Vaccination of Biological Cellulose Fibers with Glucose: A Gateway to Novel Nanocomposites

By

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ABSTRACT

This work introduces, for the first time worldwide, the means to preserve and protect the natural nanoporous structure of the never-dried plant cell wall, against the irreversible collapse which occurs due to drying.

Simultaneously, these means, used for the above-mentioned aim, provide a gateway to novel nanocomposite materials, which retain the super reactive and super absorbent properties of the never-dried biological cellulose fibers. The present work showed, for the first time worldwide, that glucose can be vaccinated into the cell wall micropores or nanostructure of the never-dried biological cellulose fibers, by simple new techniques, to create a reactive novel nanocomposite material possessing surprising super absorbent properties. Inoculation of the never dried biological cellulose fibers, with glucose, prevented the collapse of the cell wall nanostructure, which normally occurs due to drying. The nanocomposite, produced after drying of the glucose inoculated biological cellulose, retained the super absorbent properties of the never dried biological cellulose fibers. It was found that glucose under certain circumstances grafts to the never dried biological cellulose fibers to form a novel natural nanocomposite material. About 3-8% w/w glucose remained grafted in the novel nanocomposite.

Introduction and Object :-

Never dried cotton has -for the first time- been isolated from mature green unopened cotton bolls and chemically purified, by us, while it is still in its biological wet state. It was, also, characterized regarding its crystallinity and porosity (1-2). We further described the use of never dried cotton for preparation of unique cellulose derivatives (3-4).

In the never dried water-saturated state, cell walls of mature cotton fibers consist of unassociated individual elementary fibrils termed protofibrils of the magnitude 35Å (3.5nanometer). Based on an interpretation of cellulose density measured in water, it has been concluded that the protofibril consists of incompletely crystalline cellulose. When the cell wall dries, protofibrils agglomerate together and cellulose simultaneously becomes almost entirely crystalline (1-2).

Drying leads to the collapse of the natural nanostructure of the plant cell wall of never dried biological cellulose fibers. Consequently, drying causes the loss of the super absorbent and super reactive properties of the never dried biological cellulose fibers.

The present work is a serious interesting attempt to study how to preserve and protect the original natural nanostructure, of the never-dried biological cotton fibers, against cell wall collapse caused by nature air-drying. It is thought and planned to try special nanoadditves, the building units of the cellulose namely glucose, for this purpose.

Glucose, being the building unit of cellulose and having a suitable size, enters into most of the nanopores of the cell wall of biological cellulose and is entrapped and engrafted easily. When aqueous solutions of glucose are equilibrated with never-dried pulp, the glucose should be able to penetrate into every micropore or nanopore larger than 8 Å (0.8 nanometer), the volume of these glucose accessible pores amounts to 88% of the total pore volume of the micropores. Thus the dissolved glucose molecules should be distributed rather uniformly throughout the fiber cell wall, except for the pores less than 8 Å in size. These calculations are based on the solute exclusion data of Stone and Scallan and the size of the glucose molecules derived by them (9).

Results and Discussion: -

1. Isolation and Characterization of Biological Cellulose Fibers from Green Cotton Bolls: -

Unopened green cotton bolls of mature size were gathered from Egyptian cotton plants (season August 2005). They were opened by hand and the staple fibers were picked out and mixed together. Such staple fibers were designated " biologically swollen fibers or fibers in the biological state" because they included the total amount of their biological water. Hence, in this state the cell wall is in its original native volume.

The biological cotton used in the present study contained about 63% moisture content when picked from the unopened green cotton bolls. It was purified, without any previous drying, to 99.6% alpha cellulose. All the purification steps were carried out without any drying, using a solvent exchange technique (1). The purified biological cellulose fibers were stored immersed in water. A part of the purified biologically swollen fibers were left to dry in air till equilibrium moisture content was reached, which amounted to 6.8%.

