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Determination of calcium carbonate and styrene-butadiene latex content in the coating layer of coated paper

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ABSTRACT

The surface infrared spectra of coated paper with different levels of calcium carbonate and SB-latex in the coating layer were measured using ATR-FTIR. The relations between different levels of $CaCO_3$ and SB-latex and their respective characteristic peak areas were then established. The results show that the general regression neural network (GRNN) model can be used to estimate the $CaCO_3$ and SB-latex contents in coatings of coated papers. The maximum errors for calcium carbonate and SB-latex were only 3.32% and 3.39%, respectively, and occurred under conditions that are at the extreme of what might be encountered in an actual production facility.

1. Introduction

With the development of the paper industry, more attention has been paid to producing high-quality paper in a cost-effective manner. Coated paper is a kind of paper consisting of a base paper and a coating layer, to improve certain qualities to the paper, including weight, surface gloss, smoothness or reduced ink absorbency. For example, lightweight coated paper (LWC), one type of high-grade printing paper product, is a low-basis-weight and layered composite with basis weight of 51–70 g/m^2 [1–3]. The incorporation of low levels of organic latex copolymer in the coating ensures proper cohesion (binding) [2]. The pigments and binder are important components of the coating. The pigments in common use for coated paper are kaolinite, calcium carbonate, bentonite, talc, and the most widely used organic binder is styrene-butadiene latex (SB-latex).

Normally, when the formulations of the coating applied on paper are unknown, the contents of the pigment and binder in the coating layer are difficult to determine. Traditionally, the ash method [4] has been used for measuring inorganic pigments, but it is impossible to use this method to measure organic components because their low carbonation temperature overlaps that of the base paper in many cases.

Some studies have sought to develop alternative methods for determining both inorganic pigments and organic components in the coating layer. The development of surface analytical techniques [5,6] provides a means for detecting the presence and distribution of these pigments and binders on the paper surfaces [7]. The secondary ion mass spectroscopy (SIMS), X-ray methods [8–11] and Fourier transform infrared spectroscopy (FTIR) including the photoacoustic Fourier transform infrared spectroscopy (PA-FTIR) [12] and attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) [13] have generally been used to characterize compounds in the mineral charge [2]. These methods have certain limitations that could be reduced through the use of a mathematical model that could quantitatively describe the process. To date, the search for relevant models has used a variety of approaches, including the partial least squares (PLS) regression, principal component regression (PCR), multilinear regression (MLR), multiplicative scatter correction (MSC) and artificial neural network (ANN) [2,14].

Traditionally infrared (IR) spectrometers have been used to analyze solids, liquids and gases by transmitting the infrared radiation through the sample and detecting changes in the spectrum resulting from interaction with the sample. The FTIR technique can simultaneously collect spectroscopic data over a wide spectral range, which is a significant advantage over a dispersive spectrometer that measures intensively only over a narrow range of wavelength at a time. Since the IR beam information reflected from a surface of a solid sample can be collected, FTIR reflection techniques are commonly applied to ATR (i.e., internal reflection spectroscopy), specular reflection

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(i.e., external reflection spectroscopy for smooth surfaces) and diffuse reflection (i.e., combination of the internal and external reflections). Diffuse reflection relies upon the focused projection of the spectrometer beam into the sample where it is reflected, scattered and transmitted through the sample material.

In recent years the ATR technique has revolutionized solid and liquid sample analyses because it addresses some of the most challenging aspects of more traditional infrared analyses, namely, sample preparation and spectral reproducibility. Because ATR can obtain information about coated paper surface composition through radiation reflected by the surface coating rather than the whole paper, thus the paper sample does not need a separation procedure or pretreatment step [15]. In other words, the ATR technique is a nondestructive testing method that deals directly with the original sample, and has been widely used in FTIR analysis [16–18]. With the advantages of multiplexing, better signal to noise ratio and speedier measurement, ATR-FTIR can be easily used to analyze the surface composition of the coating layer for coated paper. For coatings on paper web, the ATR technique is preferred because the penetration depth in ATR mode is shallower than diffuse reflection mode [19], when the analysis focuses on the coating layer without influences of fiber and fillers.

ANN is a new information processing system for simulating the frame, character and cognitive ability of a nerve element in the cerebrum. Inspired by biological neural networks, a neural network consists of an interconnected group of artificial neurons. It is an adaptive system changing its structure and internal relations between neurons during a learning phase. Thus the neural network should be learned or trained by a set of data first, to "learn" the ability of solving certain problems. Approaches to this method include back propagation (BP), Elman network, general regression neural network (GRNN), and feed forward neural networks (FFNN) [20,21]. GRNN was firstly proposed by Specht in 1991 [22] and is a feed forward network based on non-linear regression theory and a kind of normalized radial basis function network [23]. To put it simply, GRNN is a kind of artificial neural network and used for modeling complex relationships between inputs and outputs or to find patterns in data. GRNN has been widely used in the fields of pattern recognition and forecasting because of its numerous advantages, including its strength in fitting non-linear data using a simple network structure [24,25]. In addition, GRNN is different from the traditional neural network, since it only needs to adjust a simple smoothing parameter. At the same time, the GRNN network is robust, and its computing speed is fast [26].

