Novel $CaCO_3$-polymer nanocomposite fillers for the improvement of bagasse-based papers

SHAKKTHIVEL PIRAMAN, MARUTHAIYA KARUPAIAH, RAMALAKSHMI MARIAPPAN, SRINIVASAN ALAGAR, AND KIM MIN

ABSTRACT: Polymeric inorganic nanocomposites have received considerable attention because of their potential application in diverse areas, including papermaking industries. To develop novel filler materials to improve important paper properties, polyacrylamide (PAM)-coated nano-calcium carbonate ($CaCO_3$) nanocomposite fillers were synthesized and studied for their chemical and morphological characteristics. The effect of PAM-modified $CaCO_3$ nanofillers on properties of paper made with bagasse-based pulp was evaluated and compared with papers made with pristine nano-$CaCO_3$ fillers. The Fourier transform infrared spectroscopy results confirmed the attachment of PAM/$CaCO_3$ nanocomposites with the cellulosic fiber matrix. The scanning electron microscope and light microscopic images confirmed that the PAM-modified $CaCO_3$ fillers deposited larger aggregated clusters of particles on the fiber surfaces more firmly, which caused the improved paper properties. The surface and the optical properties of the bagasse papers filled with PAM preflocculated-$CaCO_3$ nanofillers were tremendously increased without sacrificing strength properties because of the increased fiber-filler-fiber bonding.

Application: In industrial applications, PAM/nano-PCC composite fillers could be used to improve the optical and surface properties of paper.

Paper is mainly made of cellulosic fibers derived from renewable natural bioresources, including wood and nonwood lignocellulosic materials such as eucalyptus, causrina, bluegum, bagasse, and deinked pulp. Fillers are used to reduce the costlier bagasse and wood pulp content in paper and to increase the glossiness, printability, and surface, strength, and optical properties of the paper. Mineral fillers are widely used as substitutes for cellulosic fibers, particularly in printing and writing grade papers [1-5]. Increased filler loading in paper reduces the energy demand in various stages of the papermaking process and also improves optical and printing properties of papers. However, because of the interference of filler particles with fiber-to-fiber bonding in the cellulosic fiber network, the addition of fillers can have a negative impact on paper strength; this is most pronounced at high filler addition levels [6,7]. Moreover, beyond a certain addition level, fillers have other disadvantages such as poor filler retention, decreased sizing efficiency and bending stiffness, increased wire abrasion, and dusting during printing [8,9]. Such disadvantages are basically restricting the use of fillers at higher content in cellulosic paper.

To overcome the problem associated with filler addition to paper sheets, researchers have developed several techniques, one of which is filler modification or preflocculation. It has been reported that the addition of preflocculated filler to paper significantly improves the filler retention and paper strength while maintaining the functional properties of paper [10-25]. This occurs through the improved interaction between the filler particles and the cellulosic fibers with the aid of chemical additives. Various chemicals have been used for the preflocculation of fillers, such as inorganic compounds, natural and synthetic polymers, surfactants, and emulsions.

The calcium carbonate ($CaCO_3$) nanofiller can overcome the limitations of filler materials because of its abundant availability, simplicity, and low-cost production [26-28]. Nano-size precipitated calcium carbonate (PCC) has received considerable attention because of its excellent properties and market demand in many industrial applications [29-33]. A wide variety of water-soluble additives were used to control the size, morphology, and surface property of the $CaCO_3$ nanoparticles [34-39]. Additives such as chitosan, starch [40], and their derivatives [41] were used to improve the property of $CaCO_3$ and the strength properties of filled papers.

In this study, our objective was to improve the strength, optical, and surface properties of bagasse-based paper using nano-PCC without damaging the mechanical properties of papers. For this purpose, we have modified the synthesized nano-PCC by the use of polyacrylamide (PAM) to improve all the important properties of the paper. Cationic/anionic poly-

acrylamide is the best known and widely used polymer in the papermaking process. It makes sense to select a positively/negatively charged additive as a means of flocculating cellulosic materials. The ability of the charged PAM to adsorb strongly onto the anionic cellulosic fibers generates better bonding capacity between the fiber and the modified filler particles.

MATERIALS AND METHODS

Handsheets were prepared with a blend of 40% bleached hardwood pulp and 60% bleached chemical bagasse pulp. The prepared handsheets were taken to a PFI mill for the beating/refining process. The CSF of the mixed refined pulp was brought down to 300 mL, prepared in Tamil Nadu Newsprint & Papers Ltd. (TNPL), Karur, India. The anionic traceable catcher (ATC), cationic and native starch, alkyl ketene dimer (AKD), retention and draining agent (RDA), cationic PAM, and silica were purchased from Arjun Chemicals, Chennai, India, and used as received. Oleic acid, calcium chloride ($CaCl_2$), sodium carbonate (Na_2CO_3), and sodium hydroxide (NaOH) were purchased from Merck India, Mumbai, and used without any purification. The paper handsheets were prepared according to TAPPI T 205 sp-02 "Forming handsheets for physical tests of pulp."

Synthesis of nano-$CaCO_3$ filler

The synthesis of $CaCO_3$ nanoparticles (nano-PCC) was carried out by adopting a simple facile process in a round-bottom flask at 80ºC according to the method reported in the literature [42]. In a typical synthesis procedure, aqueous solution of Na_2CO_3 (0.1 M, 20 mL) was poured into an aqueous solution of oleic acid as surfactant (0.5 M, 800 mL) and the pH of the solution was maintained at 10 by adding NaOH solution. After 5 min, 20 mL of 0.1 M $CaCl_2$ solution was added into the pH-adjusted Na_2CO_3 solution under vigorous stirring in 30 s. The mixture stirred for 10 min, and then the solution was covered and allowed to stand under static condition for 12 h at 80ºC for the completion of the $CaCO_3$ formation reaction process. Finally, the obtained calcium carbonate precipitate was filtered off, washed several times with water to remove sodium chloride and sodium hydroxide, dried well, and stored for further characterization.

