2.2 Cotton Fibers as Natural Raw Materials for Cellulose Acetate Production

Shiro Saka

Graduate School of Energy Science, Kyoto University, Kyoto, Japan 606-8501
Email: saka@energy.kyoto-u.ac.jp

Summary: The commercially available cotton species are only three botanical species. For these species, the cotton fibers were described to consist of two different types of fibers termed "lint" and "linter". The structure and chemical constituents of these cotton fibers were compared, so as to use them judiciously as natural raw materials for cellulose acetate production.

Keywords: cotton fiber; *Gossypium*; lint; linter; cotton ball; 1st cut linter; 2nd cut linter; suberin-like lipid; cellulose

2.2.1 Introduction

Cotton fibers are the best as raw materials for cellulose derivatives production because of their high quality and purity of cellulose. Particularly for the production of cellulose acetate, cotton fibers and wood dissolving pulps highly purified are often used for a variety of products such as film, cigarette filter and plastics. In order to use cotton fibers judiciously as natural raw materials for cellulose acetate production, it is essential to know the topochemistry and morphology of the cotton fibers. This chapter, therefore, deals with the structure of cotton fibers and their chemical constituents.

2.2.2 General Features of Cotton Fibers

Taxonomically, cottons belong to *Gossypium* genus in *Malvaceae* family, and about 40 species of cottons are known to exist in the world. However, those that are of commercial importance are only three botanical groups, *Gosspium hirstum* L., *Gosspium barbadense* L. and *Gosspium arboreum* L. Each group has many varieties.[1]

In a cytological sense, there exist two different types of cotton fibers termed "lint" and "linter" as in Figure 1. The lint fibers are convoluted cells, 20 to 40 mm long while linter fibers are short to

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be 5 mm or less.[2] The former is mainly used for the texture of cotton fibers in the textile industries, while the latter for raw materials to produce cellulose derivertives in chemical industries.

In spite of its terminology, “commercial linters” are formed by the breaking of cotton fibers during ginning and thus, a mixture of linters and broken lints is often resulted. Figure 2 shows leaf, flower and cotton balls of the three species used for the industrial use (Table 1), being characteristic of the species, and thus easy to be identified.

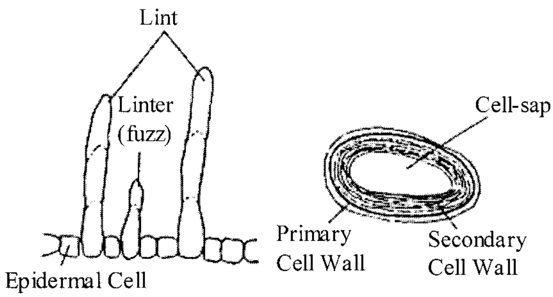

Figure 1. The structure of the cotton fibers.[2]

Figure 2. Leaf, flower and cotton balls of three cotton species.

Table 1. Cotton plants commercially available.

Species	Varieties	Sources	
G. hirstum L.	Acala SJ-2	Toyobo Co., Ltd.	California, USA
	DPL 61	Toyobo Co., Ltd.	USA
	California	Kobe University	-
	Stoneville	Kobe University	-
G. barbadense L.	Giza 45	Toyobo Co., Ltd.	Egypt
	Indian Barb.	Toyobo Co., Ltd.	India
G. arboreum L.	Norin 4	Kobe University	-
	Desi	Toyobo Co., Ltd	Assam, India

2.2.3 Separation of Cotton Balls

Figure 3 shows the separation of cotton balls for their usage. Cotton balls harvested are transferred to the ginning mill and long cotton fibers are delinted from seeds to be lints. The residual lints and linters (fuzz) which are shorter in the length remain over the surface of the delinted seeds. These seeds are then separated into the stripped seeds and linters in the oil mill by the delinting machine. The linters obtained in the first trial are called “1st cut linters”, while those in the second “2nd cut linters”. A mixture of these 1st and 2nd linters are called “mill-run linters”. The 1st cut linters consist of fibers longer than 10 mm, whereas the 2nd cut linters in a range between 3.3 and 3.5 mm and mill-run linter between 3.5 and 10 mm in length. Therefore, the 1st cut linters contain not only linter fibers in a cytological sense but also the residual portion of the lint fibers remained after the delinting treatment. The 2nd cut linters are in a range of the length in linter fibers, but contain the residual lint fibers shortened by the first delinting treatment.

