Green Nanotechnology: A short cut to beneficiation of natural fibers

By

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ABSTRACT

For the first time worldwide, it is shown that our novel nanocomposite produced from natural fibers vaccinated with glucose -by fully green nanotechnology- possesses surprising reactivity towards urea. Magic super absorbent carbamated nanocomposite cotton fabrics having remarkable distinguished properties were obtained in few minutes. It is well established that carbamates possess antibacterial effects. The produced magic nanocomposite fabrics find their use as woven or nonwoven hygienic pads, bandages or paper nanocomposites.

Introduction and Object :-

Recently, we discovered -for the first time- 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 (1). Our recent 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 to create a reactive novel nanocomposite material. 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 should also retain the super reactive properties of the never-dried biological cellulose fibers. It is worth mentioning that the distinguished reactivity of never-dried biological cellulose fibers caught high interest for study in several articles (2-5).

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. 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 (6-10).

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. (11).

The present work aims at manipulating our novel reactive nanocmposite; prepared via preservation and protection of the nanoporous structure of the never-dried plant cell walls. We thought of using simple green nanotechnology by subjecting our novel nanocomposite -produced after drying of the glucose inoculated biological cellulose- to partial carbamation (treatment with urea dissolved in water).

2. Results and Discussion: -

<u>2.1. Partial Carbamation of Air-Dried Glucose Inoculated Biological Cellulose Fibers:</u>

a) <u>Isolation and Characterization of Biological Cellulose Fibers from Green Cotton Bolls: -</u>

Unopened green cotton bolls of mature size were gathered from Egyptian cotton plants (season August 2010). 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 65% moisture content when picked from the unopened green cotton bolls. It was purified, without any previous drying, to 99.7% 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 6.9%.

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**.

b) 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 as reported recently (1). **Table 2** shows the results in case of using 15% 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**).

The results illustrate the preservation and protection of the cell wall micropores or nanostructure against the irreversible collapse during drying. This is obvious by comparing the swollen pore volume (FSP) of the novel nanocomposite, produced after drying of the glucose vaccinated biological cellulose, versus the swollen pore volume (FSP) 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 (10-16).

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.

c) Partial Carbamation of Air-Dried Glucose Inoculated Biological Cellulose Fibers (Our Novel Reactive Nanocomposite): -

Cellulose carbamate is the product of reaction between cellulose and urea (14, 15). In the present work, after several preliminary experiments, the adopted carbamation conditions were selected, fixed and studied. The amount of urea used was 1:1 based on cellulose fibers. The urea was first dissolved in the least amount of water, then mixed with cellulose fibers in a porcelain dish. The samples were then put in a circulating air oven at 135 C, for different time periods. Thereafter, the samples were washed with water and hot water for several times, and kept non-dry ready for further investigations.

Water uptake (WRV) for the non-dried, air-dried and oven-dried samples are shown in **Table 3**.

A part of the partially carbamated cotton fibers was air-dried and the nitrogen contents of the samples were determined and also reported in **Table 3.**

2.2. Partial Carbamation of *Glucose-Free* Never-Dried and Nature-Dried Biological Cellulose Fibers: -

The Results are shown in Table 4 and Table 5.

The fact that cellulose carbamate is completely non-toxic and antibacterial (14, 15) recommends the use of our novel partially carbamated nanocomposites as super absorbent fabrics for sanitary and hygienic purposes.

Experimental: -

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

Water retention values were determined according to the modified German Standard Method (14, 15).

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

Density was determined by the pycnometric method as mentioned in details in previous work (2).

- 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 (1, 6-10), 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.

- Partial Carbamation of Air-Dried Glucose Inoculated Biological Cellulose Fibers (Our Novel Reactive Nanocomposite): -

Cellulose carbamate is the product of reaction between cellulose and urea (14, 15). In the present work, after several preliminary experiments, the adopted carbamation conditions were selected, fixed and studied. The amount of urea used was 1:1 based on cellulose fibers. The urea was first dissolved in the least amount of water, then mixed with cellulose fibers in a porcelain dish. The samples were then put in a circulating air oven at 135 C, for different time periods. Thereafter, the samples were washed with water and hot water for several times, and kept non-dry ready for further investigations.

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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	118.02	1.6086
Air Dried	51.64	1.6187
Oven Dried	43.50	1.6035

Table 2

WRV (Fiber saturation point FSP) and density of the novel nanocomposite prepared from biological cellulose fibers vaccinated with glucose (15% w/w)

	FSP (WRV) %	Density g/cm^3
Never Dried	---	---
Air Dried	140.52	1.6129
Oven Dried	124.60	1.6122

Table 3

Partial Carbamation of Air-Dried Glucose Inoculated Biological Cellulose Fibers (Our Novel Reactive Nanocomposite)

Treatment Time min.	Zero (No Treatment)	5	10	15
Nitrogen Content %	----	1.64	1.88	2.06
FSP (WRV) %				
Non Dry Fibers	----	146.11	157.00	179.41
Air Dry Fibers	140.52	142.31	143.80	153.02
Oven Dry Fibers	124.60	122.55	125.62	135.61

Table 4

Partial Carbamation of *Glucose-Free* Never-Dried Biological Cellulose Fibers

Treatment Time min.	Zero (No Treatment)	5	10	15
Nitrogen Content %	----	1.01	1.46	1.68
FSP (WRV) %				
Non Dry Fibers	118.01	131.20	136.00	139.80
Air Dry Fibers	55.62	102.41	112.11	125.26
Oven Dry Fibers	43.33	90.00	105.36	108.03

Table 5

Partial Carbamation of *Glucose-Free* Nature-Dried Biological Cellulose Fibers

Treatment Time min.	Zero (No Treatment)	5	10	15
Nitrogen Content %	----	0.06	0.11	0.24
FSP (WRV) %				
Non Dry Fibers	----	57.41	59.08	61.39
Air Dry Fibers	51.64	56.02	56.60	56.99
Oven Dry Fibers	43.33	45.72	48.31	50.44