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## **Nanocomposites from Natural Cellulose Fibers Incorporated with Sucrose**

By

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## **ABSTRACT**

It is shown for the first time world wide, in the present work, that sucrose can be easily placed by simple techniques within the micropores or nanostructure of the mercerized non-dried cotton linters fibers to create a low cost cellulose substitute. Such sucrose-containing nanocomposites find their suitable uses as specialty absorbent paper. Relative to the sucrose-free paper, the sucrose-containing counterparts exhibit greater breaking length and remarkably high water uptake (W.R.V.) up to sucrose-content 8-15 % w/w. Mercerization of cotton linters, before incorporating them with sucrose, greatly enhanced the retention of sucrose in the prepared paper nanocomposites as compared to the case of unmercerized cotton linters. We assume that regions of the cell wall lamellae, on both sides of the sucrose spacers, are stressed during drying because the sucrose spacers hinder them to relax. This leads to a strain, which makes some microfibrils be partially released and protrude out of the fiber. Thus a sort of fiber beating takes place. We called this phenomenon **Incorporation-Beating** or **Encapsulation-Beating** to differentiate it from chemical and mechanical beating; and it explains the great increase in breaking length of the paper nanocomposites prepared from the mercerized non-dried sucrose-loaded linters.

**Keywords:** nanocomposites, cotton linters fibers, cell wall nanoporous structure, reversion to original cell wall nanoporous structure, mercerized non-dried state, sucrose, specialty paper, encapsulation-beating or incorporation-beating

## **Introduction and Object :-**

It has been frequently noticed that isolated plant fibers, with similar chemical analytical data, show different reactivities when subjected to one and the same chemical reaction. Fibers with similar chemical composition, obtained from different plants or from one plant by different pulping methods, display also different behavior in papermaking operations. To elucidate the reasons for the different behavior of chemically alike fibers, great efforts have been devoted to the study of the micro or fine structure of cellulose fibers. Early research work revealed that the fibers are porous bodies. Consequently, reagent molecules have to diffuse through the complex microcapillary or nanosystem of the fiber till they reach the innermost layers of the fiber and react with them. Hence, it becomes evident that the fine structure of fibers and the ease with which this structure is opened up by the reagents, influence the rate and the extent of the reaction. The same applies to the degree of fiber swellability by water, which affects the freeness and degree of conformation of fibers in paper sheet and consequently paper strength.

Several theories about the fine structure of fibers have been presented (Bonart et al. 1960; Hermans 1949; Tarkow 1950; Manely 1964). 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 (Stone and Scallan 1968). 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 (Stone and Scallan 1968). Density measurements were adopted for studying the fine structure of both the dried and the never-dried water saturated states (Fahmy and Mobarak 1971); 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 W.R.V. was adopted in the present work for studying the fine structure of the swollen and dried cell wall.

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 , as measured by FSPvolume

Y. Fahmy and F. Mobarak were the first who studied the fine structure of the biological cellulose i.e. never-dried, native cellulose in a series of research work and articles (Fahmy and Mobarak 1971; Fahmy and Mobarak 1971; Fahmy and Mobarak 1972; Fahmy and Mobarak 1976). 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  $35 \text{ \AA}$  (3.5 nanometer) rather than to crystallinity (Fahmy and Mobarak 1972).

A high fiber saturation point (F.S.P.) of about 120 % is ascribed to pure cellulose nature fiber in the never-dried state, irrespective of plant origin, as well as to never-dried regenerated cellulose (Fahmy and Mobarak 1976); and treatment with sodium hydroxide solution of about 18 % concentration (mercerization) reverts cotton cell wall completely to the original biological volume as far as (F.S.P.) is concerned. In other words, the original cell wall nanostructure could be recreated or tailored again after subjecting the air-dry cotton to mercerization and using the mercerized fibers in the non-dried state (Fahmy and Mobarak 1976). Accordingly, in the present study, mercerization of the air-dried fibers

and using them in the non-dried state was adopted to make use and benefit of the original cell wall nanostructure.

The pore structure of the cell wall of never-dried pulp fibers has been identified as a general micropackaging or encapsulation system for a broad range of both organic and inorganic chemicals (Allan and Ko 1995; Allan et al.1991; Allan et al.1992; Allan et al.1992; Balaban1980; Lee1980; Ritzenhaller 1991). These substances are entrapped in the cellulosic fiber matrix during the collapse of the cell wall pores as the pulp is dried (Allan et al.1985).

