Modified Egyptian talc as internal and surface treatments for papermaking

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ABSTRACT: Mineral fillers have long been used in papermaking. In Egypt, talc has been used, without modification, as filler or coating for bleached rice straw pulp. For this study, talc was modified chemically with starch, carboxymethyl cellulose, glycerol, dodecytrimethyammonium bromide, polyacrylamide and poly(vinyl alcohol). Talc is chemically inert; the modification was carried out to change the nature of the native talc. Researchers then studied the mechanical and optical properties for filled and coated papers. The results indicated that modified talc enhances the mechanical and optical properties for filled or coated handsheets. Scanning electron micrographs of the filled and coated sheets were investigated; results of the study showed that talc modification can improve filler-fiber-filler bond.

Application: Papers made with modified talc as additives show an improvement in mechanical properties and fiber-filler-fiber bond.

Mineral fillers have long been used in papermaking. Previously, they were used to obtain a more closed surface for writing papers and to improve writing properties. Today, the main use of fillers in printing papers is to increase printability: they produce greater smoothness and higher gloss after calendering, and higher brightness and opacity. Mineral fillers also are considerably cheaper than fibrous materials [1,2].

In many paper grades, fillers such as clay, calcium carbonate, and titanium dioxide are added to increase opacity and brightness. Fillers prevent good fiber-to-fiber contact and thus reduce paper strength, but the fillers improve other properties, rendering the paper useful for special purposes. Fillers also influence the pore structure of paper [3-6].

Two problems usually are associated with the use of fillers. First, filler particles added to fibers suspended in water are not easily retained in the forming sheet, because they are often too small to be entrapped mechanically and because filler particles and fibers are negatively charged, so they repel each other. Second, filler particles prevent fiber-fiber bonding, therefore the tensile strength of the filled paper suffers [2].

Talc, which is a hydrophobic filler, has numerous applications because of its chemical and thermal stabilities and lamellar morphology. However, the presence of talc can cause appreciable deterioration in shock resistance. This disadvantage partly can be overcome by adequate surface treatment. The objective of this study was to efficiently modify the surface reactivity of talc to enhance its use as a papermaking additive.

EXPERIMENTAL

Talc modification with starch (cooked talc-starch)

For the first modification, a mixture of 20 g of talc with 0.5 g of insoluble starch was added to 400 mL of water in a flask fitted with a mechanical stirrer. The mixture was stirred for 30 min at 95°C. After the desired reaction time had elapsed, the mixture was filtered and the residue was dried at 50°C under vacuum. The product was ground and used as a paper additive.

Talc modification with PAM

In the second modification, talc (20 g) was dispersed in distilled water (150 mL) at room temperature. To that, 0.08% ceric ammonium sulfate and a solution of polyacrylamide (PAM) (20 g in distilled water 100 mL) were added. The mixture was placed in a flask in a water bath at 55°C for 6 h. After the desired reaction time had elapsed, the product was dewatered with methanol, filtered, and the residue was air dried and stored for further use.

Talc modification with DTAB

For the third modification, we placed 5 g of dodecyltrimethylammonium bromide (DTAB) and 100 mL of water into a beaker and heated the solution to 80°C. We then dispersed 10 g of talc in 200 mL of water at 80°C. The talc dispersion was added to the solution of the DTAB, and the resulting mixture was stirred vigorously for 1 h. A white precipitate was isolated by filtration, placed into a 500-mL beaker with 400 mL hot water, and stirred for 1 h. This process was repeated twice to remove residual DTAB. The product was then filtrated and dried.

Talc modification with DTAB and PAM or PVA

For the fourth modification, talc (20 g) was dispersed in distilled water (600 mL) at 80°C. To this was added a solution of DTAB (0.05 mL) and concentrated hydrochloric acid (4.8 mL) in distilled water (100 mL). Heating and stirring continued for 1 h at a constant 80°C. The suspension was then filtered and the solid residue washed with hot distilled water until no bromide was left. The product was dried at 60°C for several days in a fan oven, then milled, and subsequently dried at 60°C under vacuum for 24 h, yielding dodecyltrimethylammonium-talc. Then, ceric ammonium sulfate (0.1 g) was dissolved in sulfuric acid, and the modified talc (5 g) and PAM or poly(vinyl alcohol) (PVA) (5 g) were added in 40 mL distilled water. The reaction flask was suspended in a water bath at 60°C for 5 h, with a condenser fitted. The powdered product was recovered from the reaction mixture by evaporation of the water, followed by drying under vacuum at 60°C.

Sheetmaking and coating

The paper sheets were prepared using an SCA-model sheet former [2]. Talc and modified talc (5%) were added to the rice straw pulp in the head box, before the sheet formation. After mixing, the sheet was formed by standard method.

