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Effective refractive index of calcium carbonate pigment slurries by a surface-plasmon-resonance sensor

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Abstract

A surface-plasmon-resonance sensor was applied in the measurement of the effective refractive index of highly turbid calcium carbonate pigment slurries. Information on the absorption of the pigment slurries as a function of the concentration was obtained by the sensor. It is suggested that the sensor can be used for monitoring the optical properties of slurries. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Various pigment slurries are widely used in industry, especially in the paper industry which consumes a significant amount of pigments. Pigments are used either as fillers or as a coating layer on body stock (non-coated paper). When used as a coating layer, the thickness of the layer is typically about 10 μm. Pigments give the paper its white colour due to their optical properties such as refractive index, extinction coefficient and light scattering. Other properties provided by pigments are opacity and gloss. These properties are closely connected to the refractive index of the pigment. Pigments are applied also in paints to give the appropriate colour. Generally, pigments increase light scattering from the surface of the material.

If the size of pigment particles is comparable to the wavelength of the light, scattering is the dominant effect when light and particles interact. Thus, pigment slurries, having pigment particles whose size centres around 1 μm, are optically opaque and turbid. In such cases, transmission of light is weak and an optical measurement method based on light transmission is not practical, whereas reflection spectroscopy is more effective because there is no need to dilute the slurry. Calcium carbonate pigments, for example, scatter most of the incoming light and, thus, their colour appears to be white. When looking for the optimal light scattering conditions: particle size, shape, refractive index, absorption coefficient, particle orientation and packing of the pigments have to be optimized if excellent opacity is to be a feature of paper products.

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In this study we investigated irregular cylinder shaped, birefringent calcium carbonate pigments in a water matrix. We prepared different loadings of slurries by weighing solid particles and mixing them in water. The object of the study was to find out a means of detecting the pigment loading, to determine the effective refractive index of the slurries and to observe the absorption as a function of calcium carbonate loading. In the pigment industry there is a desire to measure the quality of calcium carbonate slurries. Therefore, a simple on-line detection system would have significance for such an industry. Because of the high calcium carbonate loading of the slurry the optical measurement of the quality has been rather problematic, so far, due to the strong turbidity of the slurry. Therefore, the applicability of a surface-plasmon-resonance sensor (SPRS) for the detection of optical properties of high calcium carbonate loading slurries was investigated. The idea of sensing, which is based on the use of light-induced, surface-plasma wave oscillations, was introduced by Kretschmann [1] and further developed by others [2,3]. Lately, SPRS has found various applications in detection of chemical changes and physical changes [4] and also biological [5] changes of liquids and other phases. Recently, experiments have been applied to the detection of the effective refractive index of commercial calcium carbonate slurries using an ATR-reflectometer and SPRS [6]. Here the number of different calcium carbonate slurries was larger than quoted in Ref. [6]. In addition, the connection between the reflectance signal and the effective absorption of the slurries using the SPRS was investigated.

2. Theory

In the case of SPRS (see Fig. 1), the reflectance is determined in the ATR-mode, i.e. the angle of incidence exceeds the critical angle of reflection. Thus, only the evanescent component of incoming p-polarized light wave penetrates into the rarer medium, decaying exponentially along the normal of the metal film-slurry interface of the prism. The intensity reflectance can be expressed as follows [2,3]:

$$R(\theta) = \left| \frac{r_{01}(\theta) + r_{12}(\theta)\exp(2ik_z(\theta))}{1 + r_{01}(\theta)r_{12}(\theta)\exp(2ik_z(\theta))} \right|^2. \quad (1)$$

Here, θ is the angle of incidence at the interface between prism and metal, r_{01} is the electric field reflectance at the prism–metal interface, r_{12} denotes the corresponding electric field reflectance at the metal film-sample interface and k_z is the scalar wave vector component normal to the surface of the metal. The wave vector k_z is defined as

$$k_z = \left(\frac{2\pi}{\lambda}\right) n_1 d \sqrt{\left(1 - \left(\frac{n_{\text{prism}} \sin\theta}{n_1}\right)^2\right)}. \quad (2)$$

