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Determination of optical parameters of pulp suspensions by time-resolved detection of photoacoustic signals and total diffuse reflectance measurements

Research Article

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Abstract: Time-resolved photoacoustics were used to measure the optical parameters of pulp suspensions for the first time. Reconstructing stress distribution along the direction of the incident laser light allows the effective attenuation coefficient of these suspensions to be determined. Simultaneously, the total diffuse reflectance of the suspensions was measured by the same laser source. Based on the effective attenuation coefficient and total diffuse reflectance, the absorption and reduced scattering coefficients of pulp suspensions can be calculated. In this study, three kinds of pulp suspensions with different kappa number (2, 13, and 16), a measure of lignin content in pulp fibers, were diluted with water to make samples with a consistency range from 1% to 5%, and studied at 355 nm wavelength. The results showed that the optical coefficients were approximately proportional to pulp consistency; on the other hand, the absorption coefficient was linearly correlated with kappa number, but the reduced scattering coefficient was not. Therefore, by determining its optical parameters, it is possible to extract the consistency and kappa number of an unknown pulp suspension.

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Keywords: time-resolved photoacoustic • diffuse reflectance • optical parameters • pulp suspensions • kappa number • consistency

1. Introduction

Kappa number, a measure of lignin content in pulp fibers, is an important parameter during cooking and bleaching processes in the paper industry. Online measurements of kappa number are very useful in routine process control, because the number relates directly to production costs by enabling savings to be made in energy supplies and amount of chemical reagent. However, lignin contained in wood cellulose is insoluble at room temperature and atmospheric pressure. Moreover, wood cellulose probably forms flocks in a pulp suspension when the fiber consistency is higher than 1%; without careful operation, this will greatly decrease the homogeneity of suspension. In

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addition, fiber consistency has a strong effect on optical absorption and scattering in pulp suspension. All of these cause difficulty in determining the lignin content of a pulp suspension if its consistency is unknown.

In existing process measurement, the kappa number is obtained by measuring transmission light at various angles in ultraviolet wavelengths, normally at 280 nm, at which lignin has a strong absorption peak [1]. These signals are obtained at various distances from the source and at various angles relative to the optical axis, and every signal is affected by unknown amounts of scattering and absorption. During the measurement, pulp consistency is swept from a low level to a higher one. The optical signal is measured during this consistency sweep, and some of its consistency points are calibrated against laboratory data. However, this technique is incapable of separating optical absorption from scattering components and requires a consistent sweeping level and calibration of measurement points. Therefore, more convenient and effective methods need to be pursued. In this study, we applied a form of photoacoustic technique based on time-resolved stress detection. Used originally in biomedical optics to study tissues [2, 3], this technique can be used to deduce the effective attenuation coefficient of a pulp suspension. At the same time, by determining the total diffuse reflectance from a sample, we can obtain the ratio of its absorption and reduced scattering coefficients. Both measurements were carried out at the same wavelength, 355 nm, at which lignin exhibits definite optical absorption, whereas wood cellulose and aqueous matrixes do not. On the basis of these measurements, we can split out the reduced scattering coefficient and the absorption coefficient. Hence, it is possible to simultaneously determine both the fiber consistency and kappa number of a pulp suspension. Both measurements can be performed simultaneously online, simply by splitting the laser output into two beams and projecting these beams to different measurement locations.

2. Methodology

Theoretical aspects of the time-resolved photoacoustic technique have been described in detail in [4, 5]. If the turbid medium is homogeneous or at least macro-homogeneous, its effective attenuation coefficient μ_{eff} can be deduced by exponential fitting of the photoacoustic profile produced in the medium. On the other hand, in a layered medium, it is possible to deduce the distribution of the effective attenuation coefficient along the laser beam axis μ_{eff} (z).

