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Modified kaolin and polyacrylic acid-g-cellulosic fiber and microfiber as additives for paper properties improvements

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ABSTRACT

The paper manufacturing industry converts raw materials into various paper and board products by mechanical or chemical processes known as pulping. Fillers and other additives are added to improve the strength and quality of the paper. Kaolin is used as it is as filler for paper manufacture. Kaolin, in the present study, was modified with the resulting black liquor after alkaline pulping of rice straw. The modification was carried out in order to change its nature. Polyacrylamide and polyacrylic acid grafted with cellulosic fiber and microfiber were added with the modified kaolin to improve the mechanical properties and water absorption. The mechanical properties, sizability, water absorption and dewatering were studied. The results indicated that modified kaolin with the polymer enhances the mechanical properties and the water absorption. It was clear that the prepared sheets can be used for special application that needs higher absorption and faster dewatering time.

1. Introduction

Pulp and paper are manufactured from raw materials containing cellulose fibers, generally from wood, recycled paper, and agricultural residues. In developing countries, about 60% of cellulose fibers originate from non-wood raw materials such as bagasse, cereal straws, bamboo, reeds, esparto grass, jute, flax, and sisal (WORLD BANK GROUP, 1998). Rice straw is a fibrous lignocellulosic material typical of most agricultural residues. They consist mainly of cellulose, hemicellulose and lignin; however, they differ from most crop residues in its high content of silicon dioxide (SiO_2). Ash content on a dry weight basis ranges from 13 to 20%, varying according to the state of conservation of the straw after harvest (Mussatto & Roberto, 2005). However, the use of rice straw as a lignocellulosic resource has great potential in this part of the world.

The main steps in pulp and paper manufacturing are: (a) raw material preparation; (b) pulp manufacturing; (c) pulp bleaching, (d) paper manufacturing; and (e) fibers recycling (WORLD BANK GROUP, 1998). Lignin, which is one of the main constituents of the raw materials that gives its strength, is removed by mechanical or chemical processes known as puling, and the pulp fibers are bound together again to form the end product, which known as papermaking (Atchison, 1993). Thus, paper and cardboard are made from pulp by deposition of fibers and fillers from a fluid suspension onto a moving forming device which also removes water from the pulp. The shape of fillers is important for several reasons. It affects the light scattering properties, i.e. opacity and gloss, the calendaring process, the drying rate, and the air permeability of the paper. Small particles, however, have a high tendency to aggregate. Ironically, larger diameter fillers may be more difficult to retain due to their decreased specific surface. On the other hand, furnishes containing fillers of small particles are more difficult to give internal sizing since there is a higher surface area competing for the sizing agent (Crouse & Wimer, 1990; Davison, 1975, 1986; Eklund & Linström, 1991; Hodgson, 1994; Hubbe, 2005; Keavney & Kulick, 1981, chap. 13; Neimo, 1999; Reynolda, 1989).

In addition to different pulps, different fillers and/or coating materials, such as pigments, are used. Chemical additives are added to impart specific properties to paper, and pigments may be added to impart color. Many polymers, especially those with high charge densities can be used as additives for papermaking and they should be used in dilute solutions to facilitate their dispersion throughout the stock (Biermann, 1996). Polymers with high molecular weights are generally added in locations that avoid high turbulence.

A wide variety of water-soluble polymers are used for papermaking. Papermaking polymers can be categorized as naturally occurring polymers; polysaccharides or proteins, modified naturally occurring polymers, and synthetic polymers. They may also be classified as neutral, cationic, anionic, or *zwitterions* (Biermann, 1996). Polyacrylic acid or polyphosphates are often used, with anchoring cations, to decrease the zeta potential of some fillers. This helps disperse the fillers but may interfere with their aggregation

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Table 1a
XRF spectrometer for the Egyptian kaolin.

