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Nanocomposites from natural cellulose fibers filled with kaolin in presence of sucrose

Tamer Y.A. Fahmy *, Fardous Mobarak

Cellulose and Paper Department, National Research Center, Sh. El-Tahrir, Dokki, Cairo, Egypt

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Abstract

This work introduces, for the first time worldwide, an advanced nanocomposite involving two additives – a nanoadditive and a conventional additive – within a matrix of natural cellulose fibers. The first additive (the nanoadditive) is sucrose, which incorporates the nanoporous structure of the cell walls of cellulose fibers. The second additive (the conventional additive) is kaolin, the famous paper filler. Kaolin is enmeshed between the adjacent cellulose fibers. This advanced paper nanocomposite was prepared by simple techniques.

The present work shows, for the first time, that sucrose can overcome the ultimate fate of deterioration in strength of paper, due to addition of inorganic fillers such as kaolin. This deterioration was counteracted by incorporating cellulose fibers with sucrose, which leads to incorporation beating of the fibers, and thus increases the strength of the produced paper nanocomposites. In addition, sucrose was proven – for the first time – to act as retention aid for inorganic fillers such as kaolin. We called this phenomenon *incorporation retention* to differentiate it from the conventional types of retention of inorganic fillers.

Recent studies, by the authors and others, have shown that incorporating cellulose fibers, with sucrose, leads to paper nanocomposites of enhanced strength (breaking length). Also, sucrose is privileged by its small size (0.8 nm), substantial hydrogen bonding capacity, low cost, and abundance. Therefore, sucrose was chosen as a nanoadditive in this work. The present study shows that the nanoadditive sucrose may find its use as a new retention aid and strength promoter in papermaking.

Keyword: Nanocomposites

1. Introduction and object

Nanoporous materials are classified as naturally occurring nanoporous materials, and synthetic nanoporous materials. Naturally occurring nanoporous materials may be of mineral origin (such as zeolites), or of biological origin (such as the nanoporous structure of the cell walls of cellulose fibers) (Kelsall & Hamley, 2005; Vaia & Krishnamoorti, 2002).

The authors and others, in recent work, successfully manipulated the natural nanoporous structure of cellulose fibers to increase the water absorption and reactivity of cellulose fibers, to produce water absorbent paper nanocomposites, or to greatly increase the strength of paper made from cellulose fibers. This was achieved by incorporating the nanoporous structure, of water swollen cellulose fibers, by the nanoadditives sucrose and glucose (Fahmy & Mobarak, 2008; Fahmy, Mobarak, Fahmy, Fadl, & El-Sakhawy, 2006).

It was shown that sucrose and glucose molecules are entrapped in the cell wall nanopores of cellulose fibers, during the collapse of these pores, as the fibers are dried. The sucrose and glucose molecules act as spacers, and prevent the irreversible collapse of the natural nanoporous structure of cellulose fibers, which – normally – occurs during drying. Thus the incorporation of sucrose or glucose into cellulose fibers leads to nanocomposites of increased water

* Corresponding author.
E-mail address: drtamer_y_a@yahoo.com (T.Y.A. Fahmy).

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uptake (water retention value), and increased reactivity (i.e. increased accessibility to reagents) (Fahmy & Mobarak, 2008; Fahmy et al., 2006).

It was also shown that incorporating the nanoporous structure of cellulose fibers, with sucrose, leads to paper nanocomposites of enhanced strength (breaking length). The cell walls, on both sides of the incorporated sucrose spacers, are stressed during drying because sucrose spacers hinder them to relax. This leads to a strain, which makes some microfibrils partially released and protrude out of the fibers. This in turn leads to more efficient entanglement of the fibers, and hence increases the strength of the prepared paper nanocomposites. In other words, a sort of fibers beating takes place. The authors and others called this phenomenon *incorporation beating* to differentiate it from chemical and mechanical beatings, conventionally applied to increase the strength of paper (Fahmy et al., 2006).

These successful results encouraged the authors to expand the studies to a sugar industry byproduct rich in sucrose, which is molasses. Using this byproduct, as an additive for cellulose fibers, succeeded in producing paper nanocomposites of enhanced dry and wet strength and improved water absorbance (Fahmy, 2007a, 2007b).