Filler modification

The surface of the synthesized $CaCO_3$ nanoparticle was modified with PAM polymer. Typically, a known weight of the above synthesized nano-PCC was dispersed in 100 mL distilled water under stirring at 200 rpm in a round-bottom flask and a required amount of polyacrylamide (to make 1% PAM) was sequentially added to the previously described nano-$CaCO_3$ dispersed slurry (the ratio was 1:0.02 PCC to 1:0.09 PAM). The mixture was continuously stirred for 30 min for uniform coating of PAM onto the nano-PCC surface. The nano-$CaCO_3$/PAM dispersion was allowed to settle for 12 h, washed, dried at 80ºC for 6 h, and used for paper sheet formation.

Preparation of handsheets

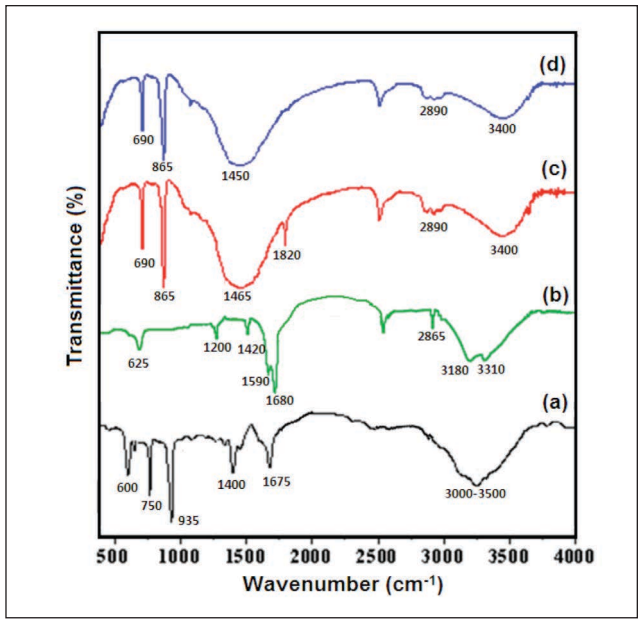
A 20% w/v slurry was prepared with PAM-modified PCC nanocomposites in water and added to the stock pulp. The handsheets were prepared by using the stock pulp containing 60% chemical bagasse and 40% hardwood refined pulp slurry with 85% brightness. The filler mixed pulp slurry was diluted to 1% consistency. A 60 g/m² handsheet was prepared according to TAPPI T 205 sp-02 by adopting the sequential approach to obtain higher filler bound ability.

The diluted pulp with 20% PAM-modified $CaCO_3$ nanofillers at 1% consistency was added with various retention aids and additives such as ATC, AKD, RDA, and starch as prescribed by the papermakers to obtain favorable adsorption of filler particle on the pores of the paper matrix. (From our trial studies, 20% nano-PCC addition showed better paper properties). The mixture was allowed to blend for 15 min (for one set). The same procedure was adopted to prepare handsheets with all modified $CaCO_3$ nanoparticles and PAM at different ratios (1:0.02, 1:0.05, 1:0.07, and 1:0.09) and with the unmodified nano-PCC fillers. The prepared sheets were dried for 6 h at 23°C±1°C and in 50±2% humidity. The prepared handsheets were examined for their morphological, structural, mechanical, optical, and surface properties.

Characterization of unmodified filler, modified fillers, and papers

The resulting nano-$CaCO_3$, PAM-modified $CaCO_3$ nanocomposites, and PAM/$CaCO_3$ nanocomposite filled papers were characterized by field emission scanning electron microscopy (FE-SEM) (model JSM-5610LV, JEOL USA; Peabody, MA, USA) with an accelerating voltage of 20 kV. The Fourier transform infrared (FT-IR) spectra were recorded on a FTIR-3600 (Jasco Inc.; Easton, MD, USA). The FE-SEM study was also performed for the bagasse-based papers prepared without fillers and with PAM-modified nano-$CaCO_3$ (at various ratios) filled papers to examine their adherence and filling properties of pores in the paper matrix.

The properties of handsheets prepared without filler, with nano-PCC, and with PAM-modified $CaCO_3$ nanocomposite at various ratios were determined after conditioning the paper sheets at constant temperature (23±1°C) and humidity (50±2%). The optical properties of the handsheets (ISO brightness, ISO opacity, and scattering coefficient) were measured on a Spectraflash 300 spectrophotometer (Datacolor; Lawrenceville, NJ, USA). The Gurley air resistance of the sheets was determined using an SE 166 air resistance tester (Lorentzen & Wettre; Alpharetta, GA, USA) as per TAPPI T 460 om-02 "Air resistance of paper (Gurley method)." A higher value means lower air permeability and porosity, and vice-versa. The Bendtsen roughness of the sheets was determined using an SE 164 Bendtsen tester (Lorentzen & Wettre) as per ISO 8791-2 "Paper and board—determination of roughness/smoothness (air leak methods)—part 2: Bendtsen method." An SE 009 Elemendorf tear tester supplied by Lorentzen & Wettre was used to analyze the tear index of the prepared



1. Fourier transform infrared (FT-IR) spectra of (a) nano-calcium carbonate ($CaCO_3$), (b) polyacrylamide (PAM), (c) PAM-modified nano-$CaCO_3$, and (d) PAM-modified nano-$CaCO_3$ filled paper sheet.

handsheets as per TAPPI T 414 "Internal tearing resistance of Paper (Elmendorf-type method)." The tensile index of the sheets was also determined on an SE 060 tensile strength tester (Lorentzen & Wettre) as per TAPPI T 494 om-01 "Tensile properties of paper and paperboard (using constant rate of elongation apparatus)." All the measurements were made three times and their average value was tabulated. The obtained results are discussed in detail in the following sections.