Analyte	Compound formula	Concentration (%)
Al	Al_2O_3	33.235
Si	SiO_2	46.136

during drainage. Neutral synthetic polymer retention aids include polyacrylamide (PAM), polyvinyl alcohol (PVA), and polyethylene oxide (PEO). PAM is the most widely used of these and adds to the dry strength. PAMs are relatively inexpensive polymers that are easily formulated to high molecular weights on the order of several million g/mol (Biermann, 1996).

In this work, in order to improve water absorbency of papermaking, modified kaolin using black liquor, starch from waste, polyacrylic acid and polyacrylamide were used as internal fillers for rice straw pulp.

At first, several different fillers, based on modifying the kaolin and the starch as well as graft polymerization of rice straw cellulosic fiber and microfiber with polyacrylic acid, were prepared. Then they were added as internal fillers to unbleached rice straw pulp and the hand-made sheets were characterized by FT-IR and SEM as well as studying their mechanical properties.

2. Materials and methods

2.1. Materials

Rice straw was the source for paper making. Commercial Egyptian kaolin was the source for the filler used as internal sizing before and after modification. The chemical analysis for the kaolin was carried out on Axios, Sequential WD_XRF spectrometer, PANalytical 2005 instrument.

On the other hand, cellulosic fibers (α-cellulose = 62.42%) were laboratory prepared from bleached alkaline pulping rice straw to be graft polymerization as cellulose and microcellulose fiber with polyacrylic acid for the use as additive for the preparation of hand-made sheets.

2.2. Methods

2.2.1. Pulping of rice straw

Pulping experiment, for rice straw, was carried out in closed bags in a method described in our patent (Nawwar, Ibrahim, & El-Zawawy, 2008). The total chemicals as NaOH were 20% (w/w), and liquor to fiber ratio was 10:1. The fibers were left in a solar source until the fibers were cooked. After the period of treatment, the black liquor was collected for further use and the pulped fiber was washed with water till neutrality then air dried.

2.2.2. Modification of kaolin

The Egyptian kaolin was treated with the black liquor resulting from our pulping method for surface modification using solar energy. After the period of treatment, the modified kaolin was washed with water till neutrality then air dried.

2.2.3. Sheet making

The paper sheets were prepared according to the (SCA) standard, by using the SCA-model sheet former (AB Lorenzen and Wetter). In the apparatus, circular sheets of 165-mm diameter and a 214 cm^2 surface area were formed by using 1.6 g oven dry pulp. The sheet was then pressed for 4 min by using hydraulic press. Sheet samples were dried in drum for 2 h. Finally, the sheets were placed for conditioning in polyethylene bags.

Native kaolin and modified kaolin as well as synthetic polymers were added in a 5%, based on the dry weight of the fiber, to the unbleached rice straw pulp in the head box, before the sheet formation. After mixing, the sheets were prepared as described according to the SCA standard, SCAN-C 26:27, SCAN-C 5:76.

2.2.4. Mechanical test of hand sheets

After conditioning, the hand sheets, filled and unfilled, were weighed, and divided into suitable pieces for the physical tests. In accordance with the standard methods, the tensile and tearing strength of the sheets were measured and then both the breaking length and the tear factor were calculated.

2.2.5. Sizing test: sizability

An indicator is prepared by mixing 1 part methyl violet dye with 45 parts sugar and 5 parts soluble starch. All ingredients are to be completely dry and finely powdered when mixed and are to be stored over calcium chloride pending use. The nearly colorless dry indicator becomes deep violet in contact with water.

The test is performed by sealing the four edges of the test specimen with wax, sprinkling a thin, uniform layer of indicator upon the surface, and then floating the specimen, indicator side up, upon a vessel of water. The time interval from the instant of contact of the test specimen with water until the rate of change in the color of the indicator is at maximum.