An industrial coating mixture was applied to the unfilled paper sheets by roll method, as was the laboratory-prepared mixture made by adding modified talc to a dilute solution of the industrial fillers. The coated sheets were dried and tested for their mechanical and optical properties.

Testing

After conditioning, the handsheets—filled and unfilled, and coated and uncoated—were weighed and divided into suitable sizes for the mechanical and optical tests [2].

The retention of fillers was calculated according to the following equation:

$$\text{Filler retention value (R.V\%)} = \frac{retained.filler}{added.amount.of.filler} \text{ X } 100$$

The sizability test was performed by sealing the four edges of the test paper 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 was at maximum.

We used a scanning electron microscope (SEM) to examine the prepared sheet.

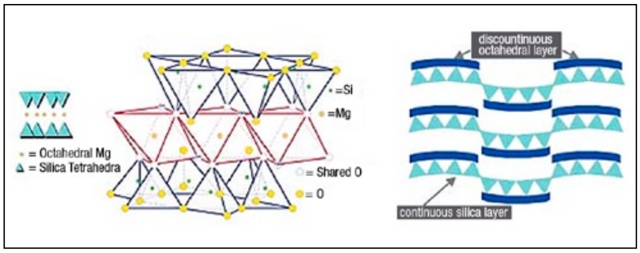
RESULTS AND DISCUSSION

Talc is soft, chemically inert, has high thermal and low electrical conductivity, and has desirable adsorption properties. The main industrial applications of talc are in the paper, cosmetics, paints, polymers, ceramics, refractories, and pharmaceuticals [7-9].

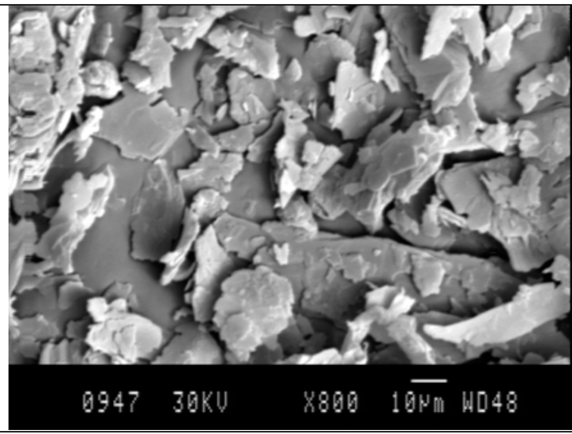
Analyte	Compound formula	Concentration %
Mg	MgO	25.393
Al	Al_2O_3	1.138
Si	SiO_2	65.768

Ignition loss = 72.8 %

I. Chemical compound of Egyptian talc.



1. Talc structure.



2. SEM of native talc.

Chemically, talc is hydrophobic and organophilic. It is a hydrated magnesium sheet silicate with the chemical formula $Mg_3Si_4O_{10}(OH)_2$ [10]. The analytical composition of the commercial talc used in this work shows 25.39% MgO and 65.76% SiO_2 (**Table I**). Talc's crystalline structure consists of a MgO/MgOH octahedral layer, which lies between two SiO tetrahedral layers (**Fig. 1**) [10]. As observed by SEM (**Fig. 2**), the crystal habit of talc corresponds to flattened tabular crystals with a hexagonal cross-section.

Talc effects on rice straw pulp sheet properties

Native talc was added to rice straw pulp at a 5% ratio to pulp. The prepared sheets were dried, and the optical and mechanical properties were investigated and expressed by brightness, opacity, breaking length, and tear factor.

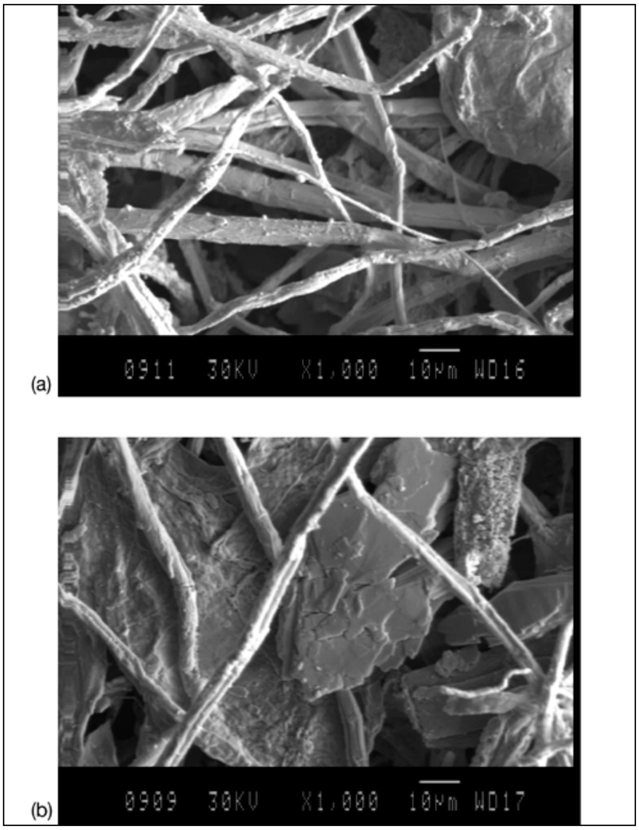
Table II shows the resulting percentage changes in optical and mechanical properties. The addition of 5% talc decreased breaking length. This change might be attributed to the chemical behavior of talc, which is chemically inert, leading to poor fiber-to-talc-to-fiber bonding and hence a decrease in the breaking length. Heating the talc to 300°C before addition to the rice straw pulp (Table II) further altered breaking length, suggesting that temperature has a negative effect on talc properties.

