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Incorporation of Never-Dried Cotton fibers with Methylmethacrylate: A Gateway to Unique Transparent Board-Like Nanocomposites

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Abstract: For the first time, it is shown that water medium allows dissolved methylmethacrylate monomer to penetrate water-swollen natural nanoporous structure of never-dried cotton fibers (biological cellulose fibers). Unique cellulose copolymer nanocomposites are obtained by green nanotechnology process (solvent is water -ideal green solvent- and reaction conducted at 25ºC). It was found that after only 2 h polymerization the conversion of MMA monomer to polymer was 42.97%, compared to zero polymer conversion in absence of never-dried cotton. Higher water uptake i.e. water retention value (WRV) of the cellulose-PMMA-copolymer nanocomposites prepared from never-dried biological cotton fibers, and microscopic investigations confirmed that the polymer was mostly grafted on the cellulose rather than homopolymer filling the fiber pores. Early products of polymerization e.g. dimmers and trimmers act as spacers and widen the porous structure of cell wall, thus increasing water retention value (WRV). We called this phenomenon *"intra-polymerization"*. As the process of polymerization proceeds, polymerization within cell walls leads to cell wall destruction, increasing WRV of fibers, giving superabsorbent end product. The produced unique biological cotton-PMMA green nanocomposite we discovered find their use in several advanced medical and pharmaceutical fields; as nonwoven pads, bandages or board-like transparent nanocomposites of bending strength up to 955 kg/cm^2.

Keywords: Green nanocomposites; Never-dried cotton fibers; Cellulose-polymethyl methacrylate -copolymer; Transparent board-like nanocomposites; Bending strength.

Introduction

Recently, we have discovered -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[1]. Our recent work showed, for the first time, 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. 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 or microfibrils which occurs during drying[1-9]. Furthermore, superabsorbent carbamated nanocomposite cotton fabrics possessing distinguished properties were obtained from biological cellulose fibers vaccinated with glucose via a fully green nanotechnology process[7].

The present work aims to study, for the first time, the Polymerization of methylmethacrylate in water in absence and presence of never-dried cotton fibers (biological cellulose). The polymerization is planned to be done in a water medium to allow the dissolved methylmethacrylate monomer to penetrate the water-swollen natural nanoporous structure of never-dried biological cellulose fibers. This leads to a green nanotechnology process, where the solvent is water (the ideal green solvent), and the reaction is conducted at room temperature (25ºC); to save energy and reduce accidents risks.

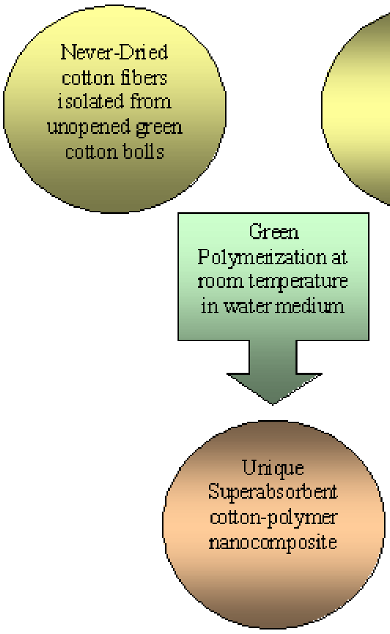
Several theories about the fine structure of fibers have been presented. Such theories about cellulose structure are based on X-ray analysis and electron microscopy. These tools are only applicable to fibers in the dry state [10]. However, water uptake can be determined for fibers in both the water-saturated and the dried states. Water uptake can be correlated to pore volume of the swollen cell wall. Accordingly, water retention value W.R.V. was adopted in the present work for studying the fine structure of the swollen and dried cell wall[2,10,14].

The following necessary overview on biological cellulose fibers integrates the background of the present work.

Never-dried cotton (obtained from unopened green cotton bolls) was -for the first time- chemically purified by us while it was still in the biologically wet state. It was, also, characterized regarding crystallinity and porosity. We further described the use of never-dried cotton, as a new cellulose source, for treatment with different reagents and preparation of cellulose derivatives[10,11,12,13].