RESULTS AND DISCUSSION

Characterization of nano-$CaCO_3$, $CaCO_3$/PAM nanocomposite fillers

The FT-IR spectra of the synthesized nano-$CaCO_3$, PAM, $CaCO_3$/PAM nanocomposite filler (1:0.09), and the paper prepared with $CaCO_3$/PAM nanocomposite fillers (1:0.09) are shown in **Fig. 1**. In Fig. 1a, the $CaCO_3$ formation with calcite phase, where the sharp peaks appeared at 600, 750 and 935 cm^{-1}, are caused by $CaCO_3$ nanoparticles (nano-PCC). In particular, the peak at 750 cm^{-1} is the characteristic IR band for the calcite phase. The peaks at 1400 cm^{-1} and 1675 cm^{-1} are attributed to the stretching and asymmetric stretching modes of CO^{-2}_3 in the calcite crystal. The larger broad absorption peak around 3000–3500 cm^{-1} is assigned to the stretching vibration and asymmetric stretching vibration of the O–H bond and can be attributed to the presence of absorbed water and hydroxyl groups on the surface of $CaCO_3$ nanoparticles.

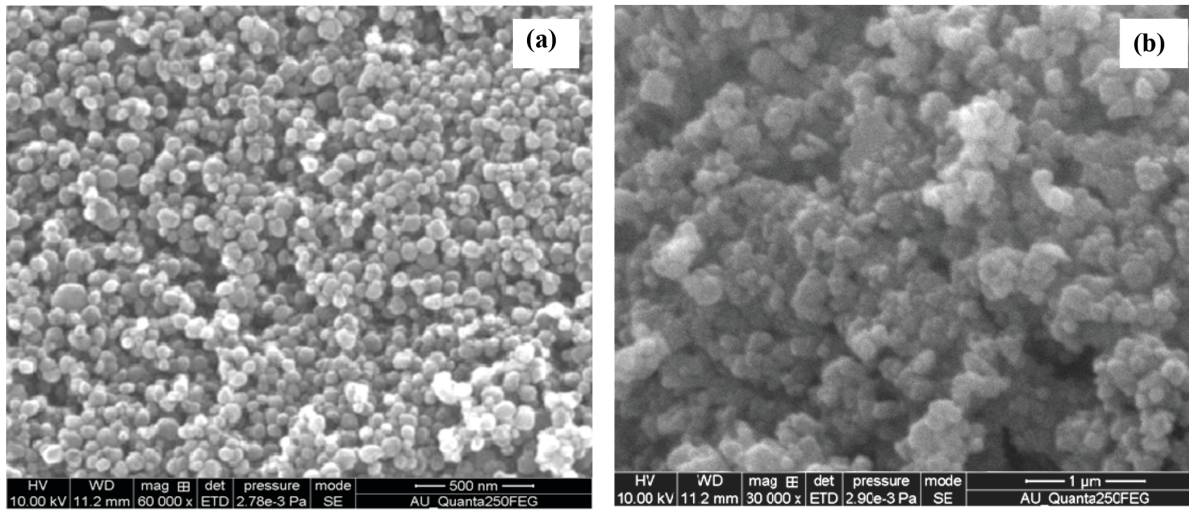
In Fig. 1b, the IR bands of PAM at 625, 1420, and 1680 cm^{-1} arise from the C–C, C–N, and C=O stretching vibrations, respectively. The peaks at 1200 and 1590 cm^{-1} are assigned for the amido (NH_2) group along with high wavenumber broad peaks at 3180 and 3310 cm^{-1} for NH_2 stretching and asymmetric vibrations, respectively. The peak at 2865 cm^{-1} corresponds to C–H vibration. After the modification of nano-$CaCO_3$ with PAM (Fig. 1c), the IR bands of PAM and $CaCO_3$ had distinct blue shifts of N–H bending vibration of PAM and CO_3^{2-} vibrations to 1465 cm^{-1}. A small blue shift of the peak for calcite of $CaCO_3$ is also observed at 750–690 cm^{-1} and 935–865 cm^{-1}. The peaks at 600 cm^{-1} (Fig. 1a) and 625 cm^{-1} (Fig. 1b) merged with the calcite peak and emerged at 690 cm^{-1}. The peak at 1820 cm^{-1} for the C=O of PAM had a red shift from 1680 cm^{-1}. These shifts of peaks and peak broadening are caused by the intermolecular H bonding and interaction of $CaCO_3$ [43,44].

In the instance of $CaCO_3$/PAM nanocomposite filled paper, the N–H bonding between PAM and cellulose exhibits the broad peak centered at 1450 cm^{-1} and 3400 cm^{-1} (merged with OH peak), confirming the bonding of polymer-modified nanofiller with cellulose matrices (Fig. 1d) [45]. A further 15 cm^{-1} blue shift of NH_2 peak (compared with Fig. 1c) is reiterated in the formation of H bonding with cellulose matrix, and the peak for C=O at 1820 cm^{-1} is overlapped in the peak broadening. These band shifts suggest that PAM-modified $CaCO_3$ and paper fiber have significant bonding. The spectral line for surface water diminished (centered at 3400) in the PAM/$CaCO_3$ nanocomposite filler and paper filled with PAM/$CaCO_3$ nanocomposite filler when compared with pristine $CaCO_3$ because the surface of the $CaCO_3$ nanoparticle was masked by PAM coating and bonding with cellulose fiber, respectively [46]. The FT-IR spectra verified the formation of $CaCO_3$ nanoparticles; coating of PAM on $CaCO_3$ nanoparticles; and PAM-modified $CaCO_3$ nanoparticles-cellulose interaction, which is responsible for the enhancement of mechanical and surface properties of the papers.