Examination of blank handsheets by SEM (**Fig. 3a**) shows a web-like structure with fiber-fiber bond for the blank sheet. In handsheets made with 5% talc (**Fig. 3b**), the talc filled the space between the web structure, but with poor fiber-to-talc-to-fiber bonding.

Samples	Mechanical properties		Optical properties		Sizability (sec)	Pigment retention (%)
	Breaking length (m)	Tear factor	Brightness (%)	Opacity (%)		
(a) Blank	7927.8	33.8	65.80	98.00	1.5	-
(b) 5% Talc	7363.8	48.3	68.80	98.41	1.44	65.5
(c) 5% Talc heated at 300°C	5467.4	53.1	67.65	97.86	0.78	15
(d) 5% Talc 1	12,839.9	24.1	66.5	98.52	1.83	77.05
(e) 5% Talc 2	14,967.9	43.4	67.75	98.47	1.45	91.25
(f) 5% Talc 3	16,399.6	67.6	67.45	98.52	1.45	70.37
(g) 5% Talc 4	12,185.3	96.5	67.40	98.87	1.17	15
(h) 5% Talc 6	15,152.6	28.9	66.00	98.75	0.78	18.25
(i) 5% Talc 7	10,170.6	86.1	71.15	97.84	1.26	15
(j) 5% Talc 8	10,340.4	97.5	69.25	98.45	1.06	23.20

Talc 1: talc with native starch. Talc 2: modified talc with starch (talc-starch cooked). Talc 3: modified talc-starch (cooked talc-starch) and carboxymethyl cellulose. Talc 4: modified talc with polyacrylamide (PAM). Talc 6: modified talc with dodecyltrimethylammonium bromide.
Talc 7: modified talc with PAM. Talc 8: modified talc with poly(vinyl alcohol).

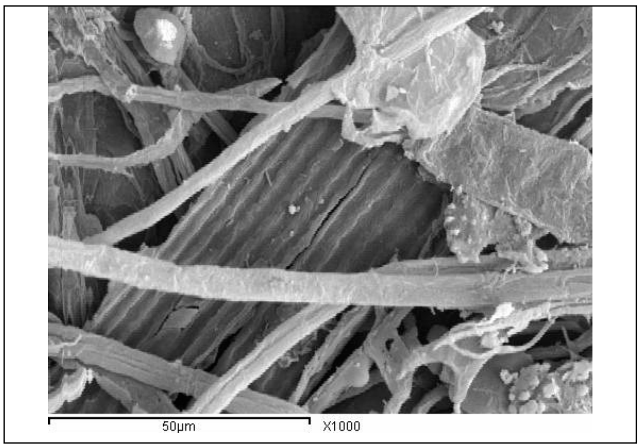
II. Optical and mechanical properties of filled and unfilled handsheets.



3. SEM for (a) blank sheet; and (b) with 5% of talc.

Effects of starch addition

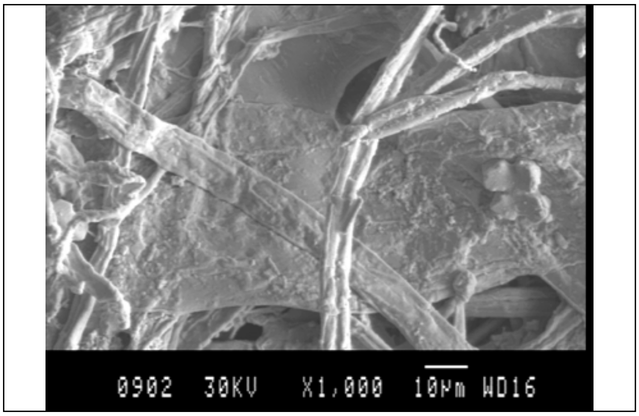
Table II also shows mechanical properties of filled paper with a 5% mixture of native talc and cooked talc-starch (modified talc with starch), and the improvements in percentages in the mechanical properties. The presence of starch was shown to increase the mechanical properties of the sheet, and breaking length improved 61.9%.



