USE OF MINERAL PIGMENTS IN FABRICATION OF SUPERHYDROPHOBICALLY ENGINEERED CELLULOSIC PAPER

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Superhydrophobic materials have a lot of interesting potential applications. The self-cleaning property is a unique feature. Rendering the water-loving cellulosic paper superhydrophobic can open the door for value-added applications. Superhydrophobic paper is a fairly new area, and only very limited scientific publications are available in the literature. Among these publications, the topics on the use of mineral pigments in fabrication of superhydrophobic structures account for a large proportion. During the fabrication process, mineral pigments, *e.g.*, silica, precipitated calcium carbonate, and clay, generally need to be hydrophobized, either directly or indirectly. Mineral pigments can be applied to cellulosic paper by surface treatment or wet-end filling, and good dispersabilities of these pigments are always highly demanded. A key mechanistic point is that by tunable particle packing or fabrication, mineral pigments may exhibit surface-roughening effects, which are critical for superhydrophobicity development. The roughening of a hydrophobic surface helps to enhance hydrophobicity. Possible concepts such as nano-structuring or controllable surface patterning of mineral pigments may help to improve superhydrophobicity. Environmental friendliness will also guide the scientific/technical development in this area.

Keywords: Mineral pigments; Superhydrophobic paper; Cellulosic paper; Surface roughening; Precipitated calcium carbonate; Silica; Clay; Fillers; Fabrication; Hydrophobic pigments

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Environment-friendly and Water-loving Natures of Cellulosic Paper

Cellulosic paper is mainly produced from water-dispersible and hydrogen-bondable pulp fibers via a filtration-driven sheet formation process. These fibers are essentially derived from chemical and/or mechanical defibration of regenerable lignocellulosic materials, including wood and non-wood plants. Due to the sustainability, renewability, and biodegradability of these natural plants, if scientifically practiced, the whole life cycle of cellulosic paper can be regarded as completely environmentally friendly, fitting well into the green/sustainable economy concept.

It is also well known that the hydrophilicity of the raw materials makes cellulosic paper inherently water-loving. The presence of hydrophilic groups, mainly hydroxyl, carboxyl, or sulfonic groups, in the paper matrixes, accounts for the water-loving nature of cellulosic paper, allowing for acceptable redispersability, redisintegrability, and recoverability/recyclability (*e.g.*, in a hydropulper) in an aqueous system. Thus, evidently this water-loving nature is of strategic significance in terms of environmental friendliness and sustainability of the papermaking industry.

Benefits and Potential Value-added Applications of Superhydrophobically Engineered Cellulosic Paper

Despite the above-mentioned benefits associated with the water-loving nature of cellulosic paper, this inherent characteristic poses obvious limitations in those practical applications where hydrophobicity is highly demanded. For example, acceptable water/moisture-resistant property of cellulosic paper is a must for packaging container applications. Although the hydrophobicity of cellulosic paper can be significantly improved by internal sizing and surface sizing, it might not be high enough to meet the requirements for such uses as food and drink packages; on the other hand, a conventional barrier coating can be an important option, but it still has possible bottlenecks, such as the need of thick coating layers (high cost), and/or poor recyclability. The fabrication of a superhydrophobic paper is a fairly new concept that has emerged only quite recently, and the resulting paper products can give much better hydrophobicity compared with the conventional ways of hydrophobilizing paper. On a flat surface, no chemical with hydrophobic property has a water contact angle of >125^o, however, a superhydrophobic surface can have a water contact angle of >150^o by combining micro and/or nano scale surface roughness with surface hydrophobicity. Due to this unique feature, superhydrophobically engineered cellulosic paper would have numerous potential value-added applications, such as liquid/food packages, cups, food plates, self-cleaning clothes, and paper boxes.

Use of Mineral Pigments in Fabrication of Cellulosic Paper's Superhydrophobic Surface

In the papermaking industry, mineral pigments are used in wet-end filling, surface filling, and surface coating applications. Significant benefits can be achieved through the pigmenting processes. These include cost and energy savings, and improved brightness/opacity/printability of the paper. Interestingly, some studies on the use of mineral pigments in fabrication of cellulosic paper's superhydrophobic surface have been reported recently.

