Olney Medal Paper

Contributions to the Chemistry and Physics of Cotton Fibers

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My interests were broad during my career. I studied both natural and manufactured fibers and researched in many areas including pyrolysis, flammability, crosslinking, and weathering. My work on cellulose included studies in which the starting products were cotton, ramie, viscose rayon, microcrystalline cellulose, and rice straw.

In this presentation, I will focus on the research I was involved with on cellulose fibers. Mostly, I will be discussing the changes in the fine structure of cotton induced by swelling, the effect of heat treatments on this fiber, cellulose-water relations, and finally, the porosity and surface area of cotton.

Cotton Structure

In the 1950s, when I first started working on the properties of cotton cellulose, the conventional way of making amorphous cellulose was to ball mill it. This destroyed the fiber structure. Swelling treatments were known to change crystallinity, but it had not been determined how extensively and how substantially the modification would affect fiber properties. The terms accessibility and amorphousness were used synonymously at that time. An exhaustive review of the literature on cotton properties,with numerous tables, was published in 1966 by the Shirley Institute.[1] Unfortunately, these tables, while giving orders of magnitude of the properties of cotton and mercerized cotton, can be misleading at times. For example, in one table, the average value for the crystallinity of cotton is given as 73%. However, if you look at the raw data, you see the average is calculated from values ranging from 39% to 95%.

Cotton has the cellulose I crystal form—mercerization will convert it to the cellulose II crystal form and amine or liquid ammonia treatments can yield cellulose III. The conversion in these cases can be done with little or no degradation. However, while the cellulose IV form was known to exist, nothing could be deduced about fiber properties, since at that time it was thought that conversion required heating the cellulose at high temperature, such as 260 °C in glycerol. Under such conditions, the fiber structure degraded. Again, the mechanism by which cellulose fibers fractured under tensile stress needed further elucidation.

I should clarify here that when I refer to mercerized products, I mean cotton fibers with the cellulose I crystal form that were treated with an alkali metal hydroxide solution of sufficient strength to cause essentially complete conversion of the lattice structure to the cellulose II form.[2–4]

Swelling Effects

First, I will discuss reduction in the crystallinity of cotton cellulose by swelling. The initial reason I studied this was because it was hypothesized by my research director at the Shirley Institute, where I was employed at the time, that by decrystallizing cotton one might be able to transform its stress-strain curve from being almost linear to break to that of cellulose acetate, which has a marked yield point. Consequently, it was thought, this would give cotton a similar draping ability as cellulose acetate.

My initial attempts at decrystalliization were to swell it with anhydrous ethylamine and then wash with water, following work at the Southern Regional Research Laboratory of the USDA using this reagent.[5] I found the change in crystallinity was relatively small and it had little effect on fiber properties. It appeared that extraction of the ethylamine by water resulted in recrystallization of the cellulose. I had better success when I kept the fiber structure open by a small degree of acetylation after the fiber was swollen in ethylamine, and then solvent exchanging the ethylamine with pyridine and acetylating in pyridine before washing with water and drying. This was true with any swelling agent I tried before and after I left the Shirley Institute. These were ethylamine,[6,7] methylamine,[8] and mercerizing-strength alkali metal hydroxide solution.[8,9] The mercerizing solution was prepared in both water[9] and alcohol.[8]

We followed the change induced by the swelling treatments by studying the rate of acetylation of the products[7,8] and comparison of x-ray diffractograms.[6–8] We also determined such properties as accessibility by moisture regain determination[6–8] and tensile properties.[7,8] What these studies showed was swelling treatments can partially decrystallize cotton, but it will recrystallize to some extent when it is washed with water. However, if the fiber is esterified, the product will not recrystallize as much. Also, when a never-dried product is reacted with a reagent, the reagent will penetrate the fiber far more uniformly and, for the equivalent degree of esterification, fiber properties will differ sharply from a fiber that is reacted without pre-swelling.[7]

In retrospect, it is difficult to introduce a marked yield point in the tensile properties of cotton. Cellulose acetate has very little crystallinity and fiber orientation. Its extensibility is high (25% to 45%) and its degree of polymerization (DP) is only 200 to 250.[10] In contrast, as I will discuss later, cotton has a very high crystallinity (around 90%) and a much higher DP, greater than 2000, normally. Also, cotton has a complex morphology.

Specifically, the cellulose molecules spiral around the fiber axis and the periodic reversal of the spiral in the secondary wall results in convolutions. While a swelling treatment such as slack mercerization will reduce crystallinity, the decrease is not large (from about 90% to 80%). Slack mercerization can increase strength and extensibility. I attributed the change induced by mercerization in part to the swelling induced by the process causing the fibers to untwist. Simultaneously, the internal stresses, which may be concentrated in regions where the convolution reversals occur, are relieved. The reduction in crystallite length that occurs on mercerization (of roughly 66%), as well as the reduction in degree of crystallinity, contributes to the relief of stresses in the fiber as well as giving a product of higher extensibility. The increased extensibility is due to greater mobility of the crystallites as their size is reduced and by the increased amount of amorphous material.[11]

However, in contrast to cellulose acetate, mercerized cotton has high crystallinity and orientation as well as a relatively low extensibility (about 12%).[8] Mercerized cotton also has a relatively high secant modulus and rupture energy.[12] Secant modulus is the ratio of tenacity to elongation and is a measure of fiber rigidity. We also determined the breaking twist

angle, a measure of brittleness, of cotton samples before and after slack mercerization and of acetate rayon. We found that the acetate rayon was the least brittle.[12] None of the decrystallization techniques we tried gave us an extensibility above 16% and all retained a significant amount of crystalline product at acetyl contents of 10%.[7–8] While the drapability issue was not resolved, the research enabled a better understanding of the effect of various swelling agents on the reactivity of cellulose and on the physical properties and accessibility of cotton fibers.