Studies on the use of nanoadditives for incorporating the cell wall nanoporous structure of the mercerized non-dried cellulose fibers, its comparison to using them in the case of air-dry fibers and properties of the paper made therefrom are lacking in the literature. The present study aims at filling this gap. The study is oriented to make use of nanoadditives to produce paper of improved water absorbency.

Sucrose is the nanoadditive we chose for this part of the work. The disaccharide sucrose is an attractive potential candidate for location within the cell wall, because of its low cost, abundance, small size and substantial hydrogen-bonding capacity. Also, the sucrose is now commercially available in quantities commensurate with the volume of paper. When aqueous solutions of sucrose are equilibrated with never-dried pulp, the sucrose should be able to penetrate into every micropore or nanopore larger than 8 Å (0.8 nanometer), the volume of these sucrose

accessible pores amounts to 86.5% of the total pore volume of the micropores . Thus the dissolved sucrose 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 sucrose molecules derived by them (Allan et al. 1999; Allan et al. 1999; Allan et al. 1999; Allan et al. 2003; Fernandez et al. 2002; Stone and Scallan 1968).

## **Results and Discussions: -**

Cotton linters pulp is the basic specialty agricultural residue pulp possessing the highest alpha cellulose content.

The cotton linters used in this work are Egyptian cotton linters, kindly provided by Abo-Zabel Mill, Cairo. The cotton linters were provided air dry (A.D.), in loose form. We have carried out chemical and physical analysis for these cotton linters. The results of the analysis and physical properties are reported in Table 1.

### **1. Effect of Incorporating Air-Dry Cotton Linters with Nanoadditive on the Properties of the Produced Paper Composites: -**

The air-dry cotton linters were first beaten till 30 °SR (55 minutes). The beaten linters were then put in the mixer and impregnated with sucrose solutions of the concentrations 5, 10, 15 and 20 % w/w and stirred for 15 minutes then paper sheets were made as mentioned in the experimental part from the pulp suspensions in the sucrose solutions. The properties of the obtained paper are shown in Table 2.

It is clear from Table 2 that the air-dry cotton linters after beating to 30 °SR then loading the beaten linters with different concentrations of sucrose solutions using suitable loading or incorporation technique during



stock preparation and sheet making, resulted generally in some improvements in the properties of the paper made therefrom. The amounts of sucrose retained in the prepared paper sheets were determined gravimetrically (Allan et al. 1999); they are also reported in Table 2. It is evident from Table 2 that the sucrose content of the handsheets was low in all cases and did not exceed 3 % by weight. However, the water uptake (W.R.V.) of the loaded paper sheets increased with increasing the sucrose content in sucrose-containing paper. The % increase in (W.R.V.) reached a maximum of about 36 % when the concentration of the incorporating sucrose solution was 15-20 % w/w. The breaking length also slightly increased in a progressive manner. The highest % increase in breaking length was about 11%. The wet breaking length also increased progressively. The highest % increase in wet breaking length was about 6%.

## **2. The Effect of Mercerization of Cotton Linters Before Incorporation with Sucrose on the Properties of the Paper Composites Made Therefrom: -**

As mentioned before, the present study on cotton linters is planned to mercerize the air-dry linters and to use them in the non-dried water saturated state after mercerization to study the effect of incorporating

sucrose into the mercerized non-dried cotton linters on the properties of the sucrose-containing paper nanocomposites.

In these experiments, the air-dry cotton linters were subjected to mercerization using sodium hydroxide solution (17.5 % w/w) at 20°C for thirty five minutes, then washed with water till neutrality and kept non-dried ready for further processing. The W.R.V. of the mercerized non-dried linters fibers was determined and found to be 119.91 %. The mercerized non-dried cotton linters were beaten in a Jokro beater till 30 °SR (45 minutes). Each of the prepared sucrose solutions was added to the mercerized beaten cotton linters in the mixer and stirred for 15 minutes then paper handsheets were made as mentioned in the experimental part from the pulp suspensions in the sucrose solutions. Properties of paper made from mercerized non-dried cotton linters beaten to 30 °SR then loaded with sucrose are shown in Table 3. The amounts of sucrose retained in the prepared paper sheets were determined; they are also reported in Table 3.