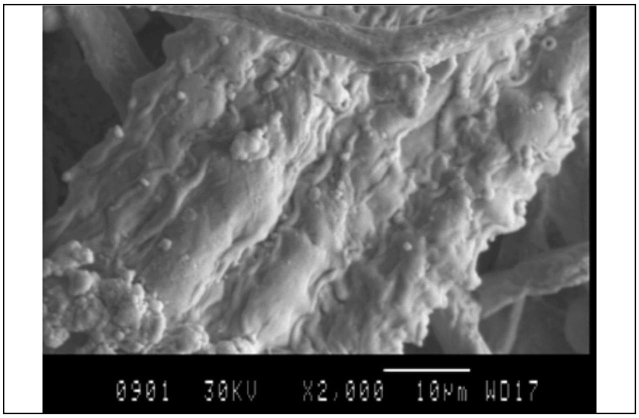
4. SEM for the addition of 5% talc-native starch to the hand-sheet.

The improvement in mechanical properties could be attributed to the cohesive property of the added starch, which promotes fiber adhesion, as seen by SEM (**Fig. 4**). The adhesive qualities of native starch for papermaking are attributable to its content of polar hydroxyl groups. These groups have a mutual attraction for the hydroxyl groups in the pulp fibers and set up a fiber-to-talc-to-starch-to-fiber bonding.

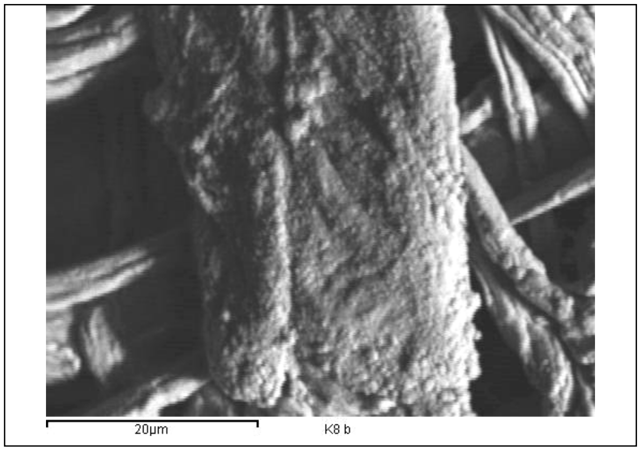
Table II further shows that the addition of cooked talc-starch with glycerol increases mechanical properties. Breaking length improved 88.8% and tear strength improved 28.4 %. **Figure 5** shows that the cooked talc-starch filler penetrates fibers to a greater extent than does native starch with the talc. This may be attributed to the nature of the modified talc in presence of the glycerol, causing depolymerization of the modified talc, which results in lower viscosity dispersions. These dispersions have lower viscosity than that in the presence of the native starch with the talc [11]. This lower viscosity cooked talc-starch filler penetrates fibers to a greater extent, thus providing additional fiber-to-filler-to-fiber bonding.



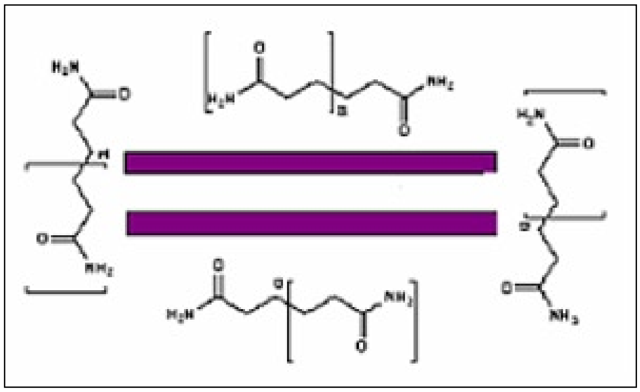
5. SEM for the addition of 5% modified talc with starch (cooked talc-starch) to the hand-sheet.



6. SEM for the addition of 5% modified talc with CMC and cooked starch to the hand-sheet.



7. SEM for the addition of 5% modified talc with poly(acrylamide) to the hand-sheet.



8. Talc-PAM.

Moreover, the presence of carboxymethyl cellulose (CMC) with the filler improves mechanical properties of the sheet (Table II). The percentage improvements of breaking length and tear were 106.8% and 100%, respectively. **Figure 6** shows that the presence of CMC with the talc and starch can form a mat-like structure, which can improve the fiber-to-filler-to-fiber bonding.

Effects of talc-PAM addition

Table II demonstrates that the addition of talc-PAM in an amount of 5% to the rice straw pulp increases the mechanical properties. The percentage increase in the breaking length and tear factor were 53.7% and 185.5%, respectively. Because of PAM's long polymer chains, the modified talc can form a long-range bridging attraction between the fibers (**Fig. 7**). Moreover, the modified surface of the talc, with the cationic acrylamide copolymer, allows the macromolecules to reflocculate the fibers, thus improving the mechanical properties. The presence of the lone pair of electrons in the nitrogen atom can form a bridge with the cellulosic fiber, in addition to the hydrogen bond between the PAM and the cellulosic fiber, increasing the mechanical properties for the sheet with the modified talc (**Fig. 8**).