Throughout the last decades, a paradox prevailed with regard to the accessibility i.e. the reactivity of celluloses isolated from different plant sources. While celluloses isolated from woody and non-woody stems possess generally high accessibility to reagents, cotton cellulose, on the other hand, possesses lower accessibility. It seemed strange that cotton cellulose stood unique among other celluloses. Therefore, we began attempts to clarify this phenomenon. Our investigations were undertaken in the framework of an integrated study about fine structure of cellulose. We started our experiments by isolating never-dried cotton from unopened green cotton bolls and by chemically purifying the fibers while still in the wet biological state. All the purification steps were carried out without any drying, using a solvent exchange technique. The purified never-dried cotton was then investigated for accessibility i.e. reactivity. It is generally known that crystallinity and porosity are the most important fiber parameters influencing its accessibility to reagents. To measure crystallinity for the never-dried fibers, we had to set forth a new interpretation of fiber water density in terms of crystallinity [10]. Our results showed that while nature-dried cotton is almost 100% crystalline, never-dried cotton is by far less crystalline. As to fiber porosity in swollen state, it is known that only cell wall pores and not fiber lumen are correlated to fiber accessibility to reagent molecules. The amount of water in cell wall pores is most accurately defined as fiber saturation point *(FSP).* We found out that the centrifugal water retention value *(WRV)* was equal to the fiber saturation point *(FSP)* in many samples, and we chose *WRV* as a simple measure for *FSP*[1,2,3,4]. Scallan performed a detailed study on this subject and confirmed our report[14]. We found *WRV* for never-dried cotton ranging from 115% to 200% and upwards. However, for mature fibers, values ranging from 115% to 150% were obtained depending on the degree of chemical purification. Since we obtained values of about 120% WRV that is 1.2 cc/g *FSP* for never-dried regenerated cellulose fibers (viscose rayon), we ascribed this value *(FSP 1.2 cc/g)* to all never-dried celluloses, whether biological or regenerated[10,11,12,13]. Treiber found that, in the case of the process of cellulose regeneration from viscose, gel structures with high *WRV* were obtained at first, then *WRV* decreased until never-dried fibrous cellulose was formed [15]. Treiber's results, added to ours, showed parallelism between fiber formation in nature and fiber formation by man, as far as *FSP* was concerned. After air drying (i.e. nature drying) of biological cotton and then soaking it in water, the measured *FSP* was only one third of the value obtained for the never-dried biological cotton. This clearly showed that upon drying of cotton from the original never-dried state a collapse of cell wall capillaries took place which was only partially reversible in water. In other words, soaking of air-dried cotton in water does not revert the cell wall to the original swollen volume it possessed in the original biological never-dried state. Since we have found a correlation between *WRV* -that is *FSP*- and cellulose reactivity[16,17,18,19,20], it becomes evident that never-dried cotton would be more reactive than nature-dried cotton. In fact this was proved by further work on reactivity of biological cotton. It was shown that cotton in the never-dried biological state is as reactive as never-dried wood pulp and never-dried rayon. In this never-dried state all mature-pure cellulose fibers possess the same accessibility and reactivity, and such reactivity is the highest for cellulose in the coherent fibrous form. However, due to drying, cotton cellulose, in contradiction to other celluloses, looses much of its reactivity. It was also shown that derivatives obtained from never-dried celluloses possessed a more or less unique character; due to the more homogeneous substitution achieved in the never-dried state. It is worth mentioning that Fahmy and Mobarak were the first to study the fine structure of biological cellulose, i.e. the never-dried, native cellulose, in a series of research work and articles. They showed 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 i.e protofibrils of magnitude 35 Å (3.5 nanometers) rather than to crystallinity[10,11,12,13]. Keeping in view the possibility of commercial utilization of never-dried cotton, we took it as a new cellulose source for patenting.

Graphical Abstract



2. Materials and Methods: -

2.1. Isolation and characterization of biological cellulose fibers from green cotton bolls:

Unopened green cotton bolls of mature size were gathered from Egyptian cotton plants. 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 include 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 work contained about 64.8 % 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 technique1. The purified biological cellulose fibers were stored immersed in water. A part of the purified biologically swollen fibers was left to dry in air till equilibrium moisture content was reached, which amounted to 6.87%. 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.

Table 1: WRV (fiber saturation point; FSP) and density of cotton staple fibers (biological cellulose) isolated from green cotton bolls.