It is worth mentioning that when aqueous solutions of sucrose are equilibrated with the water-swollen pulp (cellulose fibers), sucrose should be able to penetrate into every micropore or nanopore larger than 8 Å (0.8 nm). 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 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 from them (Stone & Scallan, 1968).

Sucrose is privileged by its low cost, abundance, commercial availability in quantities commensurate with paper, small size and substantial hydrogen bonding capacity. Therefore, sucrose was chosen as a nanoadditive in this work.

It is intended in the present work to investigate – for the first time – the strength promoting effect of sucrose as a means to counteract the ultimate fate of deterioration in strength of paper, due to addition of inorganic fillers such as kaolin. Also, the effect of sucrose on the retention of inorganic fillers (such as kaolin) will be investigated, for the first time.

To achieve these aims, we shall prepare an advanced paper nanocomposite involving two additives – a nanoadditive and a conventional additive – within a matrix of natural cellulose fibers. The first additive (the nanoadditive) is sucrose, which incorporates the nanoporous structure of the cell walls of cellulose fibers. The second additive (the conventional additive) is kaolin, the famous paper filler. Kaolin is enmeshed between the adjacent cellulose fibers. This advanced paper nanocomposite will be prepared by simple techniques.

2. Materials and methods

The cellulose fibers (pulp fibers) used in this work were high α-cellulose wood pulp fibers. We have carried out chemical and physical analyses for this pulp. The results of the analyses and physical properties are reported in Table 1.

The conventional additive (inorganic filler kaolin) used in this work was Egyptian upgraded kaolin prepared on pilot scale, kindly provided by Metallurgical Research and Development Institute, El-Tebeen, Egypt. Its specifications and analyses are: Kaolinite 92.43, Al_2O_3 35.21%, total SiO_2 44.43%, Fe_2O_3 0.92%, TiO_2 1.38%, moisture content 0.73%, ash content 87.99%, and brightness 73.90%. The bulk density of this kaolin was 0.846 before grinding and 1.1813 after grinding.

2.1. Filling the cellulose fibers (pulp fibers) with the conventional additive (inorganic filler kaolin)

In all experiments, the cellulosic fibers were mixed with kaolin and beaten for 15 min. The consistency was adjusted to 6%. The fibers were filled with increasing kaolin quantities (5, 10, 15 and 20 g of kaolin per 100 g of pulp fibers).

2.2. Incorporating the nanoadditive sucrose into the nanoporous structure of cell walls of kaolin-filled cellulose fibers (pulp fibers)

The incorporation methods used in the present work were recently established by the authors and others (Fahmy, 2007a, 2007b; Fahmy & Mobarak, 2008; Fahmy et al., 2006). After several preliminary experiments, we fixed the optimum conditions for manipulating the nanoadditive sucrose as a retention aid and strength promoter. The beaten nondried kaolin-filled fibers were incorporated with sucrose solution of the concentration 8% w/w, and stirred in the mixer for 15 min.

2.3. Paper sheet making

Paper sheet composites were made from fibers filled with kaolin only, and paper sheet nanocomposites were made from sucrose-incorporated kaolin-filled fibers. The paper sheets were prepared according to the SCA stan-

Table 1
Analysis and physical properties of the wood pulp

Alphacellulose (%)	94.81
Pentosanes (%)	4.19
Ash content (%)	0.11
Water retention value (WRV) A.D. (%)	88.40

dard, using the SCA-model sheet former (AB Lorenzen and Wetter).

2.4. Determination of the retention value of the inorganic filler kaolin

The amounts of the inorganic filler kaolin, retained in the kaolin-filled paper sheet composites and in the sucrose-incorporated kaolin-filled paper sheet nanocomposites, were determined by ignition of accurately weighed paper sheets. The retention value was calculated as the ratio of the amount of filler retained in the paper sheet to that originally added. The loss resulting from filler dehydration due to ignition was taken into consideration (Mobarak & Augustin, 1976; Mobarak, El-Shinnawy, & Soliman, 1998; Mobarak, Fahmy, & Augustin, 1976). The retention value was calculated by the formula: Retention value % = (wt. of retained kaolin/wt. of added amount of kaolin) × 100.

3. Results and discussion

3.1. Effect of filling cellulose fibers (pulp fibers) with the conventional additive (inorganic filler kaolin), in the absence of sucrose

Table 2 shows the properties of paper composites made from cellulose fibers, filled with increasing amounts of kaolin (5, 10, 15 and 20 g of kaolin per 100 g of fibers).