Here, n_1 and d are the refractive index and the thickness of the metal film, respectively, n_{prism} is the refractive index of the prism and λ is the wavelength of incoming light in vacuum. A minimum of reflectance appears at an angle θ_{SP}, due to the generation of the surface-plasmon-resonance. In the case of resonance, a surface plasmon, (a collective oscillation of a charge cloud along the metal film surface) is generated and energy from the incoming light beam is transferred to the generation of the plasma oscillation of the charges. As a result, the reflectance from the metal film–slurry interface strongly decreases at an angle of incidence that corresponds to the resonance condition. The effective refractive index of the slurry can be solved from the following resonance condition [2,3]

$$n_{\text{prism}} \sin\theta_{\text{SP}} = \sqrt{\frac{\varepsilon_1 n^2}{\varepsilon_1 + n^2}}. \quad (3)$$

Here, ε_1 is the real part of the permittivity of the metal and n is the effective refractive index of the slurry.

The reflectance (R) can be approximated as a Lorenz-curve in the vicinity of resonance angle. Now, the Lorentzian can be expressed in the following manner [3]

$$1 - R \cong \frac{4K_0''K_R''}{(k_x - K_0' - K_R')^2 + (K_0'' + K_R'')^2}. \quad (4)$$

Here, $k_x = (\omega/c)n_{\text{prism}} \sin\theta$, ω is the angular frequency and c is the velocity of light in vacuum.

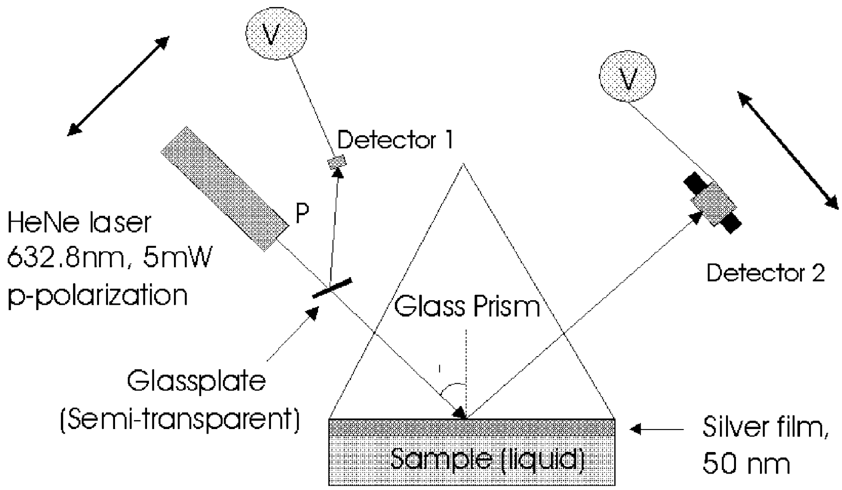

Fig. 1. A schematic diagram of the SPR-sensor.

Chen and Chen [3] obtained the following results with the aid of Eq. (4):

$$\theta_{SP} = \arcsin\left(\frac{\lambda(K_0' + K_R')}{2\pi n_{prism}}\right), \quad (5)$$

$$R_{min} = 1 - \frac{4\eta}{(1+\eta)^2}, \quad (6)$$

$$\theta_{1/2} = \frac{\lambda}{\pi n_{prism} \cos\theta_{SP}} \left|K_0'' + K_R''\right|. \quad (7)$$

Here, θ_{SP} is the surface plasmon resonance angle and R_{min} is the reflectance minimum corresponding to the SPR-angle. $K_0 = K_0' + iK_0''$ and $K_R = K_R' + iK_R''$ are complex wave numbers of the SPR-wave at the metal–sample interface that take into account the absorption of energy into the metal and medium (Joule loss) and energy leaking back into the prism. $\theta_{1/2}$ is the half-width of reflection curve. Finally, η is defined as the ratio $\eta = K_0''/K_R''$.