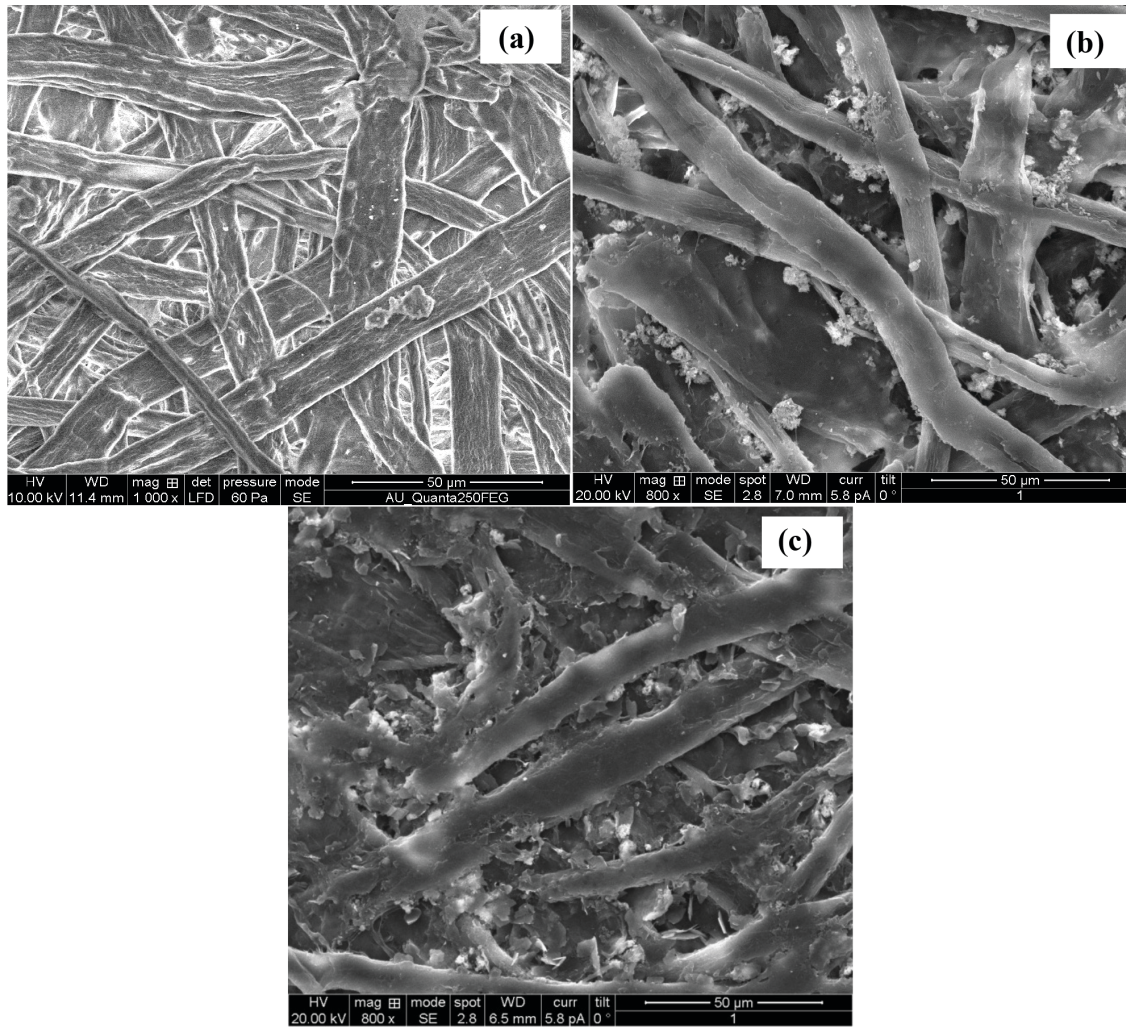
Morphological studies

The FE-SEM images of the synthesized nano-PCC and PAM-modified PCC are presented in **Fig. 2**. It is evident that the synthesized nano-$CaCO_3$ particles are freely, homogeneously dispersed discrete particles with a size range of 60–80 nm (Fig. 2a), whereas in the case of PAM-modified $CaCO_3$ nanocomposite, the $CaCO_3$ nanoparticles are covered with PAM and exhibit increased size (120–200 nm) with smaller clusters of grouped particles (Fig. 2b). **Figures 3** and **4** illustrate the FE-SEM and light microscopic images of the unfilled sheet, $CaCO_3$ nanoparticles, and PAM-modified $CaCO_3$ filled paper samples (1:0.09). The FE-SEM images of paper surfaces were taken to investigate distribution of nano-$CaCO_3$ fillers and PAM-modified nano-$CaCO_3$ (1:0.09) fillers on the cellulose matrix. The micrographs show that the amount of nano-$CaCO_3$ filler dispersion on the paper matrix is smaller compared with that of nano-$CaCO_3$ fillers modified with PAM polymer.