It is clear from Table 3 that mercerization of cotton linters, before incorporating them with sucrose, greatly enhanced the retention of sucrose in the prepared paper composites as compared to the case of unmercerized cotton linters. (Compare Table 2 and Table 3 and see Figure 1 ). It is worth mentioning that the W.R.V. of the mercerized non-dried cotton linters pulp was 119.91 % compared to 58.01 % in the case

of unmercerized air-dry cotton linters pulp i.e. the cell wall water-saturated pore volume of linters fibers, as measured by W.R.V., increased to more than twice its value due to mercerization. This is the reason for the increase in the retention of sucrose by the mercerized fibers.

The water uptake (W.R.V.) of the sucrose-loaded paper sheets increased with increasing the sucrose content in sucrose-containing paper. The W.R.V. of the sucrose-loaded paper sheets reached a maximum of about 116 % at sucrose content of about 15 % w/w. Figure 2 shows the comparison between the W.R.V. of paper sheets prepared from mercerized non-dried sucrose-loaded linters and the W.R.V. of paper sheets prepared from unmercerized sucrose-loaded cotton linters.

The breaking length also increased progressively and reached its maximum at sucrose content of about 15 % w/w. The highest % increase in breaking length was about 50 %. The wet breaking length also increased progressively and reached its maximum at sucrose content of about 15 % w/w. The highest % increase in wet breaking length was about 26 %.

It is evident from these results that the sucrose possesses an appropriate molecular size to penetrate most of the micropores in the cell walls of mercerized non-dried cotton linters and resulted in great improvement in strength and water uptake of the obtained sucrose-containing paper nanocomposites.

It can be safely concluded that sucrose functioned as cellulose substitute in paper in terms of its effect on the commercially important mechanical and physical properties. Relative to the sucrose-free paper, the sucrose-containing paper made from mercerized non-dried cotton linters exhibit greater breaking length, as well as high W.R.V., up to sucrose content of about 15 % w/w.

The present work shows that sucrose can be placed within the micropores or nanopores of the mercerized non-dried cotton linters to create a low-cost cellulose substitute and to reduce the fiber content of the specialty absorbent paper nanocomposites made therefrom.

### **3. The Role of Sucrose in Preservation of the Non-Dried Cell Wall Nanostructure of the Mercerized Cotton Linters Fibers: -**

In these experiments the mercerized non-dried cotton linters were first beaten to 30 °SR (45 minutes); then the mercerized beaten non-dried linters were incorporated with 20 % w/w sucrose solution, filtered, and left to dry in air at room temperature. The mercerized sucrose-containing air-dried linters fibers were then forwarded to the normal standard papermaking techniques and handmade paper sheets were prepared and tested. The results are reported in Table 4 and illustrated in Figure 3. The sucrose content in the prepared paper sheets was determined

gravimetrically, and it is also included in Table 4. It was found that the sucrose-content in the paper sheets prepared from the mercerized non-dried cotton linters, which was incorporated with sucrose then air-dried before papermaking, was 8 % w/w. This value is lower than that in the case of loading the mercerized non-dried linters during stock preparation, which amounted to about 15 % w/w.

It is evident from Table 4 that the breaking length of the sucrose containing paper sheets was much higher than their counterpart sucrose-free paper sheets. The % increase in breaking length amounted to about 50% in both cases of incorporation techniques whether the sucrose was placed within the non-dried mercerized cotton linters cell wall then the incorporated linters were air dried before papermaking or when the sucrose incorporated into the non-dried mercerized cotton linters cell wall during papermaking. Water uptake of the sucrose-containing paper sheets increased greatly in both cases and practically to the same extent, regardless of the difference in the sucrose content of the paper sheets due to the different loading techniques of sucrose (before or during papermaking).

It can be safely concluded that incorporation of the mercerized non-dried cotton linters with 20 % w/w sucrose solution preserves the nanostructure of the cell wall and prevent collapse of the porous structure during drying of the loaded linters. This is confirmed by the high

(W.R.V.) of the paper sheets prepared from non-dried mercerized linters incorporated with 20% w/w sucrose solution then air dried before papermaking, which was found to be as high as the (W.R.V.) of the paper sheets prepared from mercerized non-dried linters fibers loaded with the sucrose during papermaking to avoid any drying before papermaking.