Heat Treatments

Next I turn to thermal properties. Much processing of cellulose materials requires heat treatments. The question arises, is there a glass transition temperature (T_g) for cellulose even though it is a highly hydrogen-bonded product? Work had been done in this area. Second-order transitions were reported by several workers for cellulose of various forms, with values ranging up to 240 °C.[13] I obtained a value for T_g of 160 °C for ramie,[13] while on sabbatical in Dr. Menefee's lab at the Western Regional Research Laboratory of the USDA, using the torsion pendulum equipment he had built for work with wool fibers.[14] My T_g of 160 °C was lower than that of other workers. As far as data reporting, T_g is above 200 °C. I have my doubts about such data as dehydrocellulose is formed at 220 °C. Later, we looked at the brittleness of ramie fibers and found they became less brittle at about 190 °C.[15] Also, working with cotton yarn, we found its modulus decreased at about 180 °C, and its stress decay at about 200 °C.[16] Thus, a T_g of about 160 °C is reasonable for cellulose. [14]

Manufacturing of cotton products can result in conversion of its crystal structure from cellulose I to cellulose II (mercerization) or cellulose III. Products containing the cellulose IV structure are not to be found normally in commercial products because the high temperatures required to cause the conversion are avoided since fiber degradation occurs. However, we found we could cause conversion without excessive damage by heating in formamide or steam at 120 °C.[17] We compared properties of a starting cotton to the same after transformation of the crystal form to cellulose II by mercerization, to cellulose III by ethylamine treatment, and to cellulose IV from the cellulose III cotton. Although DP fell in comparison to the control when cellulose IV was formed (from 3350 to 2200), essentially all of it occurred during the ethylamine treatment. Some weight loss occurred during cellulose IV formation (roughly 8%) and accessibility increased, as indicated by moisture regain and water retention value (WRV) determinations, by about 40% and 20%, respectively. Level-off degree of polymerization (LODP) of the cellulose IV cotton had decreased to 60 from 165 for the starting product and was close to that of the mercerized cotton. Fiber strength was comparable to that of the starting cotton even though its DP was lower. Thus, cellulose IV cotton retained the strength of the native cotton, but had higher accessibility and a smoother surface as found when fibers were examined by scanning electron microscopy (SEM).

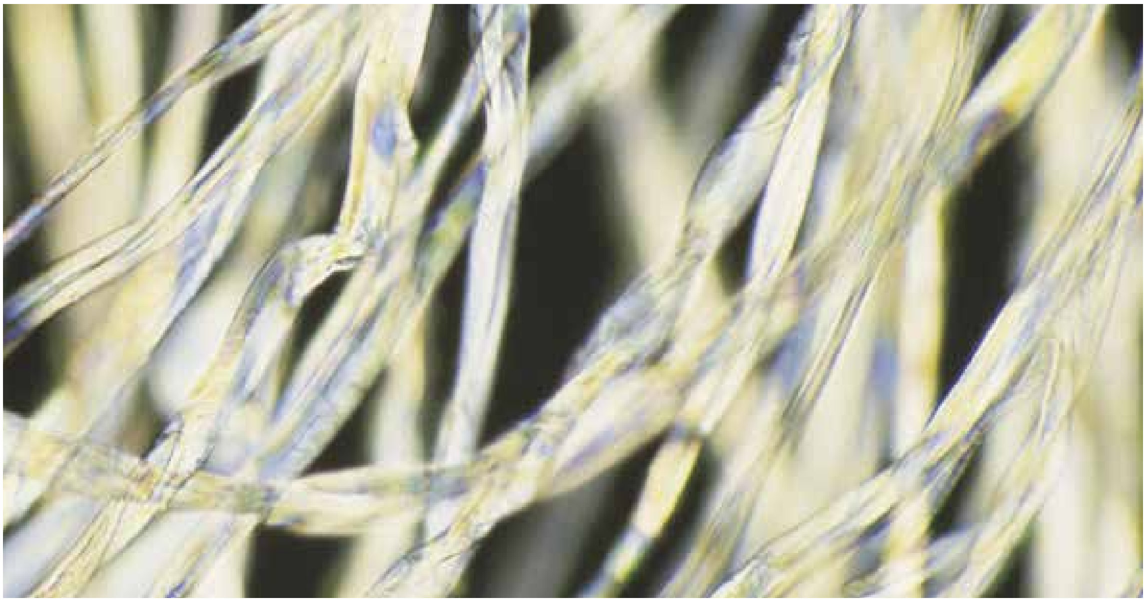
Cotton Moisture

Much work was done to study the interaction of water and cotton because of its importance in industrial processing. In this regard, I will describe our work on moisture uptake, accessibility, hysteresis, surface area, and cotton porosity.