2.2.6. Water absorbency measurement

A weighted quantity of the hand-made sheet, with and without additives, was immersed in distilled water at the room temperature to swell equilibrium, respectively. Swollen samples were then separated from unabsorbed water by filtered over a screen. The

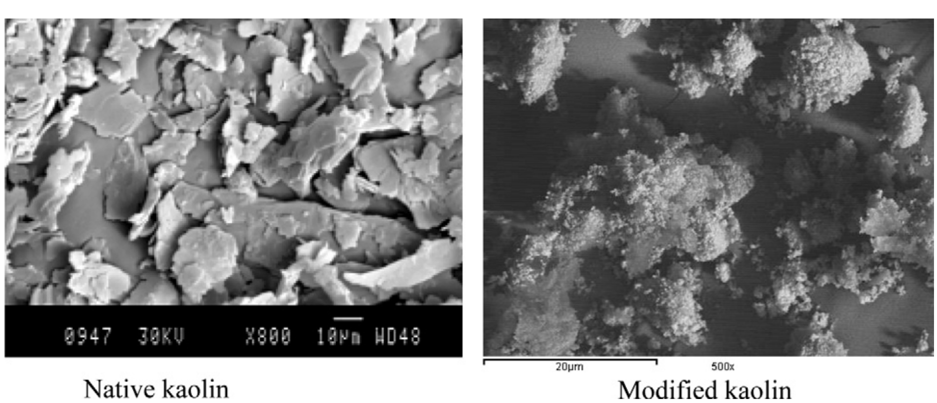

Fig. 1. SEM for native and modified kaolin.

Table 1b
XRF spectrometer for the modified kaolin.

Main constituents (wt%)	Concentration (%)
SiO_2	44.04
TiO_2	2.21
Al_2O_3	33.53
MgO	0.05
$Fe_2O_3{}^{tot.}$	1.32
CaO	0.16
Na_2O	1.09
K_2O	0.31
P_2O_5	0.27
Cl	0.01
LOI	17.01

LOI: means lost ignition.

water absorbency (Q_{H_2O}) was determined by weighing the swollen samples and calculated using the following equation:

$$Q_{H_2O} = \frac{m_2 - m_1}{m_1}$$

m_1 and m_2 were the weights of the dry sample and the water-swelling sample (g), respectively. Q_{H_2O} was expressed as grams of water per gram of sample (g/g).

2.2.7. *FT-IR spectra*

FT-IR spectroscopy was used to confirm the hand-made sheets with the addition of the synthetic polymers as internal sizing. The IR spectra were performed using a Thermo-Nicolet Model 670 Instrument (Thermo Electron, Inc, Madison, WI).

2.2.8. *Scanning electron microscope*

Scanning electron microscope (SEM) for the modified kaolin as well as the investigated hand-made sheets was studied using JEOL JXA-840A electron probe microanalyzer.

3. Results and discussion

3.1. *Kaolin modification*

Kaolin is any of a group of fine clay minerals with the chemical composition of $Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$ (Biermann, 1996) which means two-layer crystal (silicon-oxygen tetrahedral layer joined to alumina octahedral layer) exist alternately. Kaolin minerals long have been the basic raw materials used in the ceramic industry, especially in fine porcelains. Theoretically, it consists of 39.8% alumina and 46.3% silica. The analytical composition of the commercial Egyptian kaolin used in this work shows 33.235% Al_2O_3 and 46.136% SiO_2 (Table 1a).

Table 2
Physical properties for hand-made sheet from unbleached rice straw pulp.

Sheets	Tensile strength (kg/15 cm)	Tear resistance (g)	Sizability test (s)
Blank	1.5	11	1.0
With Km[a]	2.1	12	1.5
With Kn[b]	1.0	10	0.7
With Sn[c]	1.0	14	1.5
With Sm[d]	1.0	13	0.7
With Kn, Sn	1.7	22	1.0
With Km & Sn	1.5	10	1.2
With Km & Sm	1.2	11	1.0
With PAM[e]	0.9	9	1.4
With Km & PAM	1.6	11	1.3
With Kn, Sn & PAM	1.6	2	1.6
With Km, Sn & PAM	1.1	13	1.2
With Km, Sm & PAM	1.2	13	0.6

[a] Km is modified kaolin.
[b] Kn is native kaolin.
[c] Sm is modified starch (starch from the waste).
[d] Sn is native starch.
[e] PAM is polyacrylamide.

