

NANOFILLERS FOR PAPERMAKING WET END APPLICATIONS

Jing Shen,^a Zhanqian Song,^b Xueren Qian,^{a*} Fei Yang,^c and Fangong Kong^d

The papermaking industry can benefit a lot from nanotechnology. This versatile technology can also be used in the area of fillers for papermaking wet end applications. In such applications the main technological examples currently available include wet end addition of commercially available nanofillers, formation of nanofiller/fiber or nanofiller/fibril hybrids, development of novel categories of nanofillers such as high aspect ratio nanofillers, and combination of microfillers with nanostructures by specially controlled routes to obtain composite nanofillers. It is worth noting that there are certain challenges associated with nanofillers, such as high cost, difficulty in structure and performance control, poor dispersability and retention, possible severe negative effects on paper strength, possible detrimental interactions between nanofillers with some wet end additives, and the industry-related limitations. However, in the long run, the research and development in the area of nanofillers will surely create many fruitful results.

Keywords: Nanofillers; Papermaking; Wet end; Nanotechnology; Nanofilling; Challenges; Benefits; High aspect ratio; Nanostructure; Hybrids

Contact information: a: Laboratory of Pulp and Paper Engineering Subject, Key Laboratory of Bio-based Material Science and Technology of Ministry of Education, Material Science and Engineering College, Northeast Forestry University, Harbin 150040, China; b: Institute of Chemical Industry of Forest Products, Chinese Academy of Forestry; Key and Open Lab. on Forest Chemical Engineering, State Forestry Administration, Nanjing 210042, China; c: State Key Laboratory of Pulp & Paper Engineering, South China University of Technology, Guangzhou 510640, China. d: Key Laboratory of Paper Science & Technology of Ministry of Education, Shandong Institute of Light Industry, University Park of Science and Technology, Jinan 250353, China. *Corresponding author: qianxueren@yahoo.com.cn

Developments in Nanofillers for Papermaking Wet End Applications and their Benefits

The area of nanotechnology has been a very hot topic, and it has the potential to make our lives better and to make the world a better place to live in. For the papermaking industry, the existing or potential application areas of nanotechnology include coating, sizing, and paper functionalization or “smartization.” Fillers are widely used in papermaking as substitutes for pulp fibers to provide cost and energy savings, and to improve the critical properties of papers, such as optical properties and smoothness. Globally, in addition to the traditionally used microfillers, the research and development of nanofillers (i.e., fillers with at least one dimension roughly in the range of 1-100 nm, or even in the broader range of 1-400 nm), has also been of interest to many researchers. Currently, the developments (either already commercialized or still at the stage of scientific research and exploration) in nanofillers for papermaking wet end applications can mainly include the following aspects:

- Commercially available nano mineral materials (such as titanium dioxide pigment) with specifically desired properties are directly added to furnish

before the wet web formation of papers, with the goal of achieving superior paper properties such as light scattering for opacity and brightness. Under certain conditions, although nano calcium carbonate might be expected to be rather poor at scattering light due to the much lower refractive index of calcite (compared to rutile TiO_2), the use of commercially available nano calcium carbonate as a nanofiller might also be feasible.

- Nanofiller/fiber or nanofiller/fibril hybrids are formed by fiber loading (lumen and/or cell wall loading), in-situ precipitation, or other specially designed routes, and the hybrids are subsequently formed into paper. An approaches based on such hybrids can provide many benefits, such as good filler retention and alleviation of the negative effects of filler addition on paper strength. Besides optical properties, certain functional attributes (such as magnetic properties) can be conferred to papers.
- Novel categories of nanofillers such as high aspect ratio fillers have been developed to substitute for traditionally applied fillers. For example, GR International, in cooperation with several major industrial partners, has recently developed silicate-based high aspect ratio fillers named “silicate nano fibers” (SNF) that are capable of providing excellent paper properties. Also, simultaneous improvements in several critical properties including sheet bulk, porosity, smoothness, and optical and strength properties have been claimed. Another interesting and promising category of fillers, $\text{Mg}(\text{OH})_2$ nanobelts with very high aspect ratios, has recently been developed by IPST at Georgia Institute of Technology. The nanobelts have been claimed to have certain advantages of low cost, low density, high brightness, and less detrimental effects on paper strength. The novel nanobelts have the potential to be used to add certain functionalities (such as flame retardant property) to papers at low costs. Moreover, the development of nano organic fillers has also been one of the global concerns of paper scientists.
- By applying specially designed routes, the microsized fillers can be combined with nanostructures for the fabrication of nanostructured composite fillers. For example, the development of nanostructured precipitated calcium carbonate fillers (consisting of zinc-based nanostructures contacted with scalenohedral precipitated calcium carbonate particles) has recently been reported by Helsinki University of Technology (TKK), University of Oulu, and University of Joensuu, and the novel fillers have been claimed to be able to confer excellent optical properties to papers. Also, filler modification to confer organic nanostructures (containing polystyrene or a styrene copolymer) to fillers has been patented by Mondi Business Paper Services AG (Austria), and the use of the resulting nano hybrid particles in the wet end of papermaking processes has been claimed to be capable of improving process parameters, such as dewatering. The novel interesting concepts of nanostructuring might be possibly applicable to various types of fillers.

