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The influence of TiO_2/CC core/shell pigments on the properties of paper sheets

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ABSTRACT

In this work, new core-shell pigment based on precipitating a small amount of titanium dioxide on precipitated calcium carbonate (CC) were applied once as filler in paper sheet making and another time was mixed with chitosan as a coat on the papers. The prepared pigments were characterized to confirm their preparation. The mechanical and optical properties of both filled and coated paper sheets and their individual components (TiO_2 and CC) were performed to compare their effect on the paper sheets using SEM, TGA and UV aging.

1. Introduction

The benefits of using mineral fillers in papermaking, particularly for the production of fine printing and writing papers, are widely recognized and thoroughly described in the literature by partial replacement of fibers with cheaper material and improvement of the paper optical properties, bulk and smoothness. For this reason, there is a general interest of the papermaking industry in increasing the filler content of paper, but for that it is also crucial to overcome the main drawbacks related to the presence of the mineral fillers, e.g. decrease in the fiber-to-fiber bonding and as a consequence, reduction of the paper strength properties as well as additional problems of retention, dusting and whitewaters recirculation [1,2].

Precipitated calcium carbonate is a bright white mineral added to paper pulp as filler in alkaline papers or applied as a coating pigment. Like clay and titanium dioxide, calcium carbonate is added to the papermaking furnish to increase brightness and opacity. It is not as good as titanium dioxide and at the same time it is cheap as clay but with higher optical brightness. Precipitated calcium carbonate cannot be used in the manufacture of acid paper, as it is an alkaline material which reacts strongly with acidic papermaking conditions. It is used in alkaline papermaking, which is receiving increased interest due to the longer longevity of alkaline papers. Calcium carbonate is the most abundant mineral on earth that is not silicon-based; it is cheap and is commonly used as an extender in place of the more expensive titanium dioxide.

Several works have been developed on the modification of precipitated calcium carbonate (CC) by inorganic compounds (e.g. calcium-chelating agents, weak acids, aluminum salts, zinc chloride, and sodium silicate) [1–4].

Nonetheless, most of the reported modifications of PCC regarding the improvement of its performance are those related to the modification of its surface using organic compounds. Precipitated calcium carbonate has been treated/modified by organic compounds such as starch, starch derivatives, cellulose, carboxymethylcellulose, xanthan gum, water-soluble synthetic polymers, and polymer latexes [5–7].

Due to the organic, fibrous, hydrophilic and highly porous nature, paper is easily subjected to microbial attack, ultraviolet degradation and higher water vapor transmission rate. To overcome these problems, new mineral fillers are subjected to work as paper coating to meet the improved quality standards of high grade papers. Use of pigments with an appropriate binder in the coating formulation can help in filling the microvoids and offer better barrier properties [8,9].

TiO_2 is used in paper products usually to improve opacity and brightness. However, its high cost compared to clay and calcium carbonate limits its conventional usage to high value-added printing papers. Also, its low activity which leads to accelerated degradation of the matrix is an essential drawback. Hydroxyl radicals produced on hydrated TiO_2 surfaces can oxidatively convert various organic compounds in contact with TiO_2 to CO_2 and H_2O, and thus many studies on TiO_2

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Table 1
XRF analysis data for core-shell pigments.

Concentration wt.%	CT1	CT2
SiO_2	0.13	0.11
TiO_2	7.12	9.91
Al_2O_3	0.05	0.04
MgO	0.08	–
Fe_2O_3	–	0.02
CaO	50.18	46.49
SrO	0.01	0.01
Na_2O	–	0.01
K_2O	0.02	–
ZrO_2	0.002	–
P_2O_5	0.03	0.02
SO_3	0.16	0.16
Cl	0.64	3.49
L.O.I.	41.59	40.69

photo-oxidation have been carried out [10] and other volatile organic compounds (VOCs) [11,12]. Paper-based materials in particular are widely used in rooms as, e.g. wallpaper, calendars, writing papers and magazines. Many paper products containing TiO_2 photocatalyst are being marketed. However, all such products have great disadvantage that paper materials consisting of organic pulp fibers are easily damaged by TiO_2 photocatalysis, so that their physical quality deteriorates during service [13]. Thus, there is a need for commercial TiO_2-papers manufactured with an emphasis on preventing material photo-degradation. The contact area of TiO_2 with pulp is limited and the pulp degradation should be inhibited to some extent; however, the efficiency for VOC decomposition would decrease with increasing amounts of inactive TiO_2 inside the aggregates [9].