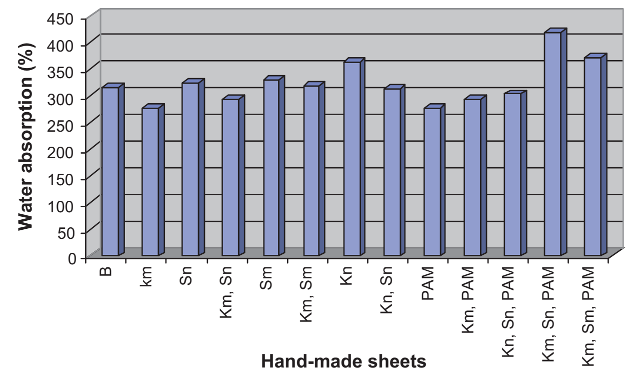

Fig. 2. Water absorption for paper sheets, where (B) for the blank sheet and the other for the filled sheet.

Table 3
Mechanical properties for hand-made sheet from unbleached rice straw pulp.

Sheets	Tensile strength (kg/15 cm)	Tear resistance (g)	Water absorption (%)
Blank	1.5	11	435
With PAA-g-cellulosic fiber and Km[a]	1.4	27	475
With PAA-g-cellulosic microfiber and Km	1.7	36	525

[a] Km is modified kaolin.

Modification for the kaolin was made by using the black liquor resulting from our pulping method. This was aimed to make another use for the black liquor besides activating the surface of the kaolin used as filler in paper making. The X-ray fluorescent spectrometer (XRF) indicated the main constituents that appear in the resulting modified kaolin, as can be seen in Table 1b. It was noticed that the percent of the silica was slightly decreased. The main difference between the native kaolin and the modified one can be noticed by the SEM, Fig. 1, where it can be seen that the plate structure of the kaolin was modified forming surface particles.

3.2. *Production of paper sheets*

Sheets were made from the unbleached rice straw pulp after the addition of kaolin and modified kaolin. On the other hand, a new starchy material was prepared from mango seeds to be used

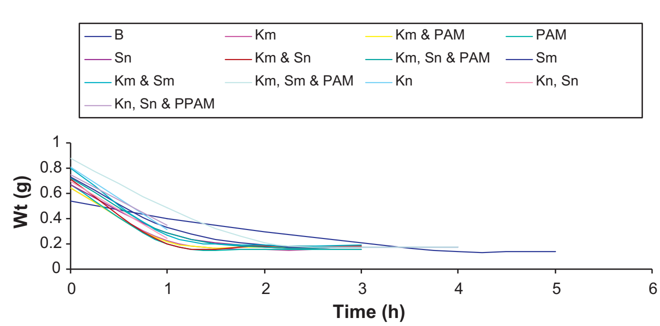

Fig. 3. Dewatering time for prepared sheets, where (B) for the blank sheet and the others for the filled sheets.