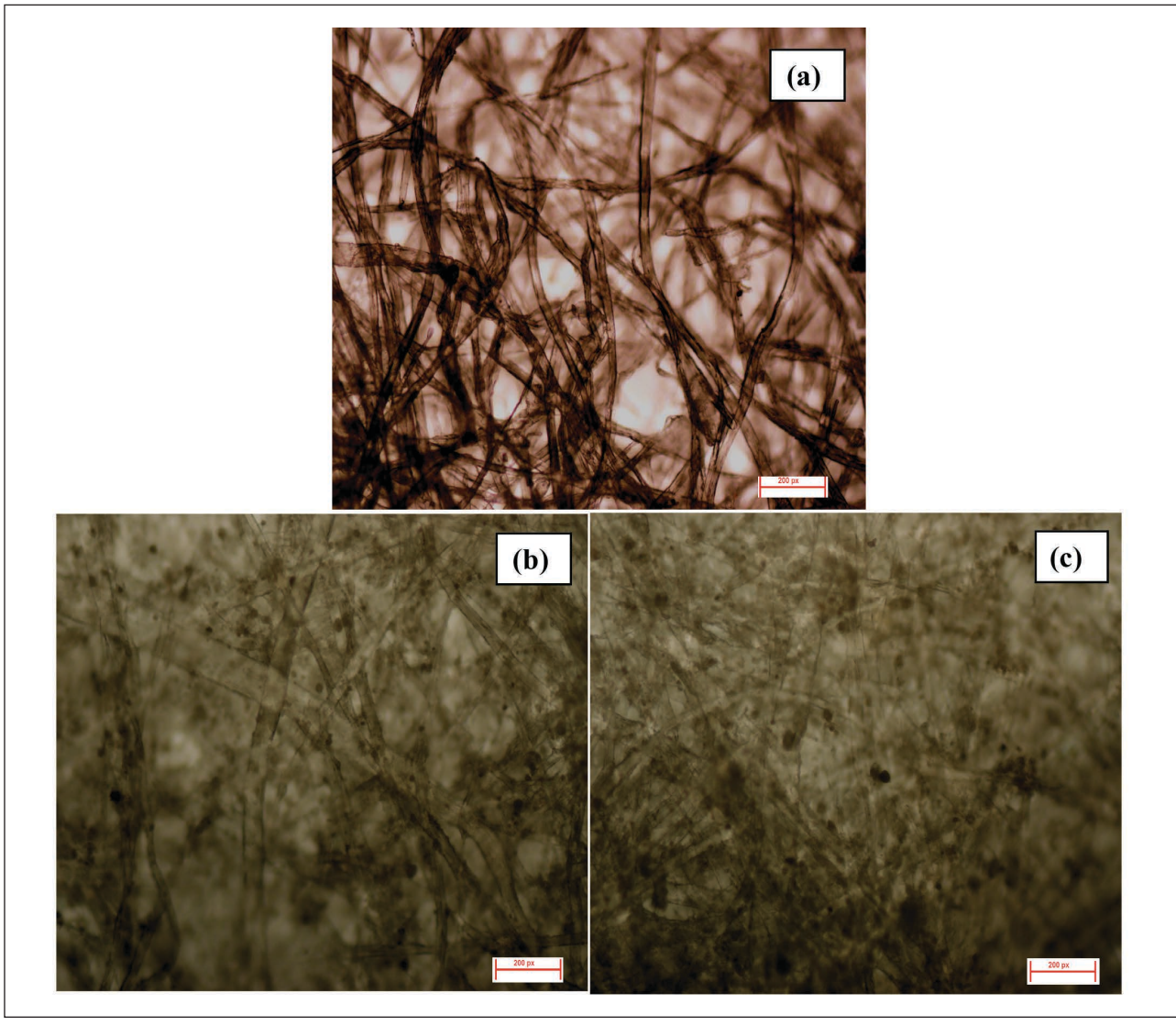
The presence of PAM during the filler modification changed the morphology of the $CaCO_3$ from nanospherical to aggregated spherical particles and led to a significant increase in particle size. Modified fillers were incorporated and deposited on the cellulosic fiber surfaces in the fiber-based



2. Field emission scanning electron microscopy (FE-SEM) images of (a) nano-$CaCO_3$ particles, and (b) PAM-modified nano-$CaCO_3$ at 1:0.09 ratio.



3. FE-SEM images of (a) blank paper, (b) nano-$CaCO_3$ filled paper, and (c) paper with PAM-modified nano-$CaCO_3$ filler at 1:0.09 ratio.



4. Light microscopic images of (a) blank paper, (b) nano-$CaCO_3$ filled paper, and (c) paper with PAM-modified nano-$CaCO_3$ filler at 1:0.09 ratio.

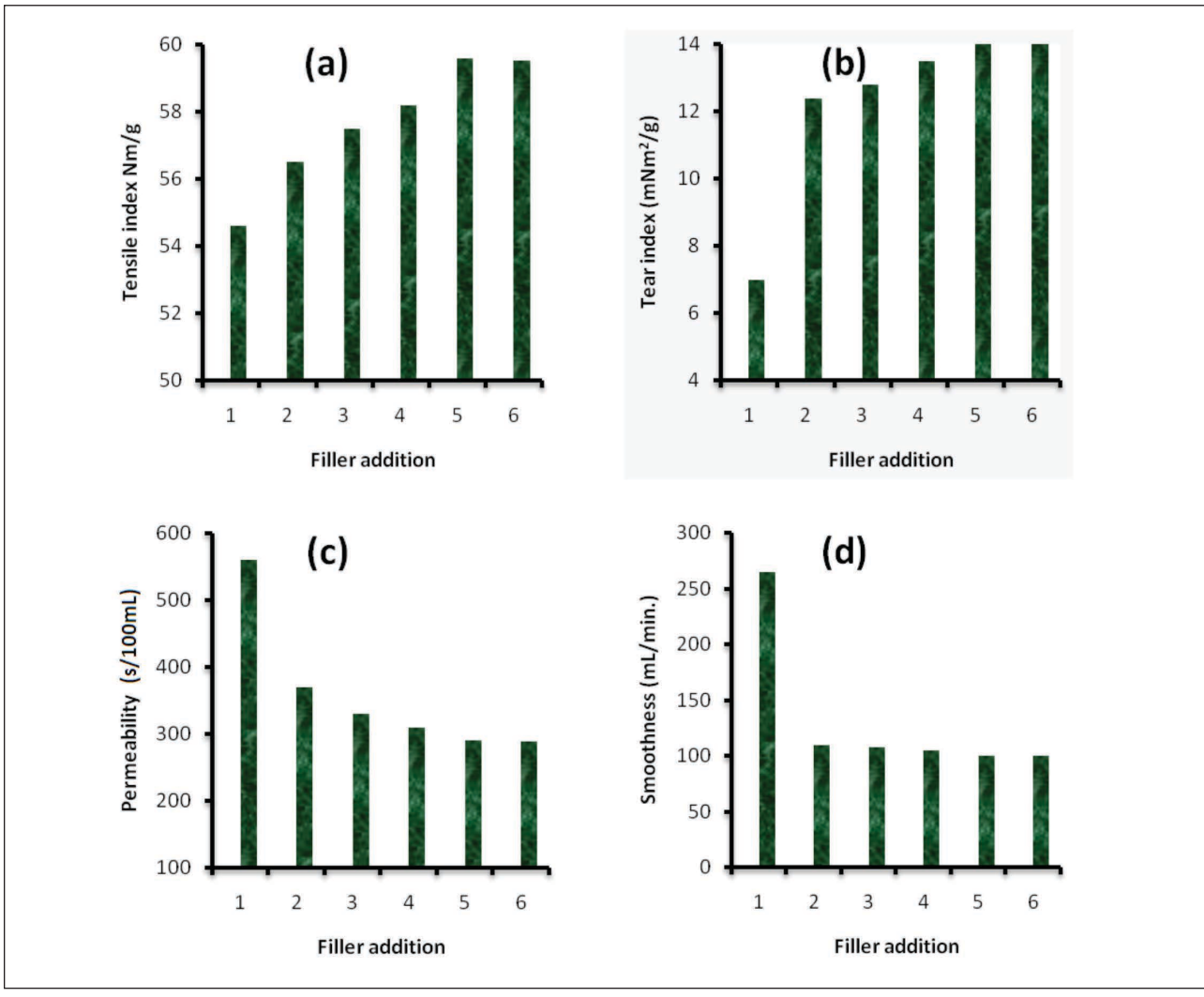
matrices. It was observed that the modified filler was adsorbed more on the fiber surfaces and caused the improved paper properties.