Chitosan is known to be nontoxic, biodegradable, antibacterial, and odorless renewable bioresource. It is a derivative of N-deacetylation of chitin which is the second most naturally abundant biopolymer next to cellulose and is readily available from seafood wastes.

The chemical formula of chitosan is 2-amino-2-deoxy-(1–4)-β-D-glucopyranose, much attention has been paid to the industrial applications of chitosan in the past decade, and it has been identified as the potential dry and wet strengthen additive for paper making. Chitosan and its derivatives (carboxymethyl chitosan and chitosan acetate) are used as reinforcement agents for both recent paper and weak historic documents [14–16].

Gradual changes in the light absorbing ability of paper can occur during its storage, even under relatively ideal conditions. Paper lose its brightness when exposed to light, considering that brightness stability is an important optical property for paper manufacturers and accurate test methods are needed to predict this characteristic of papers. For many years, it has been known that exposure of paper to very short-wavelength ultraviolet, such as 254 nm radiation induces post-irradiation effects, their specific results are influenced by both internal and external factors. Nevertheless, the fact remains that few studies have been carried out specifically to elucidate the behavior of papers subsequent to exposure to the wavelengths of visible and

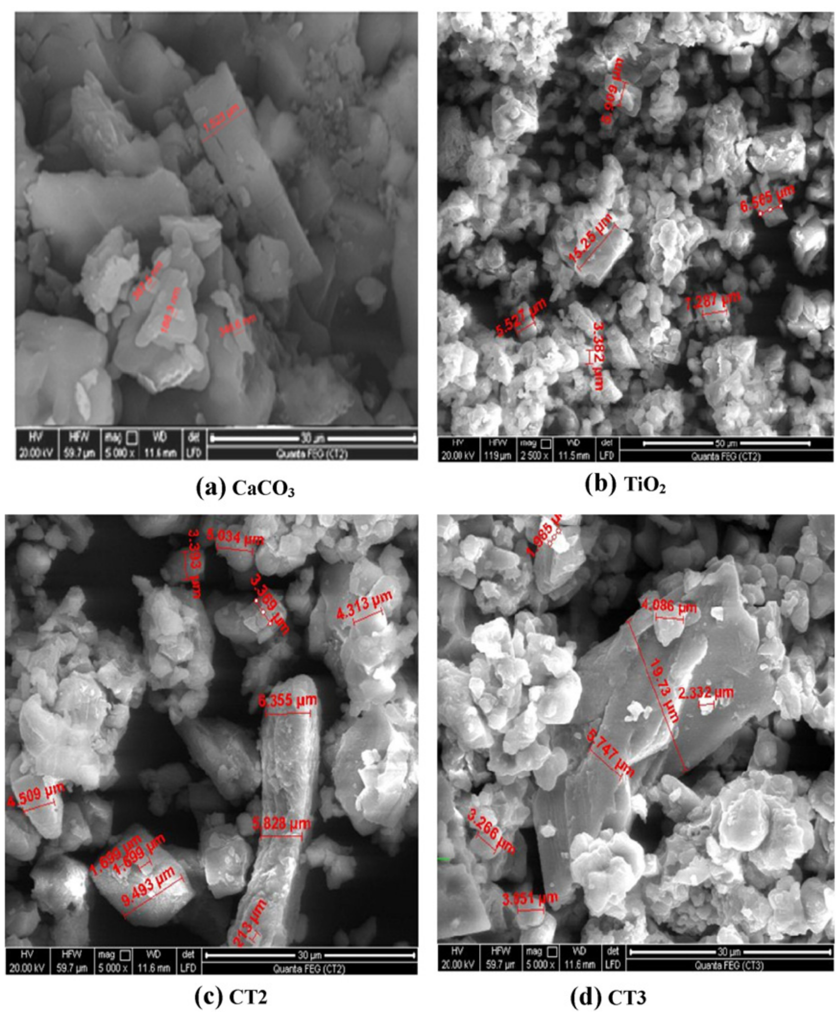

Fig. 1. SEM micrographs of (a) calcium carbonate; (b) titanium dioxide; (c) CT1; (d) CT2 pigments at magnificationn10^3X.