	FSP(WRV) %	**Density (g/cm^3)**
Never dried	119.00	1.6085
Air dried	52.16	1.6188
Oven dried	45.31	1.6040

2.2. Polymerization of methyl methacrylate monomer in presence of Never-Dried Cotton (biological cellulose) fibers:

Polymerization was carried out at 25ºC in water medium using sodium bisulfite as initiator. The polymerization was performed in a 250ml conical flask with ground joint stopper. In each experiment 4 g of the Never-Dried Cotton (biological cellulose) fibers was put in the reaction vessel, followed by 100 ml of water containing the calculated amount of sodium bisulfite (0.1 mol/l) and shacked by hand then left for 5 minutes. Thereafter 4 g of MMA monomer was added to the reaction vessel. The conical flasks were then immersed in an automatically controlled ultra-thermostat adjusted at 25ºC, and left for the desired polymerization time; during this time period the flasks were shaken by hand every 20 min. The polymerization was stopped by making the reaction medium fairly alkaline with sodium hydroxide solution. At the end of the polymerization time the product was filtered, washed thoroughly with distilled water, methanol, and finally dried at 50ºC. The monomer conversion to polymer was calculated from the relation: Monomer conversion = (CB - B) / M.100 %

Where CB, B, and M are the weights of cotton-polymer composite, cotton, and monomer respectively [21,22].

2.3. Determination of centrifugal water retention value (WRV):

Water retention values were determined according to the modified German standard Method [23,24].

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

Density was determined by the pycnometric method as mentioned in details in previous work [10].

2.5. Preparation and testing of the produced board-like biological cellulose-PMMA green nanocomposites are as mentioned in details before[8,22].

3. Results and Discussion: -

3.1. Polymerization of MMA in absence of any cotton (Blank), at 25ºC in water medium, using 0.1 mol/l sodium bisulfite as initiator:

The percentage of monomer conversion to polymer at different times is shown in Table 2. It is clear that polymerization of MMA under the conditions used in the present work, takes place slowly during the first 3h of the reaction, thereafter the rate increases considerably. After 6 h the rate of polymerization begins to slow down. After 24 h polymerization the conversion of MMA monomer to polymer was 65.7 %.

Table 2: Polymerization of MMA in absence of any cotton ((Blank), at 25ºC in water medium using 0.1 mol/l sodium bisulfite as initiator

Polymerization time in hours	**Monomer conversion %**
1	Zero
2	Zero
3	1.9
4	8.0
5	19.5
6	23.4
7	26.8
24	65.7

3.2. Polymerization of MMA in presence of Never-Dried Cotton Biological Cellulose fibers, at 25°C in water medium, using 0.1 mol/l sodium bisulfite as initiator:

The same conditions used in absence of cotton are applied here. The never-dried cotton (biological cellulose) to water ratio was 1:25.

Table 3 : Polymerization of MMA in presence of Never-Dried Cotton Biological Cellulose fibers, at 25°C in water medium, using 0.1 mol/l sodium bisulfite as initiator

Polymerization time h	Monomer conversion %	Polymer %	Swollen cell wall pore volume of the product FSP(WRV) %
1	10.97	9.37	187
2	42.97	28.84	160
3	61.50	37.14	139
5	76.84	42.02	121
7	85.30	44.61	191
24	85.55	44.65	192

It is evident from Table 3 that the presence of never-dried cotton during polymerization of MMA monomer enhanced the rate of polymerization to a great extent. While after 2 h polymerization time the conversion of MMA monomer to polymer was practically zero in absence of never-dried cotton fibers, the addition of never-dried cotton (biological cellulose fibers) improved the polymerization rate considerably. It was found that after only 2 h polymerization the conversion of MMA monomer to polymer was 42.97% compared to zero polymer conversion in absence of never-dried cotton (biological cellulose fibers). After 24 h polymerization time the conversion of MMA monomer to polymer in presence of never-dried cotton was as high as 85.55 % compared to 65.70 % in absence of the never-dried cotton fibers.

The swollen cell wall pore volume FSP (WRV%) of the produced never-dried cotton –polymer nanocomposites fibers , in the water-saturated state before any drying after polymerization was measured and reported in Table 3 as FSP (WRV %). It is clear from Table 3 that the produced never-dried biological cellulose polymer-nanocomposite possessed tremendously high water uptake i.e. high swollen cell wall pore volume (high WRV). The original FSP (WRV) of the never-dried cotton cellulose fibers used in the present work was 119%. After 1 h polymerization time of MMA, the monomer conversion was 10.97 % and the WRV of the produced never-dried cotton- polymer nanocomposite increased to 187%. This means that the cell wall swollen pore volume increased about 60 %. The produced never-dried biological cotton–polymer nanocomposites showed distinguished unique sponge-like water absorption properties, required for various uses.

