48.

TABLE 2. X-ray Diffraction of Viscose Fibers Grafted with Styrene Composed of the Diffraction of the Cellulose and Polymer Portion

2ϑ	$I(\text{Cell.}) \times K_1$ (1)	$I(\text{Polym.}) \times K_2$ (2)	$I(\text{Graft})\text{calc.}$ (1) + (2) = (3)	$I(\text{Graft})\text{ exp.}$ (4)	s in% (4)-(3)
9.0	6781	7406	14187	13974	+ 1.52
9.5	7703	7899	15602	15429	+ 1.12
10.0	8959	8115	17074	16579	+ 2.98
10.5	11352	7942	19294	18647	+ 3.47
11.0	13369	7758	21450	21717	- 1.23
11.5	17801	7388	25189	26140	- 3.64
12.0	21338	7338	28676	29841	- 3.90
12.5	21404	7167	28571	29420	- 2.89
13.0	19336	7319	26655	26435	+ 0.83
13.5	17307	7192	24499	23934	+ 2.36
14.0	17209	7423	24632	23830	+ 3.37
14.5	18264	7817	26081	24562	+ 6.19
15.0	19640	8203	27843	26684	+ 4.34
15.5	22048	9041	31089	28551	+ 8.89
16.0	22147	10046	32193	29980	+ 7.38
16.5	23305	10613	33918	31753	+ 6.82
17.0	24140	11690	35830	33340	+ 7.47
17.5	25571	12960	38531	36258	+ 6.27
18.0	28463	13907	42370	40177	+ 5.46
18.5	33930	14781	48711	46745	+ 4.21
19.0	41186	15378	56564	56719	- 0.27
19.5	51000	15616	66616	68245	- 2.38
20.0	58947	15375	74322	75760	- 1.90
20.5	61161	14170	75331	75610	- 0.37
21.0	64442	13149	77591	76303	+ 1.69
21.5	68247	11760	80007	81350	- 1.65
22.0	66584	10440	77024	79111	- 2.64
22.5	54811	9299	64110	64358	- 0.39
23.0	39293	8288	47581	46719	+ 1.85
23.5	27627	7318	34945	34110	+ 2.45
24.0	20681	6696	27377	27455	- 0.28
24.5	17073	6131	23204	23481	- 1.18
25.0	14798	5724	20522	20781	- 0.12
				$\bar{s}=$	4.73

$$K_2 = \frac{A_s(\text{graft})}{A_s(\text{polymer})} \; \frac{m(\text{graft}) \times \%\ \text{polymer in graft}}{m(\text{polymer})} \; K_2'$$

where the A_s's are the attenuation values at which the corresponding diffraction patterns on the base cellulose, on the homopolymers, and on the graft-modified cellulose fiber samples were taken. m indicates the mass of the cellulose, of the homopolymers, and of the graft-modified samples in the x-ray beam during these diffraction measurements.

We have found, as can be seen from Table 3, that for all the grafts investigated thus far, the diffraction intensities exhibited by the grafted samples are in all cases larger than expected, e.g., K_1' and K_2' were found to be larger than 1. The most probable cause for this increase in diffracted intensities over the individual diffraction behavior of the components of the grafts is an increase of the degree of order coming from compressive forces which evolve during the incorporation of the polymer into the fiber structure. This was already indicated by the fact that the increase in cross-sectional area caused by the grafting was 15 to 20% smaller than expected from the polymer add-on and the density of the corresponding homopolymers. This structure improvement most probably occurs in the less-ordered regions of the cellulose and polymer portions of the grafts. However, so far we have no evidence to decide whether this structure improvement is acting on both components or on the cellulose portion only. More information is expected to come from similar investigations on graft-modified fibers grafted to higher polymer add-ons.