Properties of papers

The properties of filled papers are dependent on the nature of fiber and filler in the paper sheets. The structural development in the paper matrix is decided by the physicochemical characteristics of the fillers. The chemical characteristics of filler are attributed to the chemical charge balance and the retention of filler in the paper, which in turn reduces the number of interfiber bonds in the paper. The response of the papers in terms of tensile index, tear index, porosity, smoothness, opacity, brightness, and scattering coefficient by the addition of nano-$CaCO_3$ and PAM-modified $CaCO_3$ nanocomposite fillers at various ratios are described in the following sections.

Strength properties of papers

Usually, when the content of the filler is increased, the fiber content is simultaneously decreased. In addition, the number of fiber-fiber bonds is also decreased as the density of fiber in a paper sheet is decreased. Moreover, the tensile and tear strength of the paper are decreased because the filler particles lie between the fibers and decrease the contact area, which then decreases the contact bonds. To overcome these negative effects, we have modified the synthesized nano-PCC with cationic PAM at different ratios to make handsheets. The effects of modified fillers addition on the tensile and tear strength in the handsheets were evaluated and the results are presented in **Fig. 5** and **Table I**. The blank paper had 54.60 Nm/g tensile index. Interestingly, the tensile index is increased about 2 Nm/g with the addition of nano-$CaCO_3$ filler; this might be caused by the increased bonding between the fibers through the higher surface hydroxyl groups present on the



5. (a) Tensile index, (b) tear index, (c) porosity, and (d) smoothness of bagasse paper filled without and with the different ratios of nano-$CaCO_3$ and PAM-modified fillers (20% filler): (1) blank paper, (2) nano-$CaCO_3$, (3) $CaCO_3$:PAM ratio 1:0.02, (4) $CaCO_3$:PAM ratio 1:0.05, (5) $CaCO_3$:PAM ratio 1:0.07, and (6) $CaCO_3$:PAM ratio 1:0.09.

nanoparticle surface. Nanofillers not only act as filler materials; they also act as binder materials for the fibers. However, the tensile index increment is higher with the PAM preflocculated nano-$CaCO_3$ filler particles addition; it reached a maximum of 59.60 Nm/g at a 1:0.07 ratio. Comparatively, the PAM-modified $CaCO_3$ nanoparticle filled papers showed significantly improved strength with increasing PAM content in filler modification up to 0.07, then decreased. These results demonstrate that the preflocculated filler or the cationic PAM improves the bonding capacity of the filler with fiber, resulting in improved tensile index, and indicate the possibility of achieving similar tensile index values for paper using preflocculated filler compared with native fillers alone (ground calcium carbonate [GCC]/PCC).

The influences of preflocculated nano-$CaCO_3$ fillers addition on the tear strength of bagasse pulp papers are presented in Fig. 5b and Table I. Similar to the tensile index, the tear strength of the paper is also gradually increased by increasing the PAM content in the PAM-modified nano-PCC fillers. The tearing index was 6.99 mN.m²/g for the blank paper, whereas with the addition of nano-$CaCO_3$ it was significantly increased to 12.40 mN.m²/g. Further, the addition of 1:0.09 $CaCO_3$:PAM-modified filler demonstrated an improved tear index of 14.30 mN.m²/g. The cationic PAM effectively encapsulated the nano-PCC filler particles. The preflocculated $CaCO_3$ filler particles are more firmly adhered onto the fiber surface and increase the fiber-filler-fiber bonding in the papers, whereas in the case of native filler (nano-GCC) the greater number of filler particles impaired the filler-fiber bonding and had the greatest negative impact on the paper strength [47-50]. Thus, increasing the dosage of PAM also increases the paper strength. For both tensile index and tearing index, lower addition of PAM showed only a marginal increase in strength property. These results showed that the impact of filler preflocculation was greater at higher filler loading levels and confirmed that cationic-polyacrylamide-preflocculated nano-PCC filler improves

Paper Properties	Blank Sheet (no filler)	Nano-Calcium Carbonate ($CaCO_3$)	Polyacrylamide (PAM):Nano-$CaCO_3$ Ratio			
			1:0.02	1:0.05	1:0.07	1:0.09
Tensile index, Nm/g (±0.2)	54.6	56.5	57.5	58.2	59.6	59.5
Tearing index, mNm^2/g (±0.1)	7.0	12.4	12.8	13.5	14.2	14.3
Porosity, mL/min (±5)	560.0	370.0	330.0	310.0	290.0	289.0
Smoothness, mL/min (±2)	265.0	110.0	108.0	105.0	100.0	99.7
Scattering coefficient, m^2/kg (±0.2)	40.3	59.0	58.1	57.5	57.0	56.8
Opacity, % (±0.1)	78.7	95.0	94.7	94.2	93.6	93.5

I. Physical, surface, and optical properties of handmade papers prepared without and with 20% addition of nano-$CaCO_3$ and PAM-modified nano-$CaCO_3$ (PAM:$CaCO_3$ ratio(s) = 1:0.02, 1:0.05, 1:0.07 and 1:0.09) in 60:40 (60% bleached chemical bagasse pulp: 40% bleached hardwood pulp) pulp mixer at 300 ml CSF.

the strength property of a paper sheet in all directions. This is a significant behavior compared with the behavior of routine fillers, which damage the strength of the papers.

