

Improvement of Bagasse Based Paper Properties Using Definite Size Effect of CaCO_3 Nanofillers



CHEMISTRY

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ABSTRACT

*The usage of fillers is attractive to the paper industries mainly including cost and energy savings. In this work, the use of inorganic fillers particularly the synthesized precipitated nano CaCO_3 (PCC) filler was used to improve the paper qualities with the refined bagasse and hard wood mixed pulp and compared with commercially available micro ground CaCO_3 fillers. And the effects of Micro GCC and Nano PCC fillers on paper strength properties of the bagasse based papers have been investigated. The XRD and FT-IR results were confirmed the formation of CaCO_3 with calcite phase. Homogeneously dispersed spherical nanoparticles with an average size of ~80 nm was observed for the synthesized CaCO_3 particles, where as the commercially available GCC particles were in the micron size (2 μm) observed through SEM analysis. The tensile and tearing strength of the papers were increased often the addition of fillers up to 20% remarkably, beyond 20%, there was no notable improvement detected. These results indicated the addition of Nanofillers showed significantly improved paper properties compared to the commercially available micro GCC fillers. * Corresponding Author, Email: apsakthivel@yahoo.com*

1 INTRODUCTION

Inorganic mineral fillers are used along with the cellulosic fibers for paper making to replace some of the expensive cellulosic fibrous material and to reduce the papermaking cost. Nanotechnology has an unforeseen impact on paper industry. Many novel materials have been developed and fundamental studies have been carried out in different areas. [1]. Nanofillers are able to add new functionalities to the papers, depend on the fillers/pigments particle size, distribution, aspect ratio, stabilization and surface modification of nano particles. The nano titanium dioxide (TiO_2), and a combination of nano- TiO_2 and beta-cyclodextrin (beta-CD) coated fillers have been used to coat the papers. The paper coated with a combination of nano- TiO_2 and beta-CD had a better effect on the degradation of paper than the paper coated only with nano- TiO_2 , and beta-CD, where the nano- TiO_2 had a significant synergistic effect on the degradation of xylene [2]. TiO_2 was recovered from the paper ash and showed that the crystal structure of TiO_2 was anatase with 10-20 nm size range [3].

In a recent study, a new type of paper with superhydrophobic surface was prepared with the addition of modified nano- TiO_2 to cellulosic fibers [4]. The light scattering properties of precipitated calcium carbonate (PCC) fillers coated with silicate and zinc sulfide nanoparticles have been examined [5]. The latest work demonstrated that the brightness, whiteness, smoothness, print density, print uniformity, picking velocity and oil absorbency of nano-ZnO coated paper showed significant improvement, compared to the bulk-ZnO coated paper [6]. The nanostructured silica produced with an open network structure by controlled precipitation from geothermal water was also investigated for their applicability in paper making process [7].

The commercially available GCC and PCC fillers in different PSD are being used by paper makers depending upon the requirement. Because of the patent nature of the reports, not much details of the experimental work and discussions are available. Hence, in the present study, considering the particle size effect and distribution, on the paper characteristics, different % (7.5, 12, 15, 20, 25 and 30%) addition of commercially available micro GCC and the synthesized nano PCC with normal and excess retention aided modified papers samples have been investigated systematically. The various particle sizes have been chosen in order to understand the effect of particle size on the strength properties of the paper sheets made from refined bagasse based mixed pulp.

2 EXPERIMENTAL

2.1 Materials

The blending of 40% bleached hard wood pulp and 60% bleached chemical bagasse pulp were taken to PFI mill for beating / refining of pulp fibers and used for hand sheets preparation. The CSF of the mixed refined pulp was bringing down to 300 ml Canadian Standard Freeness test (CSF prepared in TNPL, India). According to Technical Association of Pulp and Paper International (TAPPI) text methods, the Anionic traceable catcher (ATC), Cationic and native starch, Alkyl Ketene Dimmer, Retention and Draining Agent, Cationic and anionic poly acrylamide, and silica were purchased from Arjun chemicals, India and used as received for the hand sheets paper preparation.