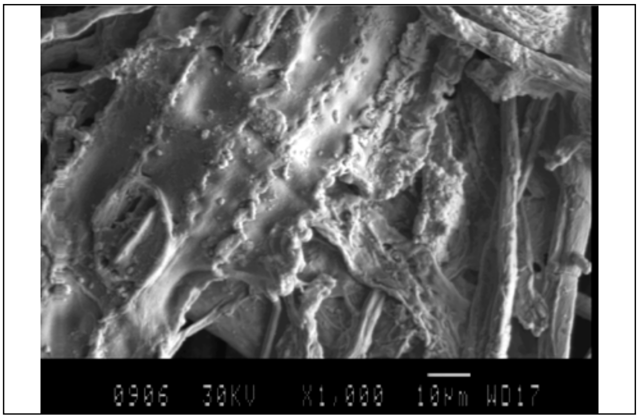
Effects of talc-DTAB

The modified talc (5% of talc-DTAB) increased the breaking length of the sheets by 91% (Table II).

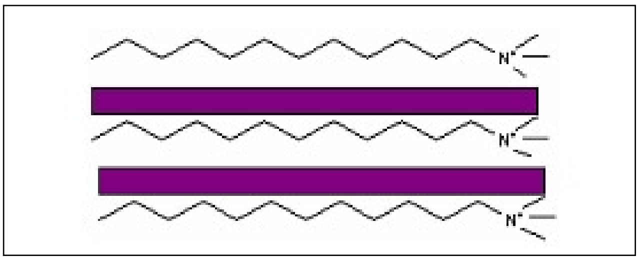
The SEM investigation suggests uniform distribution of the modified talc in the paper fibers; phase separation has not been observed in the sheet (**Fig. 9**). That might explain the improvement in mechanical properties of the obtained paper sheet, possibly resulting from the improvement of the fiber-to-filler-to-fiber bonding. This diffusion might occur because of the effect of the DTAB chains, where one end of the molecule diffuses into the other material and thus joins the particles into one.

Moreover, the presence of the alkalyammonium ions will partially expand the talc galleries; the DTAB will increase the silicate interlayer spacing of the talc and decrease the hydrophilicity of the internal surfaces of the talc. This can be noticed from the decrease of the sizability of the sheets containing the modified talc.

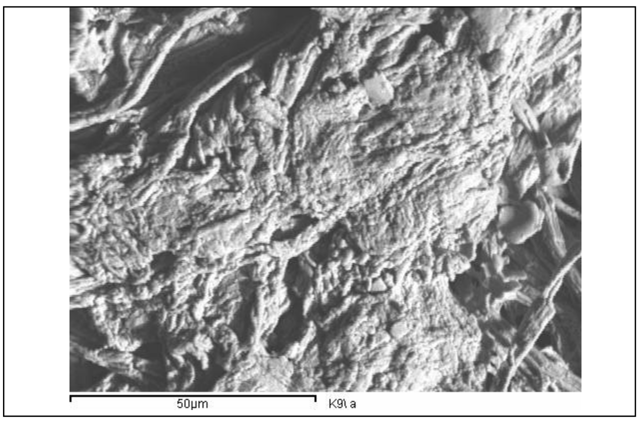
The dodecylammonium ions cannot stand perpendicular to the surface of the talc. More probably, one molecule lies parallel to each of the internal surfaces of the talc, in a bilayer orientation. In such a model, the dodecyltrimethyammonium ion exists between the talc layers in a regular fashion without delamination giving rise to the observed basal spacing (**Fig. 10**). The