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

The successful results, obtained in the case of mercerized non-dried cotton linters incorporated with 20 % w/w sucrose solution then air dried before papermaking, show that sucrose can be easily placed by simple techniques within the micropores or nanostructure of the mercerized non-dried cotton linters fibers to create a low cost cellulose substitute.

Relative to the sucrose-free paper, the sucrose-containing counterparts exhibit greater breaking length and remarkably high water uptake (W.R.V.) up to sucrose-content 8-15 % w/w. Such sucrose-containing nanocomposites find their suitable uses as specialty absorbent paper.

We assume that regions of the cell wall lamellae, on both sides of the sucrose spacers, are stressed during drying because the sucrose spacers hinder them to relax. This leads to a strain, which makes some microfibrils be partially released and protrude out of the fiber. In other words, a sort of fiber beating takes place. This can be called **Incorporation Beating** or **Encapsulation Beating** to differentiate it from chemical and mechanical beating. This phenomenon is reflected in the great increase of breaking length of the paper nanocomposites prepared from the mercerized sucrose-loaded linters in comparison to their sucrose-free counterparts.

## **Experimental: -**

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

Water retention values were determined according to the modified German Standard Method. (Jayme et al. 1958; Merkblatt IV/33/57).

### **- Incorporation of Sucrose (Nanoadditive) into the Cell Wall of Non-Dried Fibers: -**

The different methods of incorporating sucrose into the non-dried pulp fibers recommended recently (Allan et al. 1999; Allan et al. 1999; Allan et al. 1999), were applied in the present work; then we offered – after several preliminary investigations – a simple easy applicable method for sucrose entrapping in the cellulosic fiber matrix during the collapse of the cell wall pores as the pulp is 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. In all experiments, the cellulosic fibers were first beaten to 30 °SR. The beaten non-dried fibers were incorporated with sucrose solutions of the concentrations 5, 10, 15 and 20 % w/w. The retained amount of sucrose in pulp or paper was determined gravimetrically (Allan et al.1999).

### **- Paper Sheet Making: -**

The paper sheets were prepared according to the SCA standard, using the SCA - model sheet former (AB Lorenzen and Wetter).



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**Table 1**  
Analysis and physical properties of Egyptian cotton linters

Moisture Content %	5.30
Ash Content %	0.22
Alphacellulose %	98.79
Degree of Polymerization (D.P.)	971
Water Retention Value (W.R.V.) A.D. %	58.01

**Table 2**

Properties of paper made from air-dry cotton linters before and after incorporating the linters with sucrose

Concentrations of the sucrose solutions % w/w	zero	5	10	15	20
Breaking length in meters	1740	1881	1920	1925	1939
% increase in breaking length	----	8.10	10.35	10.63	11.44
Wet breaking length in meters	291	298	302	311	310
% increase in wet breaking length	----	2.41	3.78	6.87	6.53
W.R.V. of paper sheets %	53.52	60.00	68.33	72.85	73.00
% increase in W.R.V.	----	12.11	27.67	36.12	36.40
Sucrose content in sucrose-containing paper % w/w	zero	0.86	1.48	2.66	2.83

**Table 3**

Properties of paper made from mercerized non-dried cotton linters beaten to 30 °SR then incorporated with sucrose

Concentrations of the sucrose solutions % w/w	zero	5	10	15	20
Breaking length in meters	1688	2006	2225	2532	2486
% increase in breaking length	----	18.84	31.81	50.00	47.27
Wet breaking length in meters	286	304	311	363	350
% increase in wet breaking length	----	6.29	8.74	26.92	22.38
W.R.V. of paper sheets %	78.15	95.00	106.33	114.99	116.00
% increase in W.R.V.	----	21.56	36.06	47.14	48.43
Sucrose content in sucrose-containing paper % w/w	zero	3.11	6.50	9.85	14.70