To split out the absorption and reduced scattering coefficients from the effective attenuation coefficient, we can measure either the amplitude of photoacoustic generation in the medium [2] or the photon transport mean path [6]. However, the former method necessitates measuring several physical and system parameters (which are usually unknown), while the latter poses very high requirements for the transducer (ultra-wide bandwidth) and the detection channel (very fast sampling frequency). Consequently, the measurement is difficult to perform and incurs high costs. In this study, we used a simple, but effective way to measure the total diffuse reflectance R_t of a turbid medium and then deduced the ratio N' of the reduced scattering and absorption coefficients, as in bio-tissue studies [7]. However, due to the relatively high absorption of lignin at 355 nm, the ratio N' of pulp suspensions was small (usually < 3, as shown by Tab. 1 below). To improve accuracy, we applied the so-called exponential model [8]. The total diffuse reflection based on this model can be described as:

$$R_t = \frac{1}{1 + 13\frac{\mu_a}{\mu_s'}}, \tag{1}$$

where μ_a and μ_s' are the sample's absorption and reduced scattering coefficient, respectively.
It is known that

$$\mu_{eff} = \sqrt{3\mu_a\,(\mu_a + \mu_s')}. \tag{2}$$

Hence, μ_a and μ_s' can be determined on the basis of Eqs. (1) and (2), by experimentally measuring R_t and μ_{eff}.

3. Apparatus and materials

Fig. 1a illustrates the time-resolved photoacoustic setup, which employed a compact Q-switched pulse Nd:YAG laser (Brio, Quantel), operating at the third harmonic oscillation, as the excitation source. The laser's output wavelength was 355 nm, output energy per pulse was 20 mJ, and pulse duration and pulse repetition rate were 4 ns and 20 Hz, respectively. A filter (HR1064+532/45°) was used to further reflect surviving foundational and second harmonic output, and two lenses were applied as a telescope format to expand the laser beam to 12 mm in diameter, before incidence on a cuvette window. The cuvette had a height of 65 mm and a cross area of 25 mm × 25 mm. A commercial heavily damped transducer (Panametrics, V-103) was used to pick up photoacoustic signals produced by a sample placed in the cuvette. This transducer was located on the axis of the laser beam, where a drop of impedance matching gel provided an acoustic interface between the transducer and the back wall of the cuvette. Photoacoustic signals from the transducer

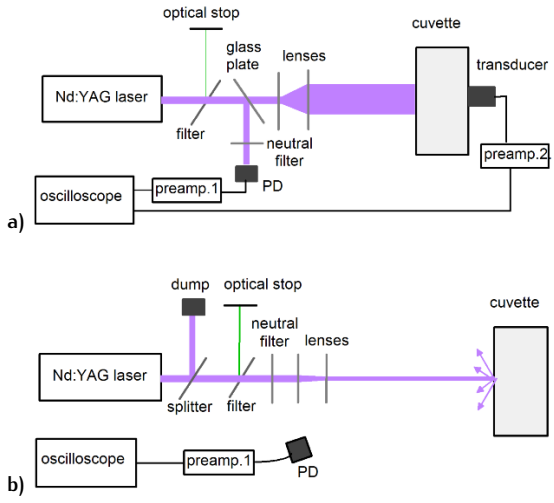

Figure 1. Experimental setup for time-resolved photoacoustics (a) and for measuring total diffuse reflectance (b).

were amplified by the pre-amplifier, and then were monitored and recorded in a digital oscilloscope (TDS794D, Tektronix), triggered by a photodiode. To avoid random noise, these recorded signals were averaged 128 times. Fig. 1b shows the experimental setup used to measure total diffuse reflectance based on the idea presented in Reference [9]. The light source system was similar to that of the photoacoustic setup shown in Fig. 1a, with the exception that pulse energy was limited to a maximum of 0.3 mJ by a beam splitter (95/5 ratio) and a neutral filter (NE05A, ThorLabs Inc.). Moreover, the laser beam's diameter was shrunk to 2 mm by an inverse telescope (consisting of two lenses) before incidence on the cuvette. A photodiode (UV-215BQ, EG&G) connected to a transimpedance preamplifier (AV-149-BW1) whose output was recorded by the digital oscilloscope, was located 60 cm away from the cuvette's incident window to pick up diffuse reflection light from a sample. The diffuse reflectance was calculated as the ratio of the signals produced by the sample and a 100%-diffuse reflection standard, where both the sample and the diffuse reflection standard were located at same place in succession.

Three kinds of pulp suspensions, provided by an industrial company, were used in this study. These pulps differed in kappa number (2, 13, and 16) and consistency (5.5 %, 5 % and 4.4 %, respectively). Before the experiment, some of the stock suspensions were diluted by distilled water to produce samples with a consistency range of 1% to 5%. Every diluted sample, stored in a plastic tube, had a volume of 40 ml. The consistencies of these diluted samples were not calibrated.