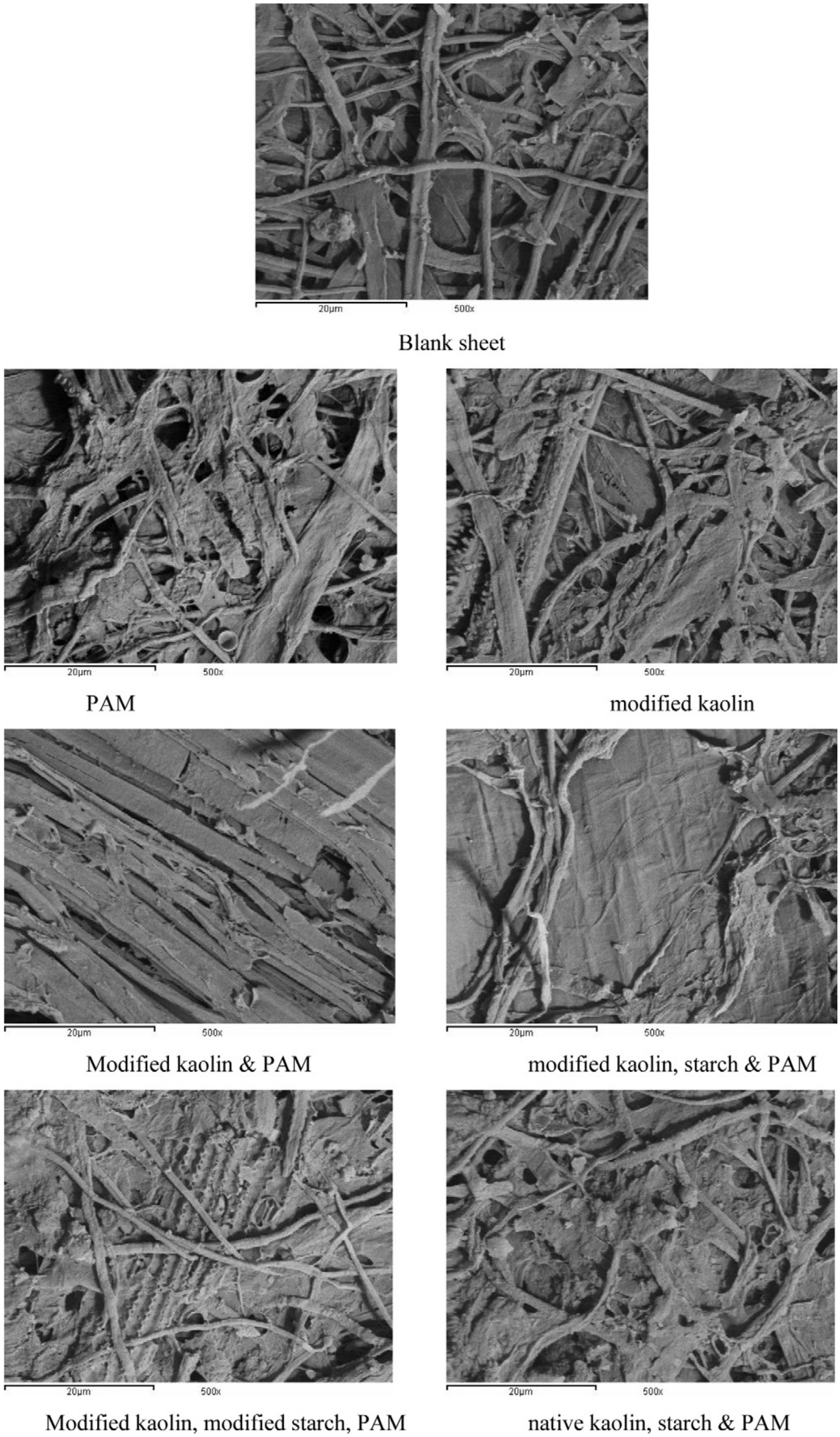

Fig. 4. SEM for paper sheets with different fillers and additives.

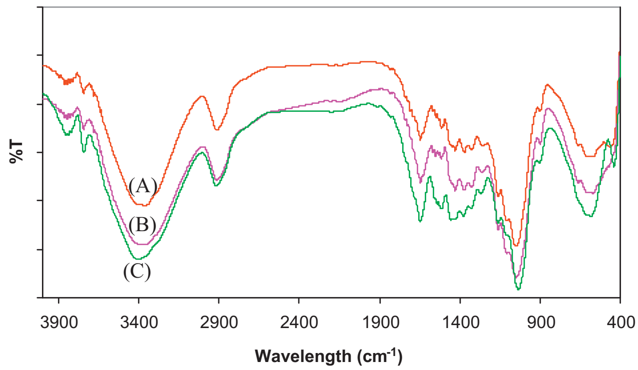

Fig. 5. FT-IR for hand made sheets from (A) blank, (B) with the addition of modified kaolin with PAA-g-cellulosic fiber and (C) with the addition of modified kaolin with PAA-g-cellulosic microfiber.

as additive for paper making. This starchy material was mentioned as modified starch and compared with the commercially available starch. A sheet of a basis weight of 80 g/m^2 was made and the physical properties were gathered in Table 2.