In addition to the above aspects, in some sense it might be reasonable to consider that some mineral nanoparticles mainly functioning as retention and drainage agents can be regarded as a special category of nanofillers. The relevant nanoparticles undoubtedly

include the world-famous colloidal silica and bentonite products, which have already been successfully commercialized. Also, certain calcium carbonate pigments with average size lower than or equal to 200 nm, claimed by Solvay (a chemical and pharmaceutical group in Belgium) to be suitable for use as a substitute for colloidal silica as a dewatering agent in the formation of paper, might also be regarded as nanofillers.

As nanofillers are nanosized in at least one dimension, one might expect that they could provide better performances than traditional fillers in applications such as adsorption, which can benefit from a high surface area; in such applications they may confer certain unique attributes and functionalities to papers, which is also one of the major concerns of papermakers when considering the use of nanofillers. The nanofilled paper could also have such attributes as high smoothness, good appearance, or even “smart” characteristics, which includes possible new security functions, superior potential for information storage, or other previously unimagined functions. It is worth noting that, in general, the available publications on nanofillers for papermaking wet end applications have been much less than those of microfillers. Also, it is fairly evident that the industrial use of nanofillers in papermaking is now only limited to a certain degree. However, the benefits associated with the use of nanofillers can be expected to encourage worldwide papermakers to pay attention to this potentially promising research area, and to make every effort to create positive breakthroughs.

Certain Challenges Associated with Nanofillers

Although the use of nanofillers in papermaking can be expected to provide certain benefits that are attractive to papermakers, there are still certain challenges lying ahead:

- Nanofillers are usually too expensive to be used. For the papermakers, cost saving is possibly the most important consideration, while the upgrading of product quality is another important concern. High cost can be a reason for hesitation when considering the use of nanofillers.
- It is generally very difficult to control the structure and performance of nanofillers. Globally, the synthesis of nanomaterials with highly controllable structural attributes (suitable for specific end uses) has not been well identified, and the mechanisms are also not well understood.
- Certain nanofillers are possibly poor in dispersability and retention, or can possibly have severe negative effects on paper strength, due to their extremely small sizes, which might be an unsurmountable obstacle to their successful commercialization.
- The potential detrimental interactions between high specific area (higher than that of traditional fillers) nanofillers and papermaking wet end additives such as strength agents, sizing agents, and dyes, might pose certain challenges and increase costs.

In addition to the above challenges, there is an industry-related challenge that is possibly worth noting. As we know, the papermaking industry is generally a classical and engineering-based industry, and until recently not many scientists have been involved in the scientific research on nanotechnology, which is possibly one of the reasons why nanofillers have been less well developed, in comparison with traditional inorganic fillers.

Future Prospects

The world is usually full of challenges and opportunities. This is also true for nanofillers for papermaking wet end applications. For nanofillers, breakthrough technologies regarding such aspects as cost reduction, bondability enhancement, paper functionalization or smartization by nanofilling, tailored wet end troubleshooting solutions, and even programmed structure and performance control, are surely capable of influencing our industry to a certain degree.

The future research and development in the area of nanofillers, together with other nano areas of papermaking such as nano polymer additives, nano pigments for coating, nano retention systems, nano sizing agents, fiber nanocoating, and nano-based smart paper, can be expected to provide certain process and product revolutions. Many nanomaterials and nanotechnologies have been studied and used in various industrials and our daily lives. Therefore, we are obviously not starting from zero, and there are many existing theories and successful examples that can be used as references. The future research work on nanofillers for papermaking wet end applications will help papermakers to better understand and design the renewable composite material — “paper” at nano levels. Though there are undoubtedly many challenges and obstacles lying ahead, in the long run, the whole industry’s never-stopping efforts can surely provide certain fruitful results, including new insights, new possibilities, and new products.

Acknowledgements

The authors would like to acknowledge support from the Fundamental Research Funds (DL09BB07) for the Central Universities of China. The authors are also much grateful to the worldwide researchers in the research fields of fillers and nanotechnology for papermaking for their relevant publications in any form, and the presentation regarding the “Developments in Nanofillers for Papermaking Wet End Applications and Their Benefits” here was in large part based on the available publications, and yet most of the relevant references were not able to be included in the “References Cited” section of the editorial due to the length limit.

References Cited

- Deng, Y. (2005). “Potentials of nanotechnologies in forest and paper industry,” Retrieved Jan. 16, 2010. URL: <http://www.esf.edu/joachim/2005forum/YDeng.ppt>
- Ball, M. (2007). “Use of calcium carbonate particles in papermaking,” *U.S. Patent Application* 20070181275, Sept. 8.
- Goldhalm, G., and Drexler, G. (2008). “Method for application of nano-particles during a papermaking process,” *E.P. Patent* 1,921,207, May. 14.
- Koivunen, K., Niskanen, I., Peiponen, K. E., and Paulapuro, H. (2009). “Novel nanostructured PCC fillers,” *J. Mater. Sci.* 44, 477-482.
- Marthur, V. K. (2006). “GRI’s fibrous filler technology,” Retrieved Jan. 16, 2010. URL: <http://www1.eere.energy.gov/industry/forest/pdfs/mathur.pdf>
- Small, A. C., and Johnston, J. H. (2009). “Novel hybrid materials of magnetic nanoparticles and cellulose fibers,” *J. Colloid. Interf. Sci.* 331, 122-126.