4. Experiments and results

4.1. Time-resolved photoacoustic measurement

The photoacoustic setup was preheated for ten minutes before the experiment. Diluted samples were first divided into three groups according to their kappa number and all measurements were conducted from the lowest kappa number group to the highest. Similarly, within each group, samples with the lowest consistency were measured first. Every sample, loaded in a plastic tube, was gently shaken up and down and then allowed to settle, to make them as homogeneous as possible, before they were loaded into the cuvette. All of the suspension in each plastic tube was poured into the cuvette to avoid sample consistency errors. For samples with a consistency lower than 2%, every measurement was finished in a few seconds to minimize the apparent sedimentation of wood fibers, while samples with a higher consistency were gently stirred to reduce air bubbles within the flock network and to allow the samples to be as homogeneous as possible. During the measurements, the apparatus was unmoved; the samples were replaced using a small spool and a suction tube. For statistical analysis, every sample with a consistency higher than 1% was measured three times. The samples with 1 % consistency were relatively homogeneous and to be measured one time.

Fig. 2 shows the transient response of the transducer in time and its frequency spectrum (measured in K_2CrO_4 solution (concentration 13 mg/cm^3, and absorption coefficient $\sim$1000 cm^{-1} at 355 nm wavelength [2]), and incident laser energy was attenuated to 1 mJ). The received signals by the transducer, which are produced in three samples (3% consistency) with kappa numbers 2, 13, and 16, respectively, are shown in Fig. 3. The exponential fitting of the signal fronts in regions with good SNR and linearity are highlighted by bold green lines. The effective attenuation coefficients of the samples can be deduced if the acoustic velocity in the sample is known. We used the acoustic velocity in water as an approximation, based on the fact that the samples consisted of more than 95% of water. Fig. 4 displays the deduced effective attenuation coefficients with errors. It needs to be noted that within the group with kappa number 2, samples with a consistency lower than 3 % are incapable of producing a photoacoustic signal which can be detected by the transducer. This is because these samples have such a low optical absorption that the frequency spectra produced by photoacoustic generation are below the response of the transducer. From Fig. 4, it can be seen that μ_{eff} increased approximately linearly with fiber consistency in the range of the error

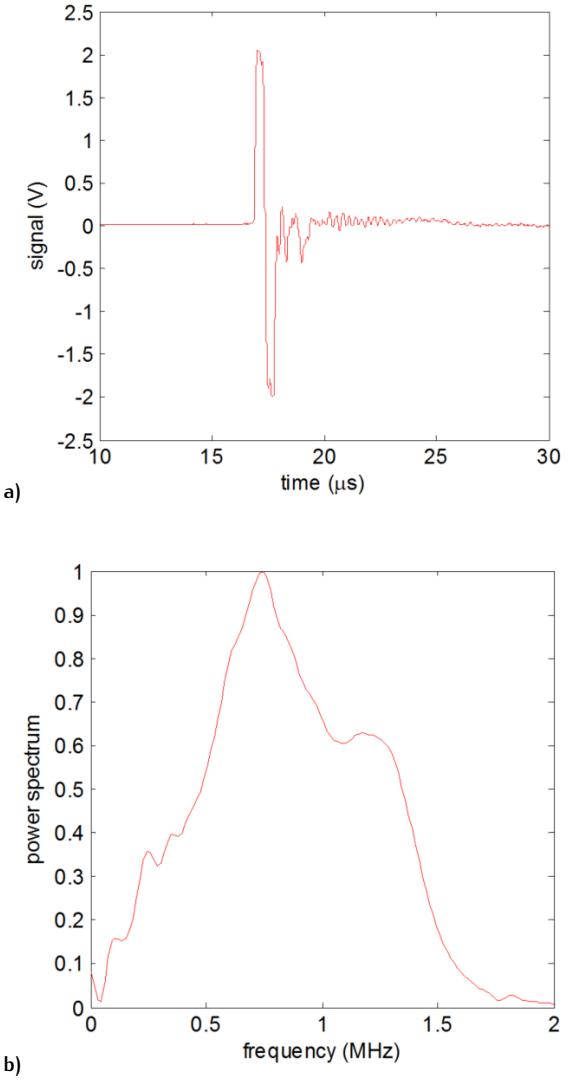

Figure 2. The transient response of the transducer in time (a) and its frequency spectrum (b).