We studied the moisture adsorption of amorphous cellulose,[18] which, as shown by Jeffries, could be formed by deacetylating acetate filament in 1% ethanolic NaOH.[19] We also tried the method on cotton by preparing a fully acetylated fiber without dissolution and then deacetylating with the NaOH/ethanol reagent.[18] The product was not completely amorphous, so I called it disordered cotton. In addition to the amorphous cellulose and the disordered cotton, we measured the sorption isotherms of the starting cotton and mercerized cotton. We also measured the sorption isotherms of microcrystalline products prepared from each product. We analyzed the water sorption data using the Brunauer, Emmett, and Teller (BET) equation, which adequately describes the sorption of water vapor in celluloses below 0.5 relative vapor pressure (RVP). We calculated the number of molecules of water adsorbed per anhydroglucose unit (AGU) when a monomolecular layer of water was formed on the amorphous cellulose (W_m). It was about 0.8 mol/AGU for amorphous cellulose, even though there are three hydroxyl groups per AGU. Using the data for amorphous cellulose, we proposed relations for calculating the crystallinity and accessibility of cellulose fibers. For our cotton, mercerized cotton, and disordered cotton, we determined their crystallinity as 0.91, 0.79, and 0.39 respectively, and their accessibility as 0.37, 0.52, and 0.78 respectively. The values for the crystallinity of cotton and mercerized cotton are close to values obtained by the acid hydrolysis technique.

We also considered the causes of moisture regain hysteresis.[20,21] In this work, a comparison was made between the BET and the Guggenheim, Anderson, and deBoer (GAB) relation for evaluating adsorption isotherms. The GAB relation fitted the sorption isotherms up to an RVP of 0.9, whereas the BET relation fitted only up to an RVP of 0.5. The GAB relation appeared to have been overlooked by cellulose chemists at that time. Using this relation, W_m was determined to be 0.9 mol/AGU for amorphous cellulose.

At least three hypotheses were put forward for explaining hysteresis. We discounted two and tested the third, which states that the internal pressure generated as a material swells or contracts affects the amount of water adsorbed. Thus, whenever there is mechanical hysteresis, there must also be moisture hysteresis. On the other hand, if elastic recovery is good, there will be little moisture hysteresis. We concluded from our study, in which we examined the elastic recovery, stress relaxation, and mechanical energy loss of viscose rayon and cross-linked viscose rayon, that the relations between mechanical hysteresis and sorption hysteresis were not simple. Of the three mechanical properties we measured, only stress relaxation at low stresses appeared to correlate well with sorption hysteresis.



Surface Area and Porosity

We determined the surface areas of cotton, and slack and tension mercerized cotton, using Direct Blue 1 as well as water as the probe.[22] Direct Blue 1 is absorbed at low concentrations in a Langmurian way, allowing surface areas to be determined using the size of the dye molecule, calculated by Dr. French as 240×10^{-20} m^2.[23] The values for cotton and slack mercerized cotton were 17.7 and 33.7 m^2/g, respectively. In contrast, the surface area of scoured cotton before and after slack mercerization was 162 m^2/g and 226 m^2/g, respectively when determined by water adsorption.[18] Clearly, the relatively large dye molecule cannot penetrate the small pores that would be accessible to the much smaller water molecule, which has a surface area of 14.8×10^{-20} m^2. The information provided by the sorption of Direct Blue 1 differs from that obtained by the sorption of water. From the data obtained, it was concluded that about 34% of the internal surface of cotton and mercerized cotton, available for water adsorption, was inaccessible to Direct Blue 1.

In addition to the presence of pores too small for dyes to penetrate, there may be other factors contributing to the large difference in surface area as measured by dye and water molecules. For example, it is feasible that there are characteristics to the pore and fibrillar surfaces which may not permit an even deposition of the dye molecules. Water molecules might be able to position themselves in regions that may be bridged or inaccessible to dye molecules. Also, there is bound water present in cellulose,[24] and if the electrolyte added to the dye solution does not effectively disrupt it, then pore diameters will be smaller. Thus, the number of pores accessible to the dye will be reduced.

We also studied other dyes to test their suitability as sensors.[25] We cautioned that care has to be taken when selecting a dye to be used as a probe for studies on the accessible surface and pore size of cellulose. Data can be affected by dye structure, dyeing conditions, and substantivity, as well as molecular volume. Molecular weight of a dye probe does not serve as a good indicator of sensor size.

To conclude, while I have made extensive studies on synthetic fibers, cotton and manufactured cellulosic fibers were the first fibers I studied. Especially cotton remained a major interest throughout my career. For this reason, I have focused on cotton here and given an overview of aspects of the research I have been involved in to provide a better understanding of its fine structure and physical properties. As instrumentation becomes increasingly advanced, more remains to be discovered.

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