It is evident from Table 2 that the strength (breaking length) of the paper composites decreased with increasing the amount of added kaolin. The breaking length of the blank (kaolin-free paper) was 2015 m, while that of the kaolin-filled paper composites decreased to 1634 m, due to addition of 20 g of kaolin per 100 g of fibers. Thus the percentage decrease in breaking length, due to addition of kaolin, reached 18.90%.

Also, the wet breaking length of paper composites decreased due to addition of kaolin. The wet breaking length of the blank (kaolin-free paper) was 403 m, while that of the kaolin-filled paper composites decreased to 316 m, due to addition of 20 g of kaolin per 100 g of fibers. Thus the percentage decrease in wet breaking length, due to addition of kaolin, reached about 21.58%.

This decrease in strength (breaking length) of the paper composites is a normal phenomenon, observed due to addition of inorganic fillers such as kaolin. These fillers are enmeshed between the adjacent cellulose fibers, and hence interrupt the inter-fiber bonding between adjacent fibers (Casey, 1962; Mobarak & Augustin, 1976; Mobarak et al., 1976, 1998; Roberts, 1996).

3.2. Effect of incorporating the kaolin-filled cellulose fibers with the nanoadditive sucrose on the properties of the produced advanced paper nanocomposites

In these experiments, the beaten nondried kaolin-filled cellulose fibers (pulp fibers) were incorporated with sucrose solution of the concentration 8% w/w. Paper sheet nanocomposites were prepared from these beaten nondried kaolin-filled sucrose-incorporated fibers, as mentioned in the experimental part. The amount of sucrose retained in the produced paper nanocomposites was determined gravimetrically (Fahmy et al., 2006). It was found to be 2.97%.

Table 3 shows the properties of paper nanocomposites made from the sucrose incorporated kaolin-filled cellulose fibers, at increasing amounts of kaolin, of 5, 10, 15 and 20 g per 100 g of fibers.

It is evident by *comparing* Tables 3 and 2 that the breaking length of paper nanocomposites, produced from sucrose-incorporated kaolin-filled fibers, is greater than that of paper composites produced from the kaolin-filled sucrose-free fibers. This is true for all the added amounts of kaolin. At addition of 20 g of kaolin per 100 g of fibers, the breaking length of the kaolin-filled sucrose-free paper composites was 1634 m, while that of the sucrose-incorporated kaolin-filled paper nanocomposites was 2187 m. Thus, there is a percentage increase of 33.84% in the breaking length, due to incorporation of the cellulose fibers by sucrose.

It is evident from Table 3 that the breaking length of the sucrose-incorporated kaolin-filled paper nanocomposites, even, surpassed the breaking length of the blank (kaolin-free paper). This was true for all the added amounts of kaolin. Even at the highest amount of added kaolin (20 g per 100 g of fibers), the breaking length of the sucrose-incorporated kaolin-filled paper nanocomposites was greater, by about 8.53%, than that of the blank kaolin-free paper.

The wet breaking length of paper nanocomposites, produced from sucrose incorporated kaolin-filled fibers, was greater than that of paper composites produced from the kaolin-filled sucrose-free fibers (compare Tables 2 and 3). This is true for all the added amounts of kaolin. At addition of 20 g of kaolin per 100 g of fibers, the wet breaking

Table 2
Effect of filling cellulose fibers (pulp fibers) with the conventional additive (inorganic filler kaolin) – in the absence of sucrose – on the properties of the produced paper composites

Amounts of the added kaolin (in grams per 100 g of fibers)	0	5	10	15	20
Breaking length (m)	2015	1885	1831	1754	1634
Decrease in breaking length (%)	–	6.45	9.13	12.95	18.90
Wet breaking length (m)	403	367	350	339	316
Decrease in wet breaking length (%)	–	8.93	13.15	15.88	21.58

Table 3
Effect of incorporating the kaolin-filled cellulose fibers with nanoadditive sucrose on the properties of the produced advanced paper nanocomposites

Amounts of the added kaolin (in grams per 100 g of fibers)	0	5	10	15	20
Breaking length (m)	2015	2237	2225	2214	2187
Increase in breaking length (%)	–	11.02	10.42	9.87	8.53
Wet breaking length (m)	403	442	438	437	433
Increase in wet breaking length (%)	–	9.67	8.68	8.44	7.44