3. Materials

The investigated pigment was PCC (precipitated calcium carbonate). The PCC particles used in this study are optically anisotropic and their shape resembles a cylinder. Furthermore, calcium carbonate is a negatively birefringent material, transparent in the spectral range 0.2–2.0 μm. Therefore, its intrinsic absorption is low in the UV–VIS spectral range. The length of particles is around 1 μm and width around 0.4 μm. Thus, their dimensions indicate light scattering in UV–VIS range. The morphology of the PCC-pigment slurry was observed with a field emission (FE) transmission electron microscope (TEM) Philips CM-200 FEG, operated at 200 kV. The samples were prepared from a diluted sample slurry that were dispersed on holey carbon coated TEM grids. A TEM-micrograph of a typical single PCC particle is shown as Fig. 2.

4. Measurement method

A schematic diagram of the SPRS is shown in Fig. 1. A thin (50 nm) silver film was evaporated onto one face of a prism (Schott FK11 glass). Optical constants of silver and other metals, as a function of wavelength are available [7]. The light source was a helium neon laser (633 nm) that produces linearly polarized light. The stability of the laser was monitored using a beam splitter, to provide a reference signal. The intensity of the probe and reference signals were measured using commercial photo-detectors. The prism was attached in a goniometer. The accuracy of the angle reading of the goniometer was 0.3°.

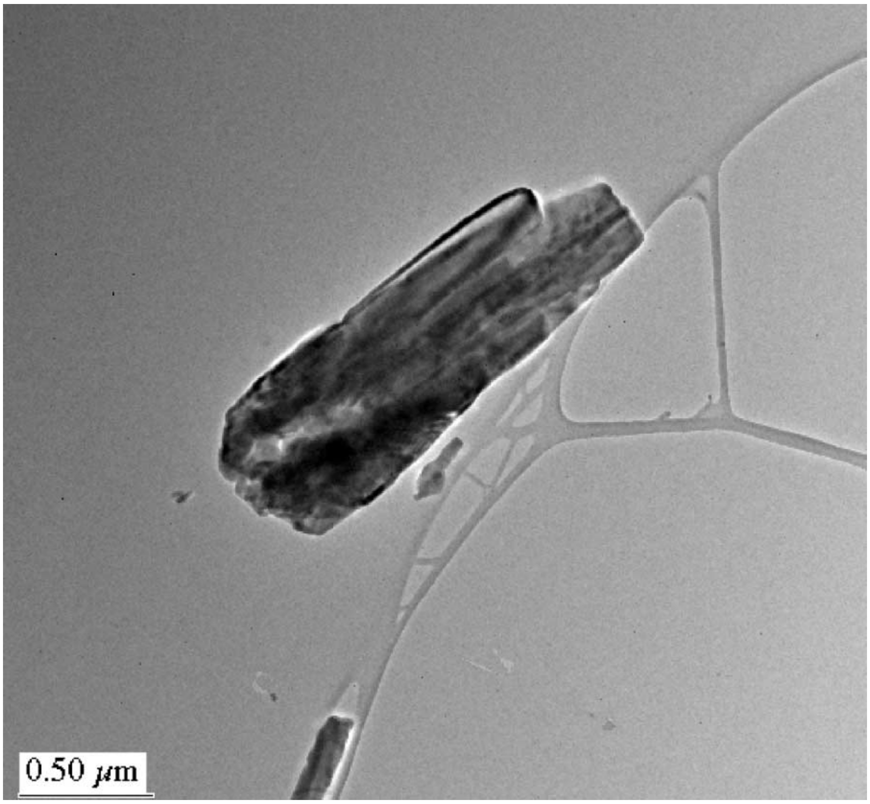

Fig. 2. A TEM micrograph of the PCC particle.