9. SEM for the addition of 5% modified talc with dodecyltrimethylammonium bromide to the hand-sheet.

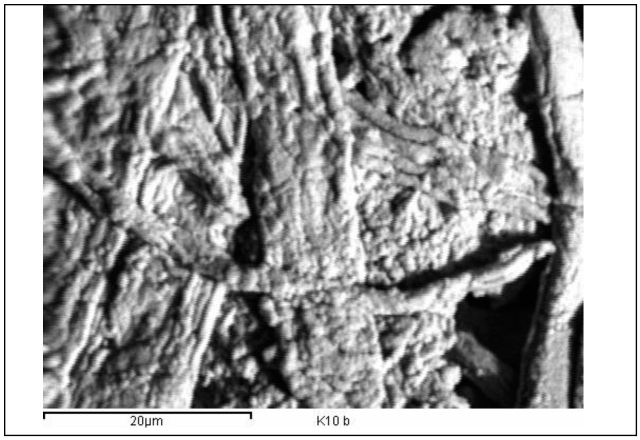


10. A model for the modified talc with dodecyltrimethylammonium bromide.

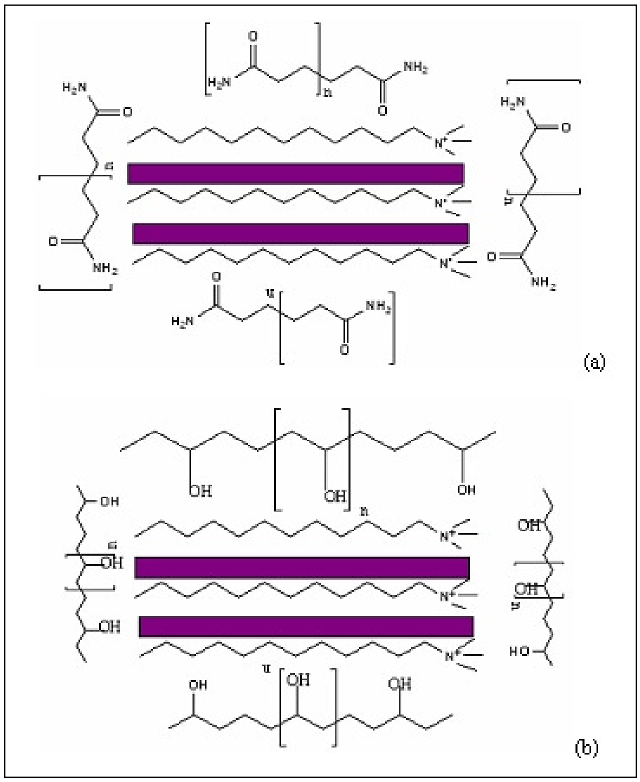


11. SEM for the addition of 5% modified talc with poly(acrylamide) and dodecyltrimethylammonium bromide to the hand-sheet.

charge of the quaternary ammonium ion will be responsible for the bond between the modified talc and the cellulosic fiber of the prepared handsheet forming a mat like structure (Fig. 9).



12. SEM for the addition of 5% modified talc with poly(vinyl alcohol) and dodecyltrimethylammonium bromide to the hand-sheet.



13. A model for the modified talc with (a) PAM dodecyltrimethylammonium bromide, and (b) PVA dodecyltrimethylammonium bromide.

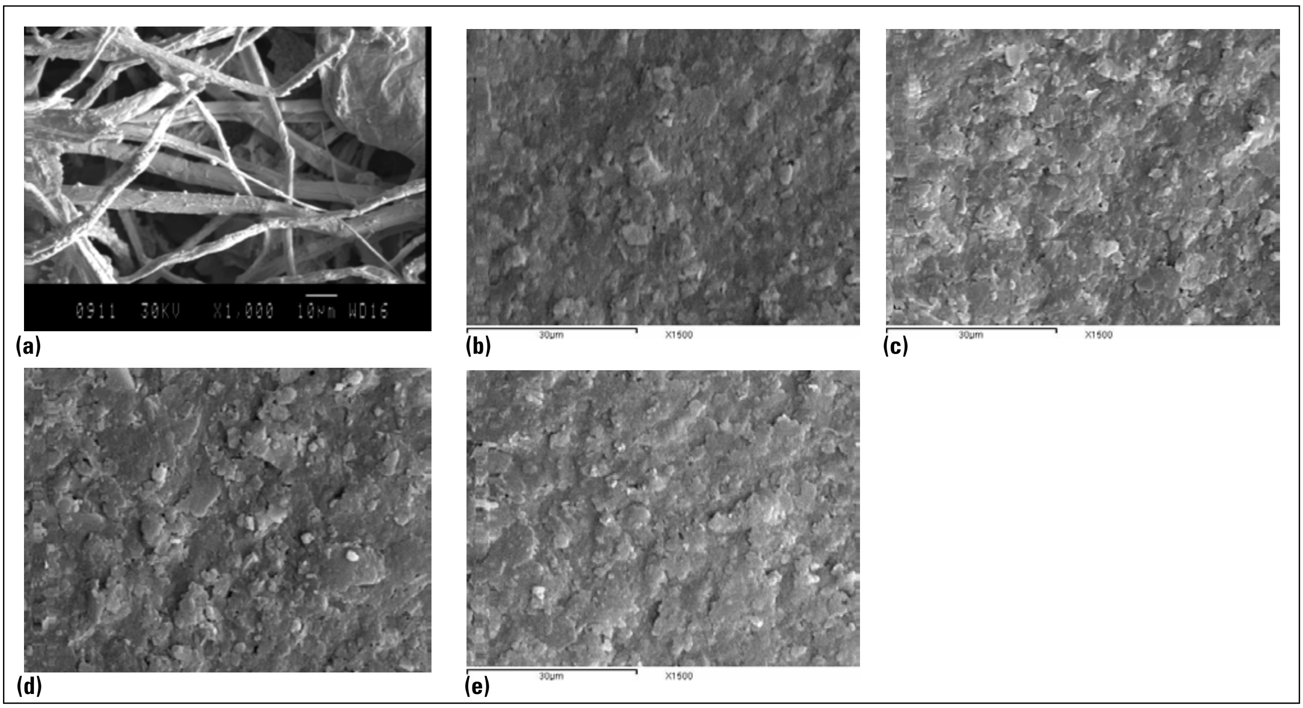
Effects of PAM and PVA addition with talc-DTAB