Surface properties of papers

The lower porosity and higher smoothness are beneficial for better printability. The influence of nano-PCC modified with PAM at different ratios (1:0.02, 1:0.05, 1:0.07, and 1:0.09) and the nano-PCC fillers on the porosity of the bagasse papers (air permeability) are shown in Fig. 5c and Table I. The addition of nano-PCC modified with PAM nanocomposite fillers drastically reduced the porosity of the paper by filling the gap or unevenness between the fiber-to-fiber bonding. Greater air resistance or lower porosity was observed for the nano-PCC and PAM-modified nano-PCC fillers where about 33% and 48% porosity reduction was observed, respectively, compared with the blank paper (560 mL/min.). As shown in Table I, the air passing through the paper structure is decreased as the PAM content in the preflocculation of nano-PCC filler (1:0.02 to 1:0.09) is increased. It was observed that the highest air resistance of paper (i.e., lowest porosity value 290 mL/min) was achieved at the 1:0.07 ratio (negligible improvement at 1:0.09), which had the higher bonding ability among all the modified fillers. The broader particle size distribution (PSD) of the nano-PCC with PAM effectively decreases the paper's porosity because smaller sizes of the fillers can fill the pores more effectively. In addition, the modified fillers effectively enhance the surface properties of the paper [51].

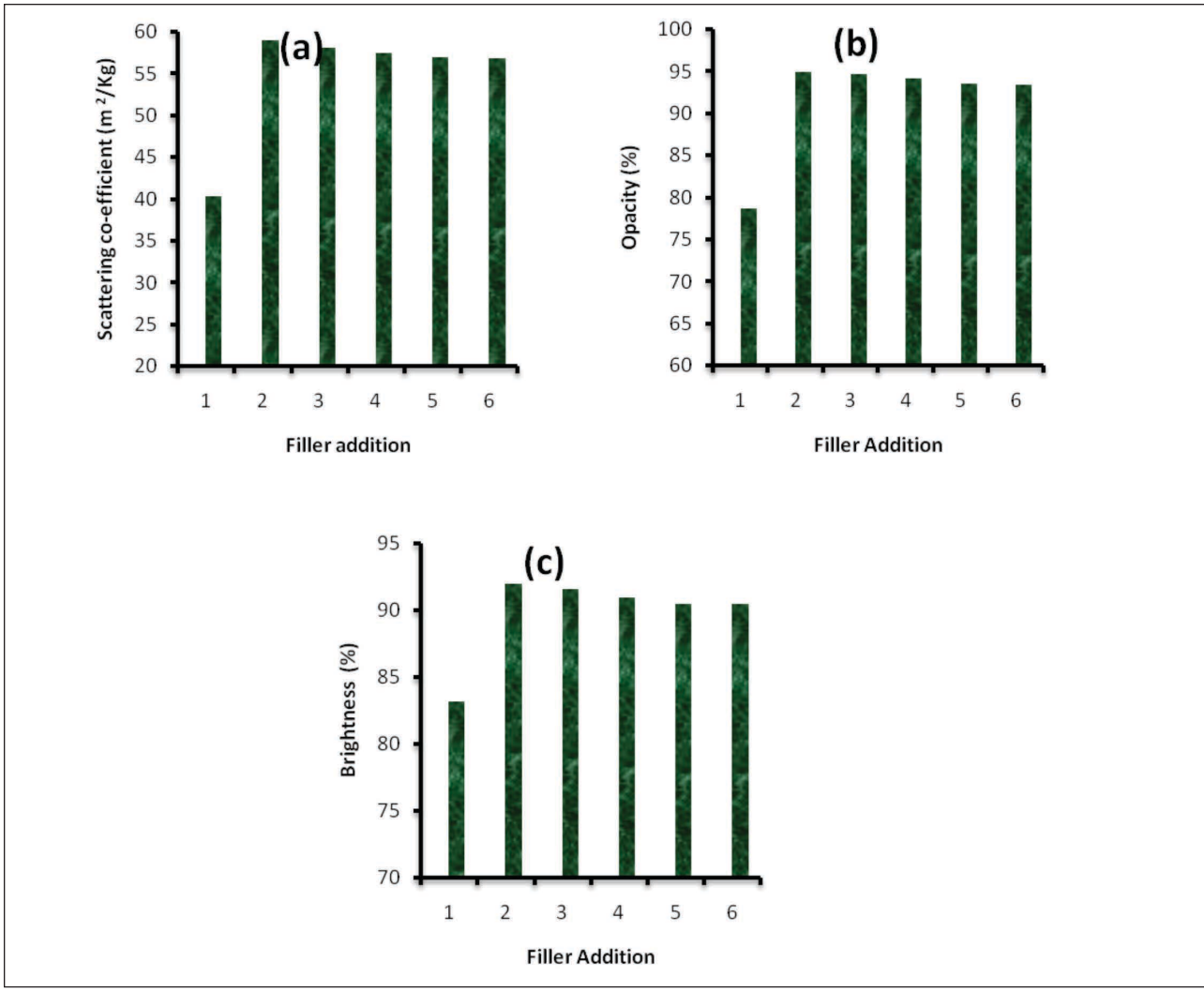
The effect of PAM-modified nano-PCC fillers at 1:0.02–1:0.09 ratio on the smoothness of the bagasse-based paper is shown in Fig. 5d and Table I. As shown, with the increase of PAM in the nano-PCC filler from 1:0.02 to 1:0.07 ratio, the smoothness of the paper sheet is also significantly increased (lower smoothness values) but beyond that the increment is small. Increased smoothness peaked at 63%, which was obtained with 1:0.07 modified filler compared with the blank sheet (265 mL/min.). The difference in the smoothness values of paper made with 1:0.07 and 1:0.09 ratios was negligible, which might be a result of minor differences in their PSD that mirrored smoothness values of the paper sheet. Because of better bonding ability between the filler particles and fibrous matrix, PAM provides better surface properties (i.e., smoothness). Under our experimental conditions, the smoothness of the papers is lower at lower PAM ratio. The smaller size effect of the synthesized nano-PCC along with the PAM has played a vital role and effectively increases the smoothness of the paper [52].