5. Experimental and discussion

The SPR-curves for six calcium carbonate loadings ranging from 0 to 50 g, mixed in 100 cm^3 of water were measured. The reflectance curves obtained from such slurries are shown in Fig. 3. Fig. 3 shows the minimum position of the reflectance curve, which gives the angle of surface-plasmon-resonance. Fig. 3 also shows that the SPR-angle shifts towards a higher angle of incidence while the loading of the pigment into the slurry increases. The reflectance minimum (R_{min}) depends also on the loading of pigment in the slurry. Measured data of R_{min} and calculated effective refractive indices of the slurries [obtained from Eq. (3)] are presented in Table 1. The effective refractive index is a non-linear function of the loading, as can be observed from Fig. 4.

An interesting feature of Table 1 is the dependence of R_{min} as a function of the loading. Initially, R_{min} decreases and then increases when the loading of the pigment particles in water increases, but R_{min} is higher for water than for lower PCC-loadings. This phenomenon can be explained theoretically. The reflectance, R_{min} was calculated using Eq. (6). The result of the calculation is shown in Fig. 5 as a function of η that describes the ratio K_0''/K_R'' (i.e. energy absorbed by the metal and sample divided by energy leaking back to the prism). Fig. 5 shows that first the R_{min} decreases and reaches the zero at the point where η is unity. After this point, R_{min} begins to increase strongly until it saturates and R_{min} changes only slightly. Thus, for absorbing liquids, R_{min} increases strongly as a function of η ($\eta > 1$) and can be used to investigate the absorption properties of liquids. The R_{min} of water is higher

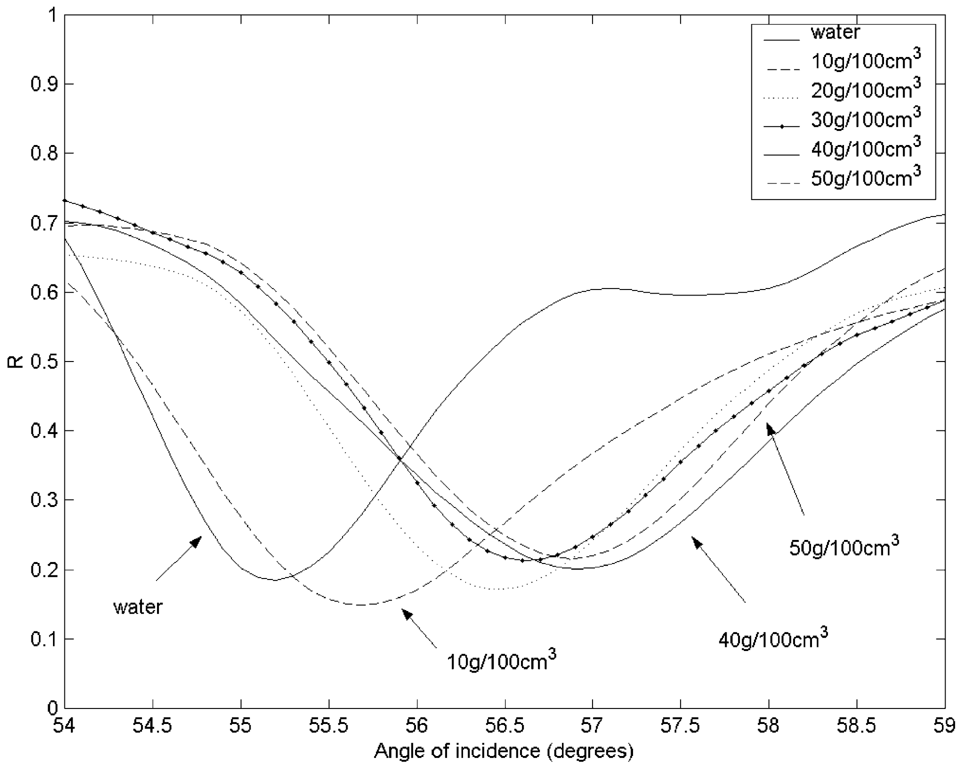

Fig. 3. Measured SPR-curves for PCC-slurry samples.