Talc-DTAB-PAM or PVA copolymers were prepared and added (5%) to the rice straw pulp. Table II shows that the addition of the modified talc increases the mechanical properties compared with those of the blank sheet. From the SEM images (**Figs. 11** and **12**), one can notice that the modified talc can form a long-range bridging attraction between the fibers. The bridge-like structure can be formed due to the long polymer chains of PAM and PVA. Moreover, the modified surface of the talc-DTAB with the PAM or PVA copolymer show a decrease in the breaking length compared to the presence of talc-DTAB alone. The presence of both polymers can form an outside coating layer around the talc-dodecyltrimethylammonium ion, which can form a hydrogen bond with the cellulosic fiber instead of the charge between the dodecyltrimethylammonium ion and the cellulosic fiber. This can explain the reduction in the breaking length compared to that from talc-do-

Samples	Mechanical properties		Optical properties		Sizability (sec)
	Breaking length (m)	Tear factor	Brightness (%)	Opacity (%)	
Blank	7927.8	33.8	65.80	98.0	1.5
Coated Blank	8906.9	20.32	73.7	99.7	360
Coated T1	8048.6	26.96	75.3	99.8	450
Coated T2	9512.9	29.96	75.4	99.83	420
Coated T3	8499.7	20.61	75.05	99.83	300
Coated T4	8820.0	27.11	75.3	99.89	510
Coated T5	9828.2	24.56	76.9	99.83	330
Coated T6	9274.3	20.63	75.7	99.94	410
Coated T7	5169.2	12.30	73.4	99.94	435
Coated T8	8261.0	15.68	75.3	99.94	390

Coated Blank: using the industrial coating mixture, T1: modified talc with native starch, T2: modified talc with dodecyltrimethylammonium bromide, T3: talc-starch cooked, T4: heated talc, T5: cooked talc-starch and carboxymethyl cellulose, T6: modified talc with phythalic anhydride, T7: modified talc with polyacrylamide (PAM), and T8: modified talc with PAM and dodecyltrimethylammonium bromide.

III. Optical and mechanical properties for handmade coated paper.



14. SEM for: (a) blank sheet, (b) coated sheet with industrial coating mixture, (c) coated sheet with the presence of T2, (d) coated sheet with the presence of T5 and (e) coated sheet with the presence of T6.

decyltrimethylammonium ion and also the increase in the sizability from 0.78 s for the talc-dodecyltrimethylammnium ion to 1.26 s and 1.06 s for both modified with the presence of PAM and PVA, respectively. **Figures 13 a** and **13 b** present a model of the structure, which represents the coating layer that can be formed from the two polymers.

The handsheet properties depend on the nature of both acrylamide and vinyl alcohol; in other words, with higher humidity more water is absorbed by the PVA. The water, which acts as a plasticizer, will then reduce its tensile strength, i.e., breaking length, but increase its elongation and tear strength. PVA has excellent film forming and adhesive properties. Adhesive materials fill the voids or pores of the surfaces and hold surfaces together by interlocking. PVA is an atactic material, but it exhibits crystallinity; its hydroxyl groups are small enough to fit into the lattice without disrupting it.

Surface treatment with talc and modified talc

The simplest type of surface treatment is coating. The coating mixture used should be composed of finely divided mineral pigments and an adhesive. The insoluble pigment, such as talc or modified talc in our study, will be in colloidal suspension.

Handsheets made from bleached rice straw pulp were coated by roll method with the industrial coating mixture and with the laboratory prepared coating mixture containing the modified talc added to the industrial coating mixture. **Table III** shows the resulting optical and mechanical properties.

A comparison of coated papers properties with those of uncoated paper made from bleached rice straw shows that all optical properties increased upon coating, while the mechanical properties decreased. The properties of the coated paper are influenced by the coating process, namely the roll method, which is time dependent. This means that the coating mixture must be spread homogeneously on the surface of the paper (i.e., the solution must be in a sol form). Thereafter, the sol must be transferred in a gel form. Therefore, the coating process is a sol-gel. The time of the sol-gel transformation defines the success of the coating process. One of the objectives of coating is to form a continuous layer of coating over the surface of the paper, as can be seen from the SEM of the coated sheets (**Fig. 14**). To do so, the coating must be retained and dried on the surface of the paper [12].