The whiteness of the fibers is decreased, and impurity due to contamination with hull and so on increased in the following order; lints, 1st cut linters and 2nd cut linters. Thus, the 1st cut linters are better in quality than the 2nd cut linters. Generally, the 2nd cut linters are used for cellulose acetate production.

The stripped seeds are then separated into the hull with the residual linters and kernel from which fiber-rich portions are collected as hull linters. The lint fibers are widely used for the textile industries, but not for the chemical usage so that the details are omitted in this section on the lint fibers.

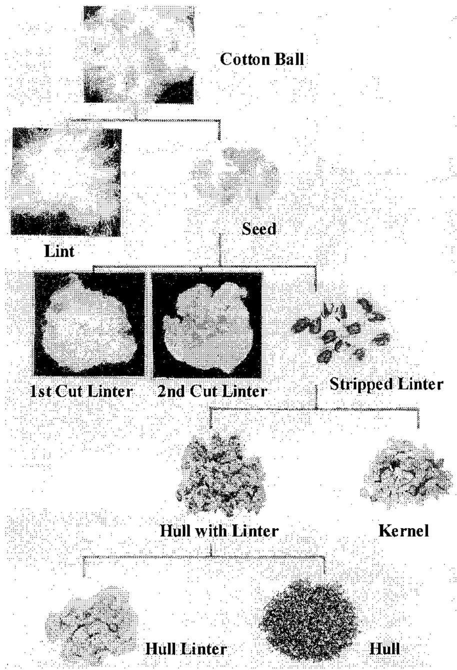

Figure 3. Separation of the cotton balls.

2.2.4 Comparisons between Lint and Linter fibers

It is important to study these two types of cotton fibers, lints and linters, to characterize "commercial linters". In this section, therefore, comparisons were made by electron microscopy and polarizing light microscopy on lint and linter fibers on their morphology and cell wall structure for three cotton species (Table 1).

Figure 4a shows a cross-sectional view of PDL 61 (*G. hirstum* L.) lint fibers. Although the primary (P) and secondary (S) walls can be seen, no visible cell wall layers were observed within the secondary wall. The inserted micrograph under crossed polars (Figure 4b) indicated more clearly that the secondary wall of lint fibers consists of one single layer.

In contrast to the lint fibers, the structure of linter cell walls is quite different. Figures 5a and 6a show cross sections of linter fibers from Giza 45 (*G. barbadense* L.) and Acala SJ-2 (*G. hirstum*

L.), respectively. It should be noted in Figure 5a that ten electron-dense concentric layers are present within the secondary wall.

Electron microscopic observations of $KMnO_4$-stained section at a higher magnification more clearly revealed an ultrastructure of these layers; in Figure 5b, each of these four layers is seen to be lamellated, consisting of several alternating electron opaque and electron translucent lamellae. Since cellulose does not react with $KMnO_4$, electron translucent layers and lamellae would consist of cellulose. On the other hand, a major component of the electron opaque stained lamellae is reported to be a suberin-like lipid biopolymer.[3] Such biopolymers are amorphous but the inserted micrographs in Figure 5c and 6b did not show multi-layered structure. This is due presumably to the presence of cellulose microfibrils within these layers.

As shown in Figures 5a and 6a, there found two types of concentric layers in linter fibers being continuous (Figure 5a) and discontinuous (Figure 6a). In both cases, however, no concentric layers were seen at the outermost part of the secondary wall.