3.3. Polymerization of MMA in presence of Air-Dried cotton fibers:

The same conditions used in absence of any cotton are applied here. The results are shown in Table 4. Comparing Table 3 and Table 4, it is evident that the higher WRV of the cellulose-polymer composite, prepared from never-dried biological cotton, indicates that the polymer is mostly grafted on the cellulose fibers rather than homopolymer filling the fiber pores. If the homopolymer fills the fiber pores and precipitates on fiber surfaces it will lead to lower WRV of the final product of the cotton-polymer nanocomposites. It is worth mentioning that in case of polymerization in presence of biological never-dried cotton no formation of homopolymer was noticed and the fibers looked free of any white powder or precipitate even at higher polymer load. On the other hand, during polymerization in presence of air-dried cotton, a white precipitate was quickly formed even during the early stages of the reaction, and by time the cotton fibers were completely covered by white precipitate or homopolymer. This indicates or explains the higher rate of homopolymerization in presence of air-dried cotton. It seems that in presence of biological never-dried cotton, grafting takes place to greater extent than homopolymerization. Grafting takes place at slower reaction rate than homopolymerization. Accordingly, the rate was somewhat lower in presence of biological cotton especially after the first 3 h polymerization time. The higher WRV of the cellulose-polymer nanocomposites prepared from never-dried biological cotton fibers indicates that the polymer is mostly grafted on the cellulose rather than homopolymer filling the fiber pores. If the homopolymer fills the fiber pores and precipitate on fiber surfaces it will leads to lower WRV of the final product of cotton-polymer nanocomposite.

Table 4 : Polymerization of MMA in presence of Air Dried Cotton fibers, at 25° C in water medium, using 0.1mol/l sodium bisulfite as initiator

Polymerization time h	Monomer conversion %	Polymer %	Swollen cell wall pore volume of the product FSP(WRV) %
1	7.53	6.63	107
2	5185	32.84	110
3	66.71	38.62	92
5	81.20	41.52	71
7	88.81	45.01	76
24	88.84	45.22	78

3.4. Percentage of grafted to homopolymer in the produced cotton-polymer composites in both cases of using Never-Dried and Air-Dried Cotton during polymerization of MMA, in water medium at 25°C, using 0.1mol /l sodium bisulfite as initiator:

Table 5 shows the results obtained after extraction of the homopolymer by suitable solvent (benzene) in the above mentioned cases.

Table 5: Percentage of grafted to homopolymer in the produced cotton-polymer composites in both cases of using Never-Dried and Air-Dried Cotton during polymerization of MMA, in water medium at 25 °C, using 0.1mol /l sodium bisulfite as initiator

Type of Cotton	Polymerization time in hours	Grafted %	Homopolymer %	Total polymer %
Never-Dried (Biological)	1	2.76	7.61	10.37
	3	10.30	26.84	37.14
Air-Dried	1	1.43	5.20	6.63
	3	5.09	33.53	38.62

The biological never-dried cotton possesses high swollen cell wall pore volume as shown from its high original WRV which amounts to 119 % (as shown in Table 1). This promotes diffusion of the MMA monomer (which possesses suitable molecular size) into the inner layers of the fibers to come in contact within or to the accessible active centers and thus grafting copolymerization is enhanced. The introduction of few PMMA in the inner structure of the fibers, leads to widening up of the fine structure and hence the WRV increase. After certain polymer loading of the fibers, introducing more PMMA blocks the fine structure, leading to decrease in the WRV. On the other hand, the air-dried cotton possesses lower original swollen pore volume as shown from its original lower WRV which amounted to about 52 % (see Table 1).

Summing up, it was found that grafting leads to higher WRV because it takes place within the inner surfaces of the fibers. Homopolymerization is a sort of filling the pores of the fibers leading to lower WRV (see Tables 3, 4, 5. Also see figure 1 and Figure 2).