The objective of the current study is to develop a method for determining the pigment (calcium carbonate) and binder (SB-latex) content in the coating layer of coated paper for analytical and testing institutions. ATR-FTIR and GRNN were together chosen as the method to analyze the concentrations of calcium carbonate and SB-latex in the coating layer. Each area under of the characteristic absorption peak of calcium carbonate and SB-latex in the ATR-FTIR spectra was obtained by using the OMNIC software.

2. Materials and methods

2.1. Materials

A commercial bleached softwood kraft pulp (BSKP) (ISO brightness of 88% and Canadian standard freeness of 700 mL) and preconditioning followed by refining chemical treatment, alkaline peroxide mechanical pulp (P-RC APMP) (ISO brightness of 70% and Canadian standard freeness of 675 mL) were collected from a high-yield pulp mill. A Level 95 ground calcium carbonate (GCC, pigment dispersion), i.e., more than 95% by weight of the GCC particles are less than 2 μm in diameter, was given by Fine Chemical Industry Co. Ltd. The carboxyl styrene-butadiene (Styronal® 302G), with an average particle size of 0.15 μm and a glass transition temperature of 10 °C, was provided by BASF Shanghai Co., China. The coating paper grade carboxyl methyl cellulose (CMC, NX-800) selected as the rheology modifier has a substitution degree of over 0.70 and a viscosity of 792 Pa s (2% solids, 25 °C), was supplied by Hengda Chemicals in Jiangsu province, China. Alkyl ketene dimer (AKD) with a solid content of 24% came from Tianjin Haoyu Agent Co.

2.2. Instruments

The standard disintegrator (Model no. 1107) was purchased from Lorentzen & Wettre Co. Ltd., Sweden. The standard sheet former (Model no. 7407) and the wire-wound rod coater (a diameter of 9 mm and width of 350 mm) were from Mavis Engineering Co. Ltd. and PK Print Coat Instruments Co. Ltd., respectively, in England. A soft calendar (NEG300) was purchased from Nanjing LIRI Technologies Co. Ltd., China. The electric hot-air heating oven (Model no. DHG-9053A) was from Shanghai Yiheng Scientific Instrument Co. Ltd. The software packages – OMNIC 8.2 and Matlab 7.11.0 – were obtained from Thermo Fisher Scientific and Mathworks, respectively.

An ATR-FTIR (Model FTIR 670), with a measurement range from 4000 to 400 cm^{-1}, was manufactured by Nicolet Instrument Co., USA. ATR-FTIR is a common FTIR spectrometer in which an ATR accessory module has been installed. In ATR, the IR beam is directed into a crystal and the test sample is placed on the outer surface of the ATR crystal. The total internal reflection occurs unless the sample has an absorption band at a particular frequency. Zinc selenide, germanium, and diamond are common ATR crystal materials. The penetration depth depends on the ATR crystal material used. The formula below presents the penetration depth [14,27,28],

$$\text{depth} = \frac{\lambda}{2\pi n_1 \sqrt{\sin^2\theta - (n_2/n_1)^2}} \quad (1)$$

where θ is the incident angle of the crystal (45° for diamond in this study), λ is the wavelength, n_1 is the refractive index of the crystal (2.4 for diamond in this study), and n_2 is the refractive index of the sample (1.0 for the coating layer with about 30% air in this study) [14,27,28]. According to these data, the calculated maximum penetration depth (at λ = 400 cm^{-1} and refractive index of n_2 = 1.0) is about 3.0 μm [14]. Typically the coating thickness of LWC is around 6 ± 2 μm equivalent to about 10 g/m^2. When measuring solids using ATR-FTIR, it is essential to ensure a good optical contact between the test sample and the crystal. In this study, the clamping force applied by the specific clamping device installed on the ATR-FTIR was adjusted to 178 N.

2.3. Disintegration

A 30.0 ± 0.5 g sample of pulp (oven-dry weight), consisting of 60% P-RC APMP and 40% BSKP, was added to 2000 mL deionized water and disintegrated in a standard disintegrator for 30,000 revolutions at room temperature.

2.4. Handsheet making

Handsheets with the basis weight of about 41 g/m^2 (oven-dry) were prepared according to the TAPPI T205 sp-02 [29]. The handsheets were filled with calcium carbonate and sized with AKD in the pulp furnish so that the calcium carbonate kept in the prepared handsheets was 4% and water absorption of the handsheets was about 20.0 ± 5.0 g/m^2. Before coating and weighing, the handsheets were air-conditioned at 23 ± 1 °C and 50 ± 2%