3. RESULTS AND DISCUSSION

3.1 XRD and FT-IR spectral studies

The XRD and FT-IR spectra of the synthesized Nano PCC and purchased micro GCC and paper sheets filled with 20% addition

of micro GCC and nano PCC fillers are presented in **Figure 1**. XRD analysis was used to prove the presence of CaCO_3 particles in the lumen of fibers. The XRD spectral lines of the paper samples clearly demonstrates the presence of strong reflection of calcite at 2θ values of 23.25, 29.35, 35.82, 39.48 and 43.27 corresponding to the (012), (104), (110), (113) and (202) planes respectively and perfectly matched with the standard data JCPDS File No. 47-1743.

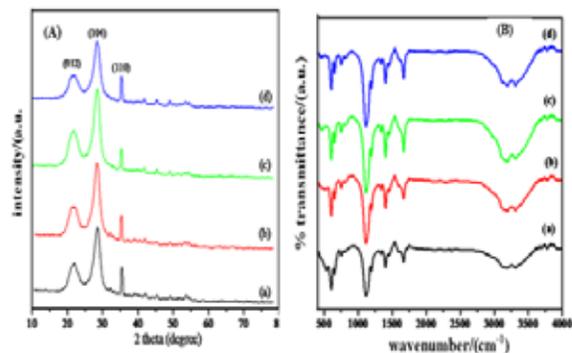


Fig. 1(A). XRD spectra of (a) Synthesized PCC, (b) Micro GCC, (c) 20% nano PCC filled paper and (d) 20% micro GCC filled paper. **Fig.1(B).** FTIR spectra of (a) Synthesized PCC, (b) Micro GCC, (c) 20% nano PCC filled paper and (d) 20% micro GCC filled paper.

In addition to the characteristic peaks of the calcite, all the XRD patterns of the paper sample did not show any other impurity characteristics, typically of vaterite or aragonite phase in the **Fig. 1A (c and d)**. These results confirmed the micro GCC and nano PCC particles are found in the paper samples. The FT-IR spectra of the synthesized CaCO_3 and the purchased CaCO_3 are presented in **Fig. 1B (a and b)**. The presence of transmission peak at 3350, 2918, 2511, 1794 cm^{-1} , broad peak at 1369-1524, 878 and 713 cm^{-1} are assigned to the stretching and vibration bands of water and CaCO_3 particles. The broad transmission peak at 3350 cm^{-1} is assigned to the stretching and asymmetric stretching vibration of OH band exhibited by the adsorbed water and hydroxyl groups present on the surface of the CaCO_3 particles [8]. The peaks at approximately 2511, 1794, 1450, 878 and 713 cm^{-1} are ascribed to the calcite transmission. According to the standard IR spectrum of CaCO_3 , the appearance of strong peak at 712 cm^{-1} is assigned to the calcite structure of CaCO_3 sample [9,10], which is well matched with our FTIR spectra and consistent with the XRD results. The presence of peak at 2918 cm^{-1} in the FTIR spectra of synthesized nano PCC is due to stretching vibration of CH_2 produced by the presence of oleic acid surfactants, which is not observed for micro GCC purchased samples. It can be confirmed that the synthesized and purchased CaCO_3 powders are calcite form of CaCO_3 with high pure. The FTIR spectra of the papers prepared with the nano PCC and micro GCC fillers are also exhibited the peaks for the calcite structure of the CaCO_3 , indicates the presence of CaCO_3 in the cellulose fiber matrix.

3.2 FE-SEM images

The FE-SEM images of the paper sheets prepared with the 20% addition of micro GCC and nano PCC fillers with normal and excess retention aids are shown in the **Fig. 2**. The SEM images of the paper sheets clearly indicated that the filler particles were more effectively adhered and bonded to the pulp fibers. When the fillers are incorporated in to the fibers, the pores of the paper sheets are filled and the filler particles deposited on the fiber surfaces in the bagasse based fiber matrices.

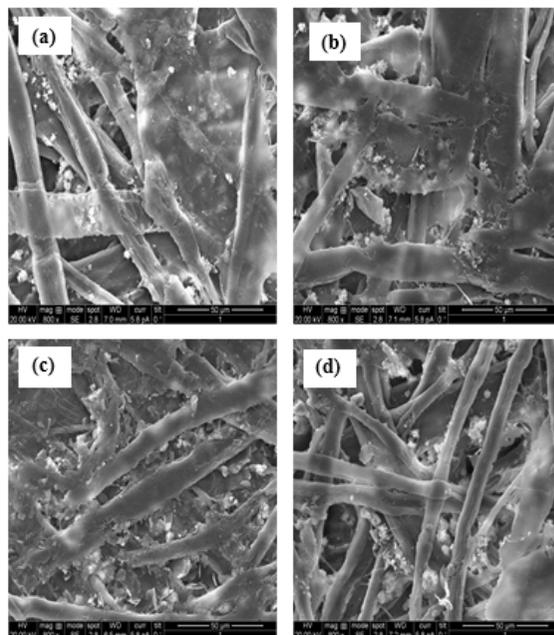


Fig. 2 FE-SEM images of papers with (a) 20% micro GCC filled with normal retention, (b) 20% micro GCC filled with excess retention, (c) 20% nano PCC filled with normal retention and (d) 20% nano PCC filled with excess retention aids