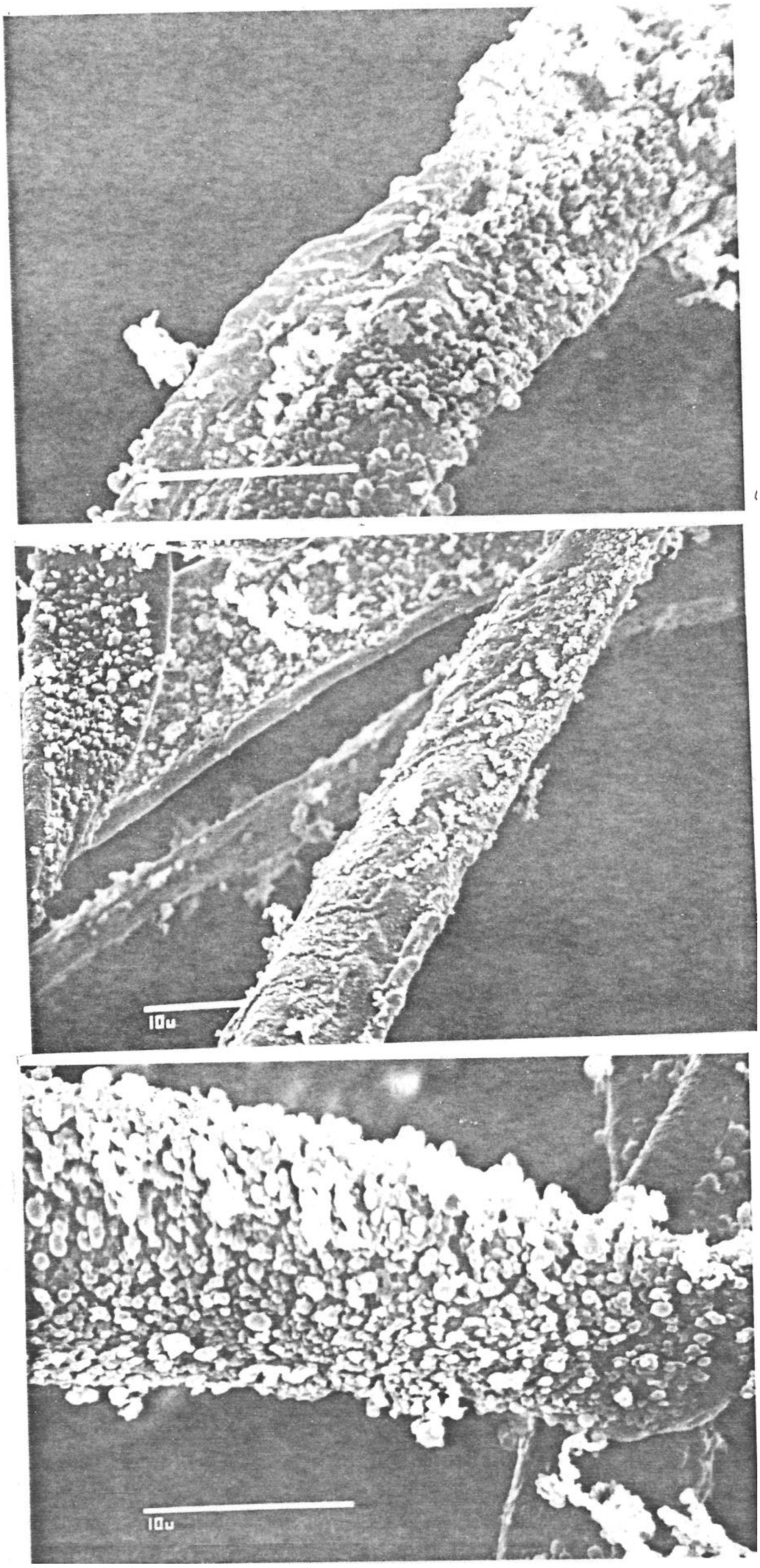


Figure 1 : Never-dried biological cotton green nanocomposite vaccinated with methymethacrylate (*before* extraction of homopolymer).