In order to clarify whether grafting changes the orientation of the structural elements in the backbone cellulose fibers, azimuthal scans through the A_0 and the A_s reflections of the base cellulose fibers and of the grafted copolymers were taken. In the evaluation of these

TABLE 3. Result of the Analysis of the X-ray Wide-Angle Diffraction of Grafted Viscose Fibers

Sample	Mass Factor	A_S-Ratio	K'		K (exp.)		K(Computer)		$\bar{s}$ in %
			K_1'	K_2'	K_1	K_2	K_1	K_2	
Styrene grafted Viscose Fibers:									4.73
– Cellulose Portion	0.580	0.996	1.215	—	0.70	—	0.69	—	
– Styrene Portion	0.354	0.708	—	1.215	—	0.30	—	0.31	
Acrylonitrile grafted Viscose Fibers:									3.62
– Cellulose Portion	0.656	0.928	1.292		0.78	—	0.74	—	
– Acrylonitrile Port.	0.394	0.761	—	1.292	—	0.39		0.41	
P-Vinyl grafted Viscose Fibers:									2.89
– Cellulose Portion	0.705	0.650	1.309	—	0.60	—	0.61	—	
– P-Vinyl Portion	0.179	2.257	—	1.309	—	0.53	–	0.52	

$$\text{Mass Factor} = \frac{m(\text{Graft})}{m(\text{Cell.})} \times \frac{\%\,\text{Cell. in Graft}}{100} \quad \text{or} \quad = \frac{m(\text{Graft})}{m(\text{Polym.})} \times \frac{\%\,\text{Polym. in Graft}}{100}$$

$$A_S\text{-Ratio} = \frac{A_S(\text{Graft})}{A_S(\text{Cell.})} \quad \text{or} \quad = \frac{A_S(\text{Graft})}{A_S(\text{Polym.})}$$

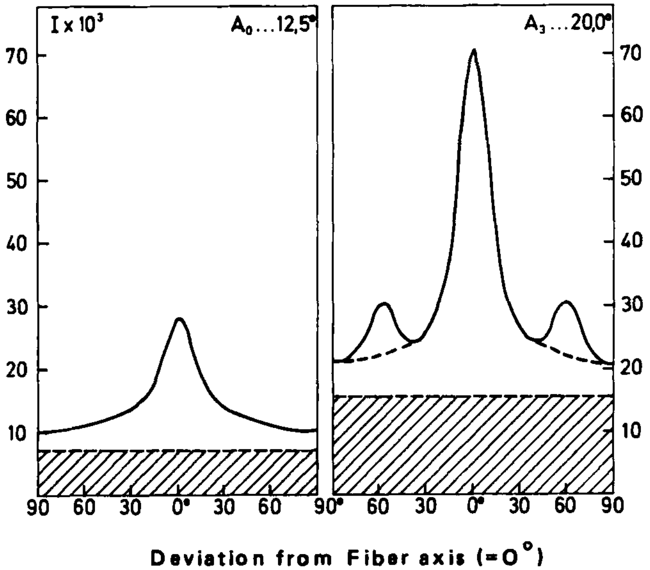


FIG. 2. Separation of the azimuthal diffraction distribution into the diffraction of the amorphous grafted styrene (cross-hatched area) and the diffraction of the cellulose fiber backbone.

azimuthal scans a contribution of the nonoriented polymer fraction at the corresponding Bragg angles has been deducted as illustrated in Fig. 2. The remaining diffraction distribution coming from the cellulose portion in the graft was evaluated in accordance to Hermans and Weidinger for the orientation factor f_r.

The values obtained, listed in Table 4, indicate that only a slight disorientation of the structural elements of the base cellulose fibers occurs during the polymer addition by grafting. This statement surely applies only for grafting to a polymer add-on of approximately 30 to 40%. Additional investigations on graft samples with higher polymer add-ons, which have been started, will show whether changes in the degree of order or in the degree of orientation may occur with higher additions of polymer.

In conclusion, we can state that the grafting of polymer side chains to fibrous cellulose substrates occurs, at least at lower levels of grafting, mainly on the surface and/or in accessible regions of the fibrillar elements. At low levels of add-ons apparently no destruction of the crystalline order occurs. The addition of polymer at these levels does also not disorient the fibrillar elements of the fiber either.

TABLE 4. Effect of Grafting on the Crystalline Orientation of Modified Viscose Fibers

Sample	Orientation Factor[1) f_r
Unmodified Viscose Fibers	0.460
Styrene grafted Viscose Fibers	0.423
Acrylonitrile grafted Viscose Fibers	0.443
P-Vinyl grafted Viscose Fibers	0.407

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