Table 1
Measured θ_{SP}, R_{min} and refractive index

Pigment loading (g/100 cm^3)	R_{min}	θ_{SP}	Half-width	Refractive index
0	0.19	55.2	2.06	1.334
10	0.15	55.7	3.00	1.341
20	0.17	56.5	2.43	1.352
30	0.21	56.6	2.73	1.354
40	0.20	56.9	3.09	1.358
50	0.21	56.9	2.58	1.358

than it is for the lower slurry loadings because η is at the left wing of the curve in Fig. 5. However, when the loading increases then R_{min} shifts through the minimum to the right wing of the curve in Fig. 5. The reason for the small increase in the speed of R_{min} is the weak absorption of light in the slurry. Simulations were made with the aid of the theory of surface-plasmon-generation [Eq. (1)] by applying different complex refractive indices of the slurry. It was observed that when the extinction coefficient increases, the level of R_{min} also increases. This confirms the experimental results of Table 1.

The half width, defined by Eqs. (5) and (7), of the curves shown in Fig. 3 was also investigated. A practical problem concerns the choice of the base line for the determination of $\theta_{\frac{1}{2}}$. Nevertheless, the variation in the magnitude of $\theta_{\frac{1}{2}}$ as a function of pigment loading, may not be a coincidence. The pigments carry an external electric charge, designed to improve the orientation of the pigments on the paper. It is believed that there appears some kind of self-organization of the pigments at the slurry–silver film interface. This, in turn, has an effect on the absorption cross section due to the net effect of the orientated dipoles. Harrick has clearly stated the possibility of such a phenomenon in the context

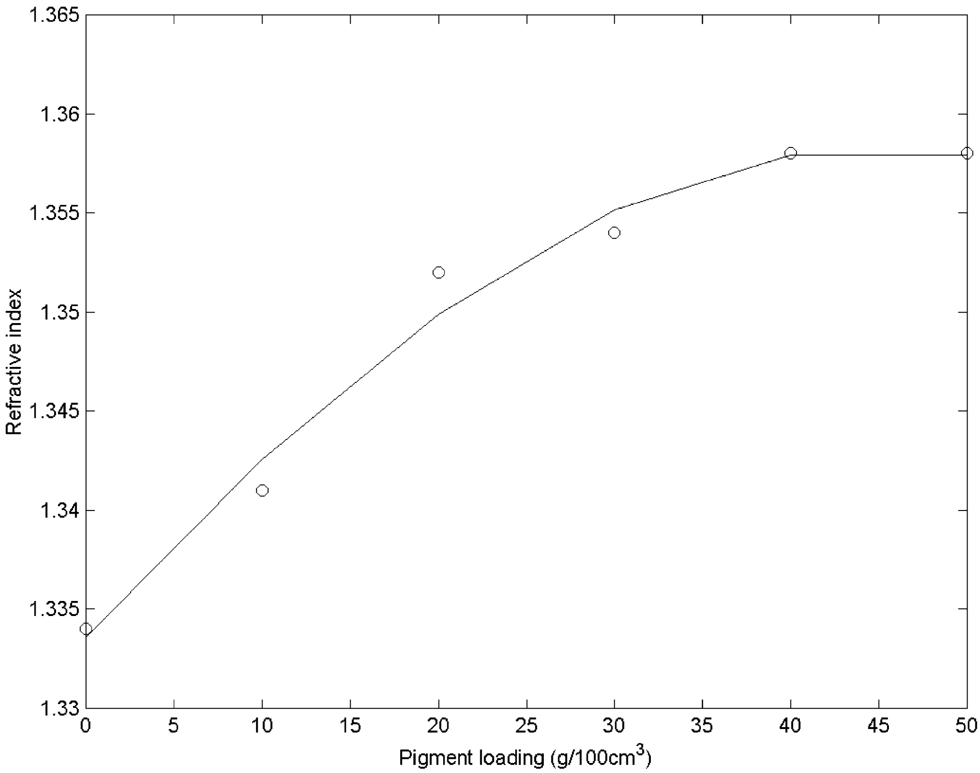

Fig. 4. The effective refractive index as a function of the pigment loading. The solid line is only a guideline for the eye.

of the ATR-spectroscopy [9]. Note that, in optical region, there is no light interaction with permanent dipoles. The sensitivity of the sensor with respect to the pigment orientation, via absorption, may be important also in the study of light scattering from a collection of partially organized pigments on the paper surface.