The discrete white particles within the fiber matrix represent the presence of fillers. As the particle size of nano PCC fillers became finer, the particles were more adsorbed on the fiber surface (**Fig. 2c and d**) as compared to that of coarser size micro GCC fillers (**Fig. 2a and b**). It is clear that the synthesized nano PCC in the paper structure are distributed much more uniformly than the micro GCC filler [11]. In addition, the nano PCC fillers are appears to be more compatible with the cellulose fibers. The adherence of fillers on fiber was a little higher with the excess retention aid compared to normal retention aid. Among the fillers, the nano PCC has more distribution on the paper due to its smaller size effect. Noticeably, the synthesized nano PCC particles are more firmly and effectively adhered and bonded to the fiber surfaces compared to the micro GCC particles [12], which was expected to deliver good strength property of the papers made with bagasse based pulp. **(B)**

3.3 Strength property of the micro GCC and nano PCC filled papers

The strength properties such as tensile and tear index of the bagasse based paper without and with the addition of different percentage of nano-PCC and micro - GCC fillers were studied and their results are presented in the **Fig. 3**.

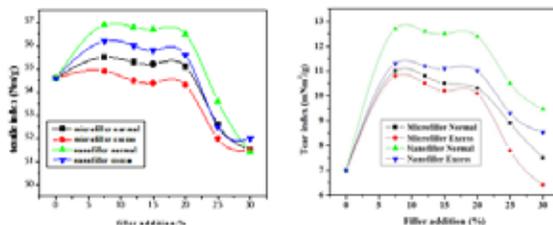


Fig. 3 Tensile and Tear index of the papers filled with the different % of micro-GCC and nano-PCC with normal and excess retention aids

The tensile and tear indexes were increased with increasing the filler addition, beyond 20% addition of filler the strength was

dropped. As the APS distribution was decreased from nano PCC to micro GCC, the tear and tensile index were decreased, which was different from the previous assertion that "smaller particle size has more detrimental effects on tensile strength". The experimental procedure used here comparatively reduced the particle size to nano range and broadened the PSD of nano PCC, which improves the packing ability of filler particles and makes particles that are likely filled in the pores surrounding the fibers, thus decreasing the paper porosity and improving the strength index. Moreover, the broad distribution of particle sizes allows the particles to pack more tightly together affecting fiber bonding to a lesser extent. So, we can state that filler average particle size, particle size distribution and particle shape (morphology) have influenced in a combined way to the paper's tensile strength. Aggregated fillers (micro GCC) introduce void volume into the sheet causing a more severe debonding, so there is a greater loss of sheet strength. And also, particles with narrow particle size distributions exhibit low packing efficiency resulting in greater disruption of inter-fiber bonding. [13,14]. Thus the prepared nano PCC exhibited good paper strength properties compared to the unfilled bagasse based paper and commercially available GCC fillers filled papers. It can be suggested that the nano PCC prepared with nano size range is to be better filler for the industrial applications.

4 CONCLUSIONS

Calcium carbonate spherical nanoparticles have been prepared and their characteristics as paper fillers and their effect on the bagasse based paper strength properties were determined.

The FT-IR, XRD analysis and FE-SEM observations of the micro GCC and nano PCC filled papers confirmed the occurrence of surface encapsulated fillers in the paper matrix. On the basis of the above results, it can be concluded that nano PCC is potential paper filler that can impart in the paper products with good strength and also it can able to provide better surface and optical properties. The surface encapsulating and higher penetrating power of the synthesized nano PCC are thought to be favorable for the enhancement of the compatibility and affinity of filler particles to the cellulosic pulp fibers. In addition, adapting the filler blending concept by taking advantages of the morphology/ characteristics of different sizes of GCC may be of commercial interest.

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