Starting from the biologically swollen state, changes in fine structure of the isolated mature cotton fibers - due to drying - were traced by means of

centrifugal water retention value (WRV), and also by density measurements. The results are reported in **Table 1**.

Several theories about the fine structure of fibers have been presented (5-8). Such theories about cellulose structure are based on X-ray analysis and electron microscopy. These tools are only applicable to fibers in the dry state (9). Cellulose fibers are, however, worked up in water-swollen state in most industrial processes. In papermaking, all operations – till the last stage of drying the paper sheet – are carried out while the fibers are saturated with water. For chemical conversion usually the cellulose fibers have to be pre-swollen with water or other liquids before being subjected to the chemical reaction. Therefore the fine structure of the swollen, respectively water-saturated fibers could be of more bearing on fiber behavior in papermaking and during chemical conversion than the fine structure of dry fibers. Accordingly, the fine structure of fibers in the water-saturated state has attracted the attention of research workers (9). Density measurements were adopted for studying the fine structure of both the dried and the never-dried water saturated states (1); and the interpretation of densities in terms of fiber crystallinity and porosity are laid down. Water uptake can be determined for fibers in both the water-saturated and the dried states. Water uptake can be correlated to pore volume of the swollen cell wall. Accordingly, water

retention value (WRV) was adopted in the present work for studying the fine structure of the swollen and dried cell wall.

A high fiber saturation point (FSP) i.e. WRV of about 120% is ascribed to pure cellulose nature fiber in the never-dried biological state, irrespective of plant origin, as well as to never-dried regenerated cellulose (4).

Consequently, it is clear from **Table 1** that water treatment of the air dried cotton fibers -to determine their WRV and density- failed to return the cell wall to its original biological volume, as measured by FSP (WRV). This shows that the basic morphological structural element in air-dry fibers is not the original protofibril but predominantly an aggregate of closely associated microfibrils i.e. compound microfibril. It is, also, clear from **Table 1** that drying of the biological cellulose fibers to practically zero moisture content -via oven drying- decreased both the density and the WRV. This is attributed to formation of enclosed pores.

Fahmy and Mobarak were the first to study the fine structure of the biological cellulose i.e. never-dried, native cellulose in a series of research work and articles (1-4)**.** They have shown that cellulose in the biological, native state is much more reactive than air-dried or conventional cellulose, and that in the biological state, cellulose fibers are as reactive as the never-dried regenerated cellulose. They also indicated that the reactivity of cellulose is correlated to the degree of dissociation of

microfibrils to elementary fibrils or protofibrils of the magnitude 35 Å (3.5 nanometer) rather than to crystallinity (3).

Our recent work (10) on nanoadditives in papermaking, coupled with our interest in studying the fine structure of biological cellulose fibers, and keeping in view the possibility of commercial utilization of never dried cotton, all these facts led us to take the never dried biological cotton -as a new cellulose source- to patenting. In the present work we extended our studies and conducted several trials to preserve and protect the original nanostructure of the never-dried biological cotton fibers from cell wall collapse caused by nature air-drying. This is shown in the following section.

2. Vaccination of the Never-Dried Biological Cellulose Fibers (i.e. biological cotton staple fibers) with Glucose (the building unit of the cellulose molecule): -

The vaccination was performed in a 250 ml Conical flask with ground joint stopper. In each experiment, 4g of the never dried biological cotton staple fibers were put in the reaction vessel, and left for 1 hour in a sunny summer time at 35ºC. This was followed by addition of 100 ml of water containing the calculated amount of glucose (5,10,15 and 20% w/w). The mixture was shaken by hand then left overnight at room temperature (30ºC). The vaccinated biological cotton staple fibers were then

centrifuged under the same conditions used for determination of FSP (WRV). The centrifuged vaccinated never dried fibers were then air dried at room temperature. The produced nanocomposite was characterized for water uptake and density.