An observation was made to the effect that the silver film was degrading to some extent during the measurements. Therefore, the sensor was calibrated by measuring the reflectance from a reference liquid, water, before and after the measurement of a slurry. After that 50 g/100 cm^3 slurry was removed from the measurement compartment, which was first rinsed by water before measuring the reference, a small shift of about 0.3° of the resonance angle was observed. It has been shown that a fast measurement of the slurry is preferred when using the present sensor in order to maintain the thickness of the silver film. However, it should be noted that, for industrial, on-line measurement, the silver or generally speaking the metal film can be coated by a thin dielectric over layer in order to prolong the age of the probe. Another attractive prism set-up for absorption measurement is based on the waveguide sensor [8]. In principle, SPRS can provide a sensor that is to monitor the quality of a slurry either in the process line of pigment manufacturing or in the process slurry quality inspection in paper making. The advantages of the SPRS are, (1) relatively high loadings can be measured (beyond the concentration limit where normal ATR is no more reliable), (2) simultaneous information of the absorption and refractive index of the slurry is obtained, (3) the light beam can be focused on the metal film–slurry surface which simplifies the system (see e.g. www.bionsensor.com), (4) the sensor is simple, (5) the sensor is relatively cheap and (6) the sensor is easy to construct.

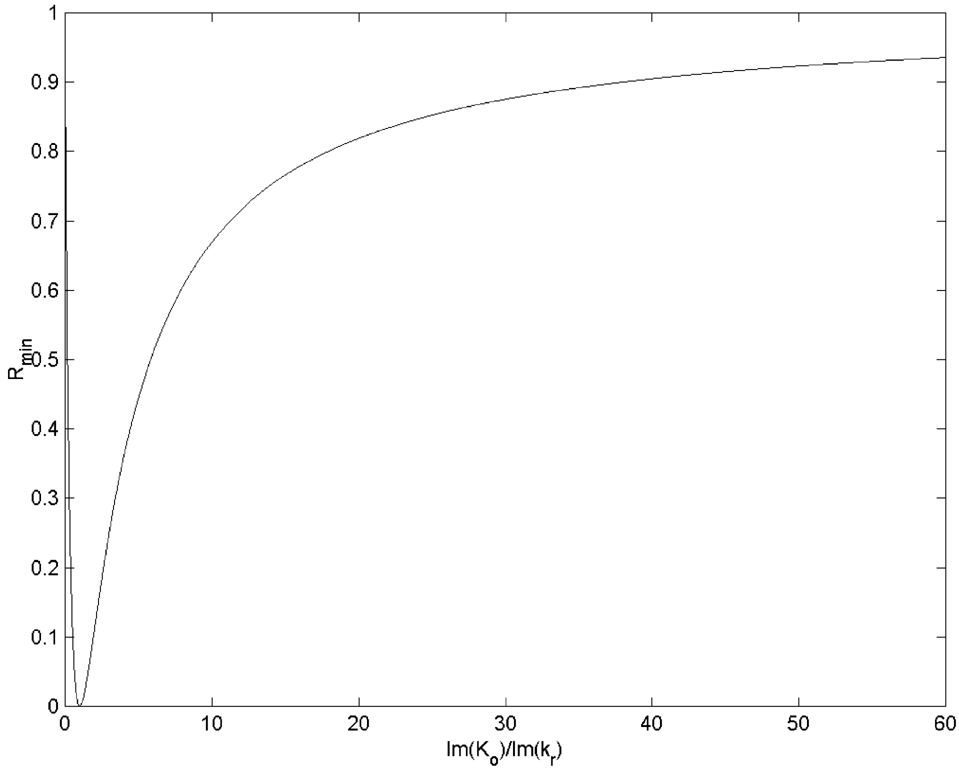

Fig. 5. Reflectance minimum R_{min} as a function of the parameter η.

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