- As reported by researchers at Georgia Institute of Technology (USA), superhydrophobic paper can be prepared by multi-layer self-assembly and sequential deposition of a cationic polymer (poly (diallyldimethylammonium chloride) and anionic silica nanoparticles onto the cellulosic paper surface, followed by subsequent surface treatment with a hydrophobic material, *i.e.*, 1H,1H,2H,2H-perfluorooctyltriethoxysilane. Also, the preparation of superhydrophobic paper using a simple procedure of spray-deposition of hydrophobic silica nanoparticles onto the paper substrate has been demonstrated by the researchers at Tokyo Institute of Technology (Japan).
- The researchers in New Zealand (Scion Research) and Sweden (SCA R&D Center; Karlstad University) have co-demonstrated that hydrophobic clay used in the plastics industry can be used as a pigment in water-based dispersion coatings for linerboard, where the pigment can exhibit acceptable dispersibility under controlled conditions, and combining the hydrophobic

pigment with a low dose of wax can result in the fabrication of superhydrophobic coating structures on the cellulosic substrate.

- According to findings of the researchers at Georgia Institute of Technology (USA), micro-sized precipitated calcium carbonate (PCC) particles can be hydrophobically modified with a fatty acid (stearic acid), the hydrophobic pigment can be used for coating of cellulosic paper with the aid of a polymer binder (styrene-acrylate copolymer latex), and superhydrophobic paper can be prepared by immersing the surface coated paper in a potassium stearate solution for hydrophobicity improvement.
- The preparation of superhydrophobic paper by using hydrophobically modified pigment as a wet-end filler has been reported. The researchers at South China University of Technology (China) and Georgia Institute of Technology (USA) have found that hydrophobic modification of titanium dioxide with a coupling agent (3-(trimethoxysilyl) propyl methacrylate) followed by its addition to the pulp slurry for sheet formation can render cellulosic paper superhydrophobic.

It should be noted that as superhydrophobic paper is a fairly new area, and up to now there have been very limited scientific publications. Among these publications, the topics concerning the use of mineral pigments in fabrication of superhydrophobic structures account for a large proportion. Other publications include for example simultaneous surface roughening and hydrophobication of cellulosic paper with alkyl ketene dimer (AKD), a widely used sizing agent in papermaking; in this sense, it may be valid and interesting to think that for the traditional use of sizing agents, the sizing efficiency is dependent upon micro/nano-scale surface roughness of the sized paper.

The use of mineral pigments in fabrication of superhydrophobic paper has some unique advantages, for example:

- Due to the fact that mineral pigments are usually cheaper than organic hydrophobic materials used for surface hydrophobication of cellulosic paper, by depositing the costly organic materials onto the surface of mineral pigment, the efficiency of these materials can be enhanced, thus lowering the cost associated of the paper product.
- As inspired by the well-known "lotus effect", roughening of hydrophobic surface is of critical significance in superhydrophobicity development. Mineral pigments tend to work well in this regard, as their tunable packing structures are expected to provide controlled roughening effects.

As the hydrophobicities of the commonly used mineral pigments in the papermaking industry are generally poor, direct or indirect hydrophobication of these pigments is essential for the preparation of superhydrophobic paper. However, the use of hydrophobically modified pigments as wet-end filler materials is challenging, as their dispersabilities are rather poor in an aqueous system. Although strong shear can be applied to homogenize the aqueous filler/fiber mixture, significant loss in fiber strength would discourage practical applications. Fortunately, the use of hydrophobically modified pigments for the formulation of a water-based coating color has been increasingly possible, as new binder systems would help to improve the dispersibility of these pigments. In general, rendering cellulosic paper superhydrophobic by surface treatment (*e.g.*, pigment coating) with mineral pigments and other additives can be expected to be a preferred process concept.

Possibilities

For the fabrication of superhydrophobic cellulosic paper using mineral pigments and other additives, some possibilities might be anticipated. The nano-structuring of micro-sized mineral pigments can be integrated with the hydrophobication process, providing possibilities of effective roughening of hydrophobic surface for superhydrophobicity development. The hydrophobication agents and coating binders can be increasingly environment-friendly and biodegradable. In particular, natural or semi-natural resources will eventually play a key role. In this case, starch, fatty acid, and other natural resources have great potential for practical applications. However, it is also possible that mineral pigments use in the superhydrophobication process will be partially replaced by pigments derived from natural resources, such as hydrophobic starch and hydrophobic cellulose nano-crystals. Nevertheless, future R&D works on both mechanistic and practical aspects of superhydrophobic paper in terms of fabrication and recycling for example, will sooner or later lead to new possibilities, new developments, and successful commercial applications.

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