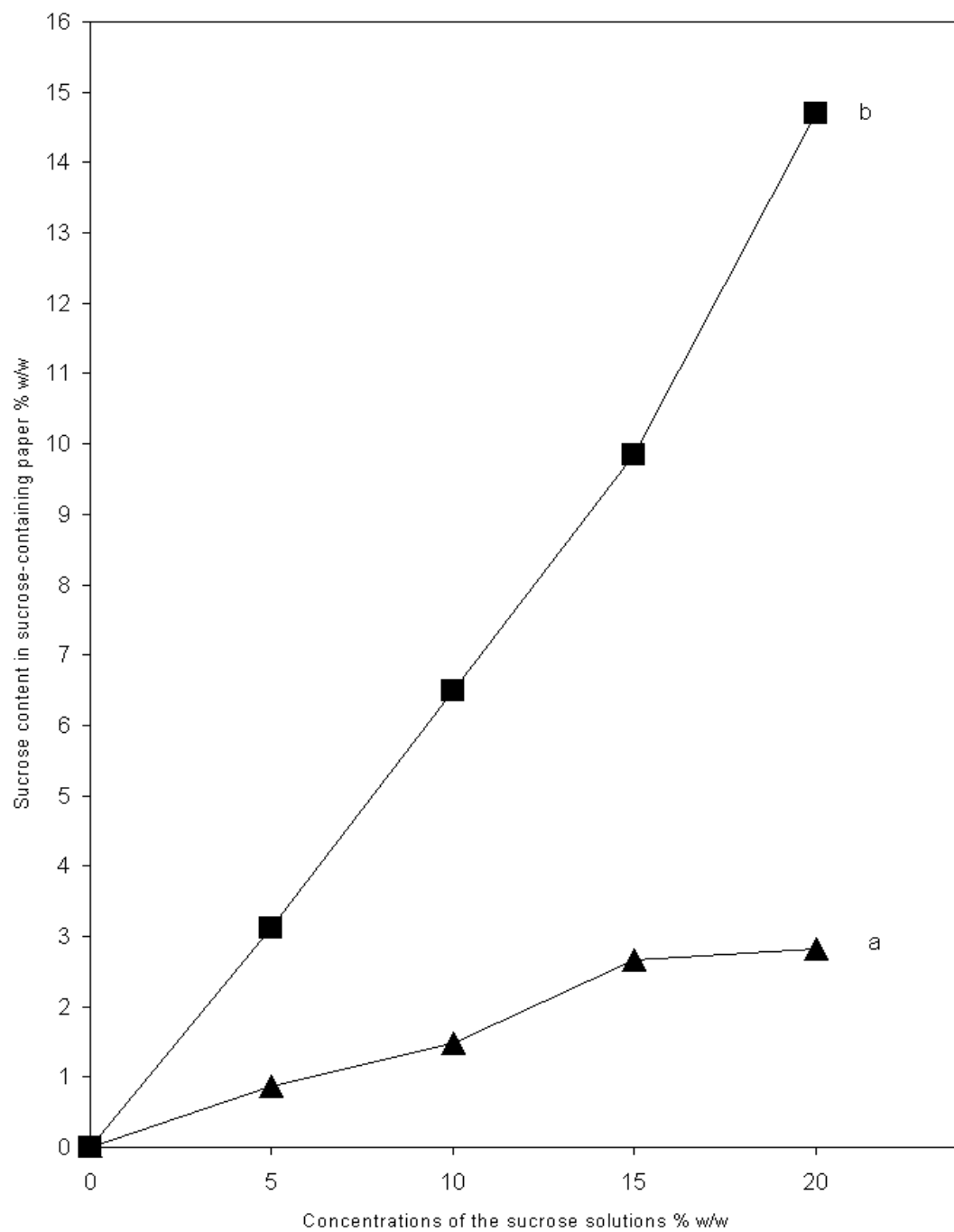
**Table 4**

Properties of paper made from mercerized non-dried cotton linters incorporated with 20 % w/w sucrose solution then air dried at room temperature before papermaking, compared to the properties of paper made from mercerized non-dried cotton linters incorporated with 20 % w/w sucrose during papermaking

Concentrations of the sucrose solutions % w/w	zero	20	20
Incorporation technique	Blank (Sucrose-Free)	During papermaking	Before papermaking
Breaking length in meters	1688	2486	2501
% increase in breaking length	----	47.27	48.16
Wet breaking length in meters	286	350	348
% increase in wet breaking length	----	22.38	21.68
W.R.V. of paper sheets %	78.15	116.00	118.62
% increase in W.R.V.	----	48.43	50.99
Sucrose content in sucrose-containing paper % w/w	zero	14.70	8.15