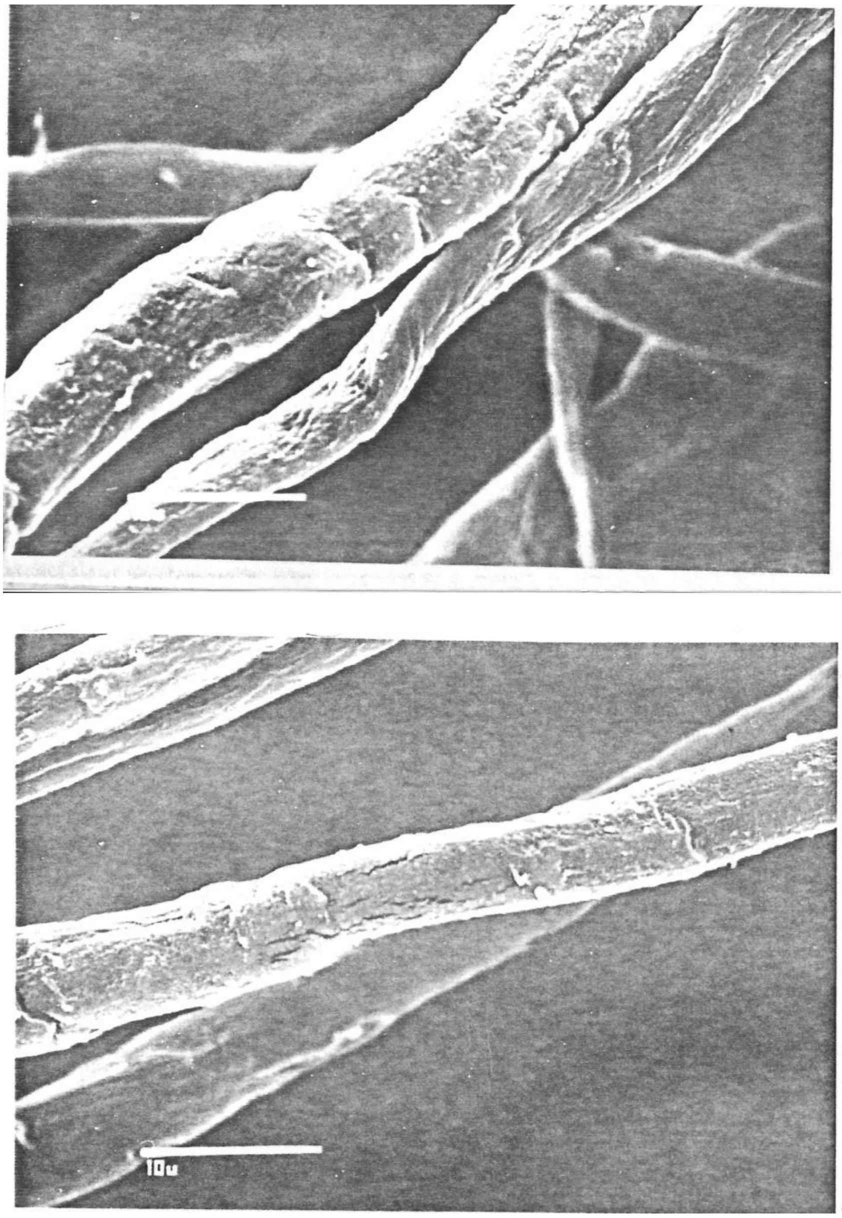


Figure 2: Never-dried biological cotton green nanocomposite vaccinated with methymethacrylate (*after* extraction of homopolymer).

Moreover, pressing of the produced composites in a closed die, at specific conditions [8,22], resulted in board-like transparent nanocomposites of bending strength up to 955 kg/cm^2.

Conclusion:

The molecular size of MMA is small enough to diffuse and penetrate within and into the cell wall pores of the cotton fibers. These molecules begin to polymerize within the cell wall and the early product of polymerization e.g. dimmers and trimers act as spacers and widen the porous structure of the cell wall. We called this phenomenon or process *"intra-polymerization"*. This leads to increase in WRV. Simultaneously, polymerization on the external surfaces of the fibers leads to polymerization products which penetrate into the fibers and clog some of the cell wall pores leading to decrease in WRV. We called this phenomenon *"inter-polymerization"* i.e. polymerization outside the cell wall. As the process of polymerization proceeds, the polymerization within the cell wall leads to cell wall destruction as indicated by the increase of the WRV of the fibers, leading to sponge-like structure of the fibers. Higher water uptake i.e. water retention value (WRV) of the cellulose-PMMA-copolymer nanocomposites prepared from never-dried biological cotton fibers, and microscopic investigations confirmed that the polymer was mostly grafted on the cellulose rather than homopolymer filling the fiber pores (See Figures 1 and 2).

Compliance with Ethical Standards:

The authors declare that they have no conflict of interest.

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