Table 4
The role of the nanoadditive sucrose as a retention aid for the inorganic filler kaolin

Amounts of the added kaolin (in grams per 100 g of fibers)	0	5	10	15	20
Retention value of kaolin in case of paper composites produced from kaolin-filled sucrose-free fibers (%)	–	25.2	23.5	21.9	27.8
Retention value of kaolin in case of paper nanocomposites produced from sucrose-incorporated kaolin-filled fibers (%)	–	60.2	62.3	63.8	65.4
Percentage increase in the retention value of kaolin, due to sucrose-incorporation into the kaolin-filled fibers (%)	–	138.88	165.10	178.60	135.25

length of the kaolin-filled sucrose-free paper composites was 316 m, while that of the sucrose-incorporated kaolin-filled paper nanocomposites was 433 m. Thus, incorporation of the cellulose fibers, with sucrose, led to a percentage increase of 37% in the wet breaking length.

Table 3 shows that the wet breaking length of the sucrose-incorporated kaolin-filled paper nanocomposites, even, surpassed the wet breaking length of the blank (kaolin-free paper). This was true for all the added amounts of kaolin. Even at the highest amount of added kaolin (20 g per 100 g of fibers), the wet breaking length of the sucrose-incorporated kaolin-filled paper nanocomposites was greater, by about 7.44%, than that of the blank kaolin-free paper.

It is clear from these results that incorporating cellulose fibers, with sucrose, succeeded in counteracting the deterioration in strength of paper, that occurs due to addition of inorganic fillers such as kaolin. Sucrose acted as a strength promoter in the paper nanocomposites, produced from the sucrose-incorporated kaolin-filled fibers. The strength (breaking length) of these paper nanocomposites, even, surpassed that of the blank (filler-free paper). Incorporating cellulose fibers, with sucrose, leads to incorporation beating of the fibers, and thus increases the strength of the produced paper nanocomposites.

3.3. The role of the nanoadditive sucrose as a retention aid for inorganic fillers such as kaolin

Table 4 shows the retention value of kaolin for both the kaolin-filled sucrose-free paper composites, and the kaolin-filled sucrose-incorporated paper nanocomposites.

It is evident from Table 4 that incorporation of cellulose fibers, by sucrose, resulted in an increase in the amount of kaolin retained in the produced paper nanocomposites, relative to the case of the sucrose-free kaolin-filled paper composites. This was true for all the added amounts of kaolin. There was a percentage increase of about 178.60% in the retention value of kaolin, due to incorporation of the cellulose fibers by sucrose (at added amount of kaolin of 15 g per 100 g of fibers). The retention value of kaolin in the case of sucrose-free kaolin-filled paper composites was 21.9%, however, it increased to 63.8% in the case of the sucrose-incorporated kaolin-filled paper nanocomposites.

These results show clearly that sucrose acts as a retention aid for inorganic fillers such as kaolin. It is assumed that, during paper sheet formation, sucrose decreases the collapse of the nanoporous structure of the fibers. This collapse – normally – takes place at paper sheet formation, due to drying of the fibers. Thus, during paper sheet formation, the sucrose-incorporated fibers are more swollen and thicker, relative to the sucrose-free fibers. This fiber swelling decreases the size of the gaps present between the fibers, during paper sheet formation. Therefore, lesser amount of inorganic filler can escape through these narrowed gaps, during the water drainage, which occurs at paper sheet formation. Eventually, more inorganic filler is enmeshed between these swollen thickened sucrose-incorporated fibers. We called this type of retention "*incorporation retention*" to differentiate it from the conventional types of retention of inorganic fillers.

4. Conclusions

This work introduces, for the first time worldwide, an advanced nanocomposite involving two additives – a nanoadditive and a conventional additive – within a matrix of natural cellulose fibers. The first additive (the nanoadditive) is sucrose, which incorporates the nanoporous structure of the cell walls of cellulose fibers. The second additive (the conventional additive) is kaolin, the famous paper filler. Kaolin is enmeshed between the adjacent cellulose fibers. This advanced paper nanocomposite was prepared by simple techniques.

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The present study shows that the nanoadditive sucrose may find its use as a new retention aid and strength promoter in papermaking.

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