Table 2 shows the results in case of using 20% w/w glucose for vaccination of the never-dried biological cellulose fibers (i.e. never-dried biological cotton staple fibers). It is obvious that vaccination of the never-dried biological cotton staple fibers with glucose, using our simple technique, protected the cell wall nanoporous structure against the attack of collapse due to drying. (Compare FSP values in **Table2** and **Table1**).

Table3, also, illustrates the preservation and protection of the cell wall micropores or nanostructure against the irreversible collapse during drying. This is obvious by comparing the pore volume of the novel nanocomposite, produced after drying of the glucose vaccinated biological cellulose, versus the pore volume of cotton staple fibers dried without vaccination with glucose.

It is most probable that as the glucose-loaded cell wall dries, the glucose molecules prevent neighboring lamellae from collapse. These glucose molecules hinder the hornification of cellulose by acting as spacers and thus prevent the irreversible coherency of lamellae which occurs during drying (10).

The present work shows that even after soaking the produced nanocomposite in hot water and washing it with hot water, about 3-8% glucose remains engrafted in the biological cellulose, as measured by the increase in weight gravimetrically.

Our novel natural nanocomposite, produced from the biological cellulose fibers vaccinated with glucose, finds a lot of uses: especially as super absorbent natural fibers for medical and hygienic purposes and as reactive cellulosic source. Such uses are under investigation by us.

Summary and Conclusions: -

The present work shows, for the first time worldwide, that the never-dried biological cellulose fibers can be vaccinated, by glucose, against the attack of drying. Drying, normally, leads to the collapse of the natural nanoporous structure of the plant cell wall of never-dried biological cellulose fibers. Consequently, drying causes the loss of the super absorbent and super reactive properties of the never-dried biological cellulose fibers. Inoculation of the never-dried biological cellulose fibers, by glucose, prevented the collapse of the cell wall nanostructure during drying.

Drying of the glucose inoculated biological cellulose fibers, leads to novel nanocomposites, which retain the super absorbent properties of the never-dried biological cellulose fibers.

This achievement was accomplished by new and simple techniques.

Experimental: -

- Determination of centrifugal water retention value (WRV): -

Water retention values were determined according to the modified German Standard Method (11,12).

- Determination of density of non-dried and dried fibers: -

Density was determined by the pycnometric method as mentioned in details in previous work (1).

- Determination of porosity of dry fibers: -

Pore volume of dry fibers was determined through the density of fibers in water and in xylol, as mentioned in details in previous work (1).

- Incorporation of glucose (the nanoadditive) into the cell wall of biological never-dried cellulose fibers: -

The different methods of incorporating sucrose into the non-dried pulp fibers recommended recently (10), were applied in the present work; then we offered -after several preliminary investigations- a simple easy applicable method for glucose entrapping in the biological cellulosic fiber matrix during the collapse of the cell wall pores as the fibers are dried. We have shown in the section concerned with the results and discussion that our new approach and simple incorporation technique preserves and makes benefit of the original nanoporous structure of cellulose fibers cell walls.

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Table 1

WRV (Fiber saturation point FSP) and density of cotton staple fibers (biological cellulose) before vaccination with glucose

	FSP (WRV) %	Density g/cm^3
Never Dried	116.55	1.6089
Air Dried	52.00	1.6190
Oven Dried	44.35	1.6041

Table 2

WRV (Fiber saturation point FSP) and density of the novel nanocomposite prepared from biological cellulose fibers vaccinated with glucose (20% w/w)

	FSP (WRV) %	Density g/cm^3
Never Dried	---	---
Air Dried	135.31	1.6128
Oven Dried	122.25	1.6120

Table 3

Relation between pore volume of air-dry fibers and fiber saturation point

	Cotton staple fibers without vaccination	Novel nanocomposite from biological cellulose vaccinated with glucose (20% w/w)
Pore volume %	1.905	5.240
FSP (WRV) %		
Air Dry Fibers	52.00	135.31
Oven Dry Fibers	44.35	122.25