Moreover, when comparing the properties of the coated paper made from the industrial coating mixture and those from the addition of modified talc (Table III), the comparison indicates that the addition of modified talc with DTAB (T2), starch and carboxymethyl cellulose (T5), and phythalic anhydride (T6) increases the optical and mechanical properties of the paper coated with modified talc over that coated with the industrial coating mixture.

Applying the modified talc to the industrial coating mixture as a surface coating acts as a dispersive adhesion (Fig. 14), also known as adsorption, in which two materials are held together by van der Waals forces. In the simple case, such molecules are polar with respect to average charge density, although larger or more complex molecules might have multiple poles or regions of greater positive or negative charge [13]. These positive and negative poles might be a permanent property of a molecule (Keesom forces) or a transient effect, which can occur in any molecule, as the random movement of electrons within the molecules can result in a temporary concentration of electrons in one region (London forces) [13]. This might explain the reduction of the mechanical properties on applying coating. Furthermore, the talc-containing

INSIGHTS FROM THE AUTHORS

Mineral fillers, such as talc, have long been used in papermaking. They are used to obtain a more closed surface for writing papers and to improve the writing properties. Talc is chemically inert, which leads to poor fiber-to-filler-to-fiber bonding and a decrease in the breaking length. In this research, we carried out trials to modify Egyptian talc and characterize the effects of the addition of native and modified talc as internal or surface treatments, concentrating on using commercially available bleached rice straw pulp.

One difficult aspect of the work was the chemical nature of the talc that led to poor mechanical properties. We solved this by using a different reactant to modify the nature of the talc. The use of different types of polymers with the talc causes a change in the talc, resulting in a bond formation between the modified talc and the cellulosic fibers, which led to improvements in the mechanical properties for the papers tested.

When either polyacrylamide or dodecyltrimethylammonium bromide is used, the breaking length increased by 53.7% and 91.1%, respectively. The performance of modified talc depends on the change of the surface of the talc caused by the reacted polymer or compound with the talc.

Mills can benefit from this information by using modified talc to be chemically reactive, forming better fiber-to-filler-to-fiber bond in papermaking, and leading to the improvement of the breaking length and sizability.

Our next project will be to produce indicator paper for humidity by modifying kaolin with transition metals. Another modification for the kaolin will be carried out to change its nature for enhancing the mechanical properties of the produced paper.

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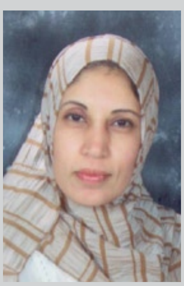

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coatings exhibited a slightly mottled appearance, which might indicate variations in the amount of polymer film covering the talc particles close to the surface of the coating (Fig. 14).

CONCLUSIONS

The results of this study indicate that modified talc gives higher results when used as internal treatment for papermaking, compared with the native talc. Changes in the chemical nature of the native talc improved mechanical and optical properties. The addition of modified talc as a pigment in the industrial coating mixture improved surface treatment. **TJ**

Received: April 20, 2008
Accepted: October 10, 2008

LITERATURE CITED

1. Rojas, O.J. and Hubbe, M.A., *J. Dispersion Sci. Technol.* 25(6): 713(2004).
2. Al-Mehbad, N.Y., *Polymer-Plastics Technol. Eng.* 43(3): 963(2004).
3. Mobarak, F., El-Shinnawy, N., Soliman, A., et al., *J. Sci. Ind. Res.* 57: 316(1998).
4. El-Shinnawy, N., Mobarak, F., Soliman, A., et al., *J. Sci. Ind. Res.* 56: 35(1997).
5. Sefain, M.Z., Mobarak, F., Fadl, M.H., et al., IPPTA J. 18(1): 33(2006).
6. Li, L., Collis, A., and Pelton, R., *J. Pulp Paper Sci.* 28(8): 267(2002).
7. Madson,W.-H., *White Hiding and Extender Pigments*, Unit 7, Federation of Societies for Paint Technology, Blue Bell, Pennsylvania, USA, 1967.
8. Martens, C.R., Ed., *Technology of Paints, Varnishes, and Lacquers*, Robert E. Krieger Publishing, Melbourne, Florida, USA, 1974, p. 344.
9. Virta, R.L., Talc and pyrophyllite, in *Minerals Yearbook*, Vol. I, U.S. Geological Survey, Reston, Virginia, USA, 2001. Available at http://minerals.usgs.gov/minerals/pubs/commodity/talc/talcmyb01.pdf.
10. Ciullo, P.A., *Paint Coating Ind. Mag.* January 2003.
11. Whistler, R.L., BeMiller, J.N., and Paschall, E.F., Eds. *Starch Chemistry and Technology*, 2nd edn., Academic Press, Orlando, Florida, USA, 1984.
12. Al-Turaif, H. and Lepoutre, P., *Prog. Organic Coatings* 38: 43(2000).
13. Schuman, T., Karlsson, A., Larsson, J., et al., *Prog. Organic Coatings* 54: 360(2005).