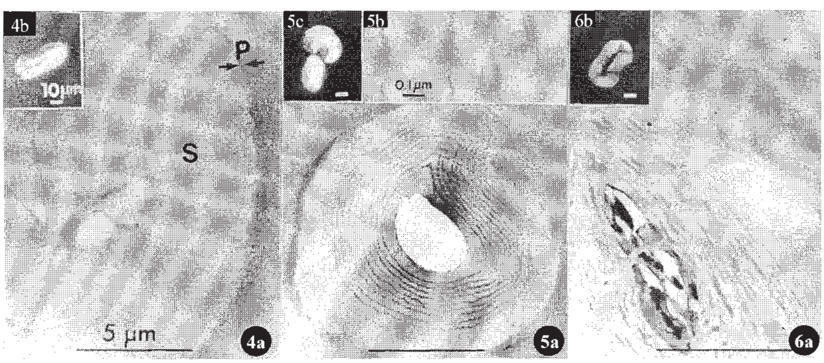

Figure 4. Transverse sections of lint fibers from (a) DPL 61 (*G. hirstum* L.), Pt-Pd shadowing, and (b) Giza 45 (*G. barbadense* L.), under crossed polars.

Figure 5. Transverse sections of linter fibers from Giza 45 (*G. barbadense* L.) (a) Pt-Pd shadowing, and (b) $KMnO_4$ staining, and (c) under crossed polars.

Figure 6. Transverse sections of linter fibers from (a) Acala SJ-2 (*G. hirstum* L.), $KMnO_4$ staining, and (b) Stoneville (*G. hirstum* L.), under crossed polars.

Described in Table 2 is a summary of the cotton fiber structure of lint and linter secondary walls for eight varieties studied in this work. Interestingly, the secondary wall of lints was found out to be mono-layered structure (Figure 4a) for all varieties investigated, whereas that of linters generally revealed $KMnO_4$-stained concentric layers (Figure 5a) except for Norin 4 (*G. arboreum* L.). Among concentric layers, continuously concentric layers were found in all varieties in *G. barbadense* L. and Desi (*G. arboreum* L.), whereas discontinuously concentric layers were only in *G. hirstum* L. This structural difference would be, therefore, characteristic of cotton species.

A study by Roser and Holloway[3] indicated that suberization is a common feature of the seed-coat epidermis. In the fiber cell walls, however, it is restricted to the wild species and to the green lint mutant in cultivated species. This green lint mutant has a character of linter fibers rather that lints themselves because of its relatively short and fine fibers.[4]

Based on these observations, Ryser and Holloway[3] have proposed that suberization at the base of cotton fibers may influence fiber length and thickness of the secondary walls by modifying the import of nutrients. Our present finding that only short fibers, linter hairs, possess concentric layers composed of suberin-like lipid biopolymers strongly supports their proposal.

Table 2. The fiber structure of lint and linter secondary walls for eight varieties of cotton fibers.

Species varieties	Lint		Linter		
	Monolayer	Concentric layers	Monolayer	Concentric layers	
				Discontinuous	Continuous
G. hirstum L.					
Acala SJ-2	+	-	-	+	-
DPL 61	+	-	-	+	-
California	+	-	-	+	-
Stoneville	+	-	-	+	-
G. barbadense L.					
Indian Barb.	+	-	-	-	+
Giza 45	+	-	-	-	+
G. arboreum L.					
Desi	+	-	-	-	+
Norin 4	+	-	+	-	-

2.2.5 Chemical Constituents of Cotton Fibers

Major constituents of cotton fibers (lints) are, needless to say, cellulose, as in Table 3. Minor constituents of the cotton fibers are very small in amount even in the raw fibers, consisting of wax, fat, cuticle containing protein and polyphenol, and ash.[5]

The chemical constituents of linters are not known in the literature. However, as indicated in a previous section, they contain suberin-like lipid biopolymer,[3] in addition to the minor constituents of lint fibers. These minor constituents in lint and linter fibers can be readily removed with hot alkaline aqueous solution, thus the commercial cotton linters are high in purity of cellulose.

Table 3. Chemical constituents of the cotton fibers (lints) in wt%.[5]*

Lint	Cellulose	Wax/fat	Protein	Cuticle	Ash
1	98.6	0.55	0.72	-	0.12
2	98.2	0.43	0.54	0.68	0.13

* in oven-dried basis.

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