Optical properties of papers

The optical properties of the papers are influenced by the amount, particle size, PSD, and shape of the filler particles. **Figure 6** represents the scattering coefficient of the papers filled with modified fillers (PCC:PAM) at different ratios (1:0.02–1:0.09). It was presumed that the aggregated fillers or the synthesized nano-PCC modified with PAM fillers were permitted higher light scattering; for the blank paper the value is 40.30 m^2/kg and for nano-PCC and PAM-modified nano-PCC the values are 59.00 m^2/kg and 57.00m^2/kg, respectively, which are higher compared with the commercial PCC/GCC fillers. However, all the filler particles do not contribute to the light scattering in the paper because of their heterogeneous distribution and positioning in the paper matrix. Typically, smaller filler particles can be located in interfiber pores or on the fiber surfaces between adjacent fibers, where they influence the light scattering ability.

In our study, the nano-PCC and PAM were shown to maximize the light scattering ability of paper and to have limited contact with the adjacent particles, providing more solid-air interfaces. It was also reported that the smaller pores or uniform particles are not beneficial for light scattering. Comparatively, the light scattering and opacity of the polymer-modified $CaCO_3$ fillers are lesser than the synthesized nano-PCC filler, but their values are in the range of world standard.

Opacity is an important property in fine papers to avoid showthrough; therefore, these papers should have low light absorption coefficient and high brightness. Light scattering is



6. (a) Scattering co-efficient, (b) opacity, and (c) brightness of the bagasse paper filled without and with the different ratios of nano-$CaCO_3$ and PAM-modified fillers (20% filler): (1) blank paper, (2) nano-$CaCO_3$, (3) $CaCO_3$:PAM ratio 1:0.02, (4) $CaCO_3$:PAM ratio 1:0.05, (5) $CaCO_3$:PAM ratio 1:0.07, and (6) $CaCO_3$:PAM ratio 1:0.09.

the main mechanism for opacity production; it is known that the opacity of paper depends upon the grammage and the specific light scattering of the paper [53,54]. As shown in Fig. 6b and Table I, the trend of opacity in PAM-modified nano-PCC fillers filled paper was also comparable to that of the scattering coefficient. The opacity value for the blank sheet was 78.7%, and the addition of nano-PCC filler resulted in a 16% increase to 95%. The opacity of the papers made with PAM-modified nano-PCC fillers was increased to 91% (a negligible difference).

The influence of the filler modification on the brightness of the paper was also examined and the results are presented in Fig. 6c and Table I. The brightness of paper was increased about 9% with the addition of nano-PCC compared with that of the blank sheet. All ratios of PAM-coated nano-PCC exhibited good brightness at the higher filler addition (90.5%) (negligible variations) because it has more intrinsic brightness [55]. The application of combined nano-PCC filler and PAM at 1:0.07 and 1:0.09 ratios retained the brightness of the filled papers at the desired standard values. The reason for the slight decrease in the brightness with the nano-PCC is caused by the increased filler-to-fiber coverage and surface encapsulation.

CONCLUSIONS

The surfactant assisted $CaCO_3$ nanoparticle was synthesized by simple coprecipitation technique and its surface was modified with PAM (0.0%–0.09%) through in-situ technique. The FT-IR spectral lines were clearly evident in the formation of $CaCO_3$, PAM/$CaCO_3$ nanocomposites, and the dispersion of PAM/$CaCO_3$ nanocomposites on the cellulosic fiber matrix. The aggregated clusters of particles with distortion morphology of the PAM- modified $CaCO_3$ nanoparticles were dispersed on the pores of the cellulosic matrix more densely. Tensile index and tearing index of the PAM/$CaCO_3$ nanocomposites filler were significantly increased to 59.60 Nm/g and 14.20 nN.m²/g, respectively. A 48% reduction of porosity and

63% increase in smoothness were observed with the PAM-modified nano-PCC. The nano-PCC and PAM maximized the optical properties of the paper and were shown to have limited contact with the adjacent particles, thus providing more solid-air interfaces. The impact of filler preflocculation was greater at higher filler loading levels. It was confirmed that the cationic-polyacrylamide-preflocculated nano-PCC filler improved strength and surface and optical properties of paper sheets in all directions because of its better bonding ability between the filler particles and fibrous matrix. It is suggested that the use of polymer-coated PCC filler could be an effective alternative to improve paper quality. **TJ**

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ABOUT THE AUTHORS

We chose to research this topic because of the interest in nanotechnology as a means to improve paper as well as reduce wood consumption. Our previous work was synthesis of nanoparticles for various applications. This work differs because we chose to focus on improving paper quality without sacrificing the mechanical properties of paper.

Our most difficult challenge was that optical and surface properties cannot typically be improved without affecting tear and tensile properties of the paper. We demonstrated that all the important paper properties can be improved and we highlighted that in our article. Nanoparticles, particularly precipitated calcium carbonate ($CaCO_3$) nanoparticles, can lead to improvements in the cheaper bagasse-based papermaking process, with the addition of polymeric nanocomposite. Our most interesting finding was that the nano-$CaCO_3$/polyacrylamide (PAM) nanocomposite demonstrated the ability to improve all of the critical paper properties.

Significantly, mills could adopt the suggestions in this article in terms of reducing the amount of pulp by increasing the filler content to produce high-quality paper. Our next step is to test the adoptability of the processes.

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