The results of both blank sheets, i.e. without fillers or additives, and those with the presence of fillers and additives, i.e. kaolin, modified kaolin, starch and modified starch, indicated that fillers and additives play a role in the properties of the prepared sheets. The higher tensile strength was noticed for paper filled with the modified kaolin, 2.1 kg/15 cm, compared with 1.0 kg/15 cm for that prepared with native kaolin. Moreover, using the new starchy material results in the same tensile strength compared with those prepared using the native starch. This means that the waste starch can give the same results as the commercial starch. On the other hand, the sizability was increased in case of using modified kaolin and decreased in case of using the waste starch.

From Fig. 2, one can noticed that the higher water absorption can be obtained on using the native kaolin compared with the modified one. Also, using waste starch results in higher water absorption compared to the unfilled sheets. In general, the presence of the modified filler as well as the waste starch results in better water absorption compared to the unfilled sheets. This means that changing the surface of the modified kaolin has a role in the water absorption.

Moreover, synthetic polymer, i.e. PAM, was used as internal sizing with and without the presence of the kaolin, modified kaolin and starch. It was noticed that, the use of PAM with both modified kaolin and waste starch results in a good tensile strength, as can be seen in Table 2. From Fig. 2, one can noticed that the higher water absorption can be obtained on using modified kaolin with starch and PAM. In general, the presence of the modified filler as well as the waste starch results in better water absorption especially in the presence of the PAM.

On the other hand, our aim was not only to get higher water absorption but to get paper with faster dewatering time. The results illustrated in Fig. 3 show the time for dewatering. It was noticed that the use of the modified kaolin and waste starch results in a faster dewatering time. Within maximum of 2 h one can reach the original weight of the paper sheet. This means that the prepared sheets can be used for special application that needs higher absorption and faster dewatering time for several time uses.

Furthermore, the SEM for the prepared sheets was investigated to see the change in the morphological structural of the prepared sheets to find an explanation for the results (Fig. 4). The results indicate the presence of tube canal in the sheets made from modified kaolin with PAM which gives indication for the higher water absorption.

On the other hand, graft copolymers of acrylic acid with cellulosic fiber and microfibers were used with the modified kaolin as additives and hand-mad sheets were studied for their mechanical properties and water absorption. It can be seen from Table 3 that the addition of grafted polyacrylic acid with cellulosic fibers and microfibers results in an increase in the tear resistance as well the water absorption. The grafted microfibers shows better mechanical properties as well as higher water absorption percent.

The FT-IR, Fig. 5, for the hand-made sheets with and without the addition of modified kaolin and grafted PAA indicated that an increase in the —OH peaks, 3430 cm^{-1}, was noticed in case of grafting with microfibers. This can be in agreement with the higher water absorption noticed for the sheets filled with modified kaolin and PAA-g-microfibers (Table 3). One can come to a conclusion that surface modification of kaolin as well as using of synthetic polymers can results with better mechanical properties as well as higher water absorption percent.

4. Conclusions

The results indicated that the black liquor resulting from pulping process can find useful application by modifying the kaolin which can be used as filler additives for paper making. The modified kaolin with the waste starch and the synthetic polymer was noticed to give higher mechanical properties and higher sizability with higher water absorption and faster dewatering time when used as internal filler for paper making compared to the native kaolin. Changing the chemical nature of the native kaolin by modification and used with the synthetic polymers resulted in higher mechanical and water absorption properties due to the nature of the new product. On the other hand, the addition of the modified kaolin with the waste starch, as filler, results in a special paper that can be used for several times in absorbing and dewatering phenomena.

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