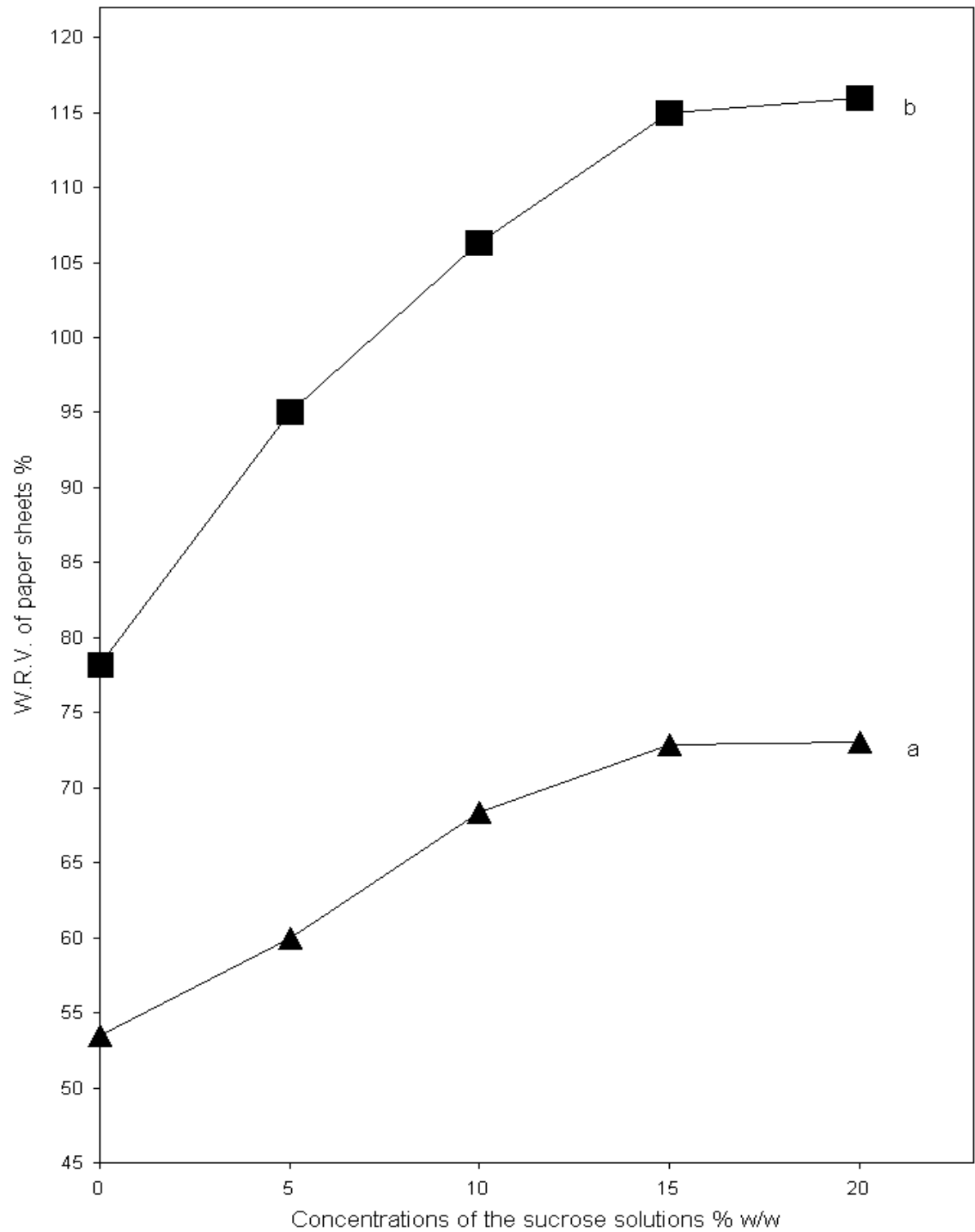
**Fig. 1**

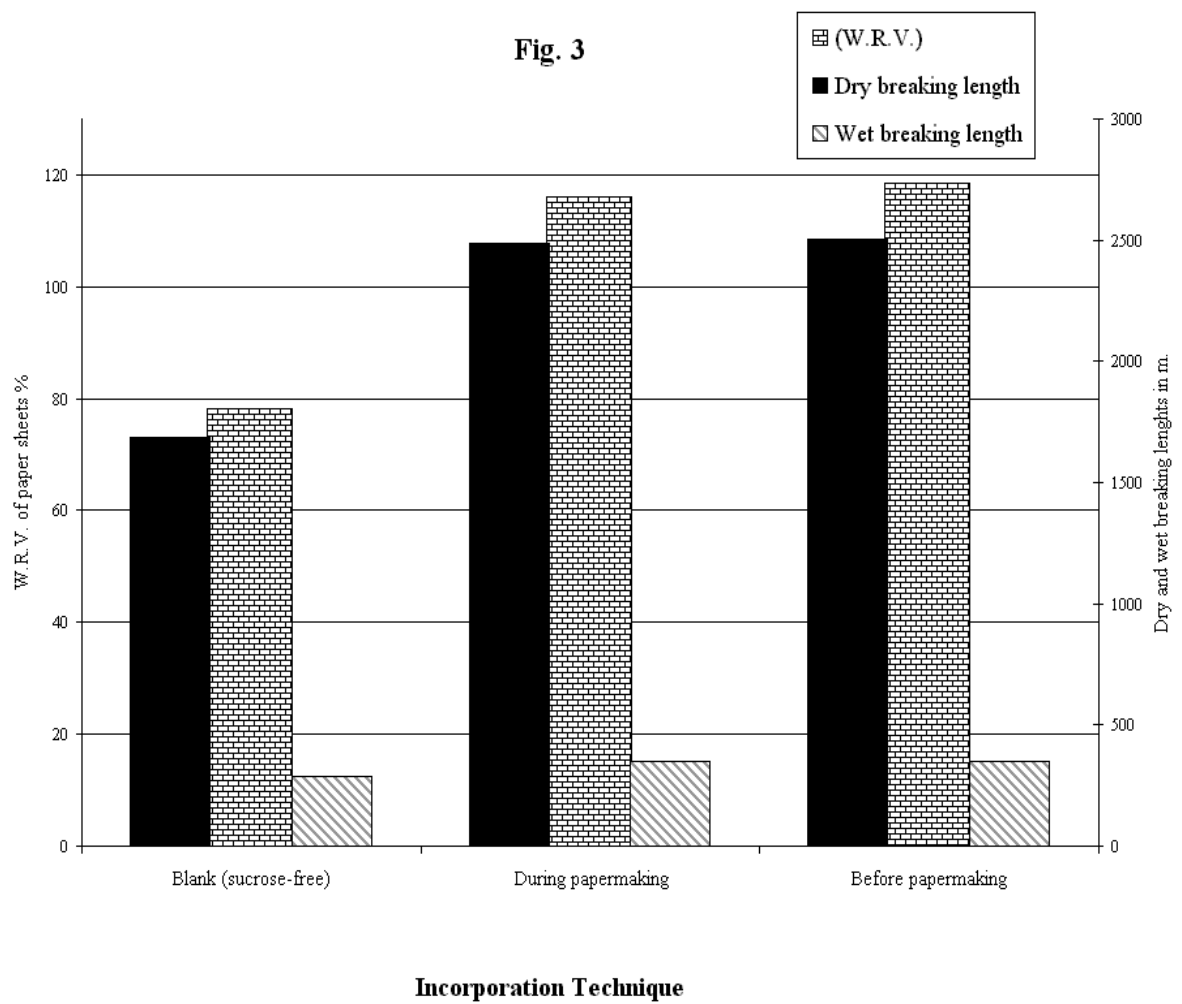
Comparison Between Mercerized b  
and Unmercerized a



**Fig. 2**

Comparison Between Mercerized b and Unmercerized a







## **Figure Legends**

- Fig. 1** Comparison between mercerized b and unmercerized a
- Fig. 2** Comparison between mercerized b and unmercerized a
- Fig. 3** Properties of paper made from mercerized non-dried cotton linters incorporated with 20 % w/w sucrose solution then air dried at room temperature before papermaking, compared to the properties of paper made from mercerized non-dried cotton linters incorporated with 20 % w/w sucrose during papermaking