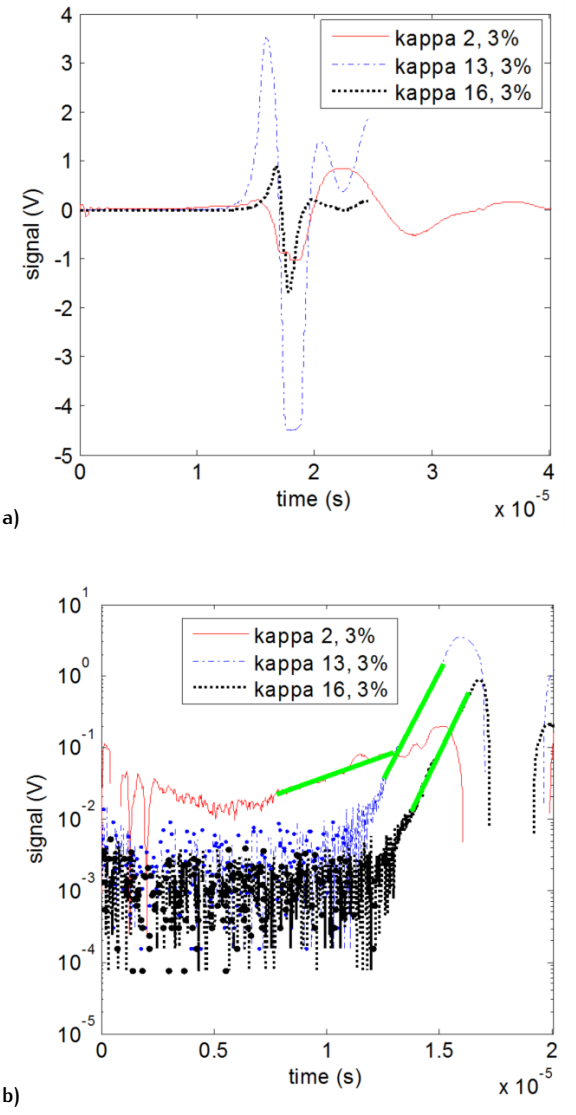

Figure 3. The signals received from three samples with 3% consistency, where the gain of the transducer's preamplifier is 53 dB for the samples with kappa numbers 2 and 12, and 40 dB for the sample with kappa number 16 in (a), and the y-axis in (a)is changed to the logarithmic scale in (b) (the bold green lines highlight the exponential fits of signal fronts).

bars.

4.2. Measuring total diffuse reflectance

In this part of the experiment, pulp samples were loaded into the cuvette to measure their total diffuse reflectance. The measurement order and sample replacement procedure were the same as in the photoacoustic experiment described above, but the cuvette was washed with distilled water between samples with a different kappa number. Stray light from the foundational and second harmonic wavelengths of the laser was absolutely isolated from the photodiode. Every sample was gently stirred and measured seven times. Fig. 5, presenting the experiment results, shows that, in the range of the error bars, R_t was almost identical for samples with a different fiber consistency but identical kappa number. This is probably due to the fact that both the absorption and reduced scattering coefficients increase together with sample consistency, while the ratio of the two coefficients remains unchanged. In accordance with Eq. (1), this results in identical R_t values. A similar phenomenon can be seen in the so-called fish-tank experiment [10].

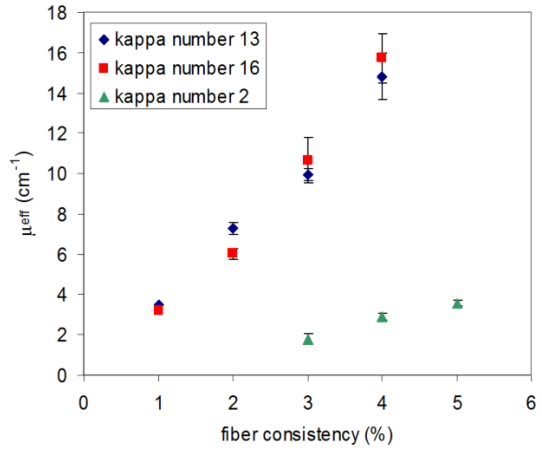

Figure 4. Deduced effective attenuation coefficients of samples with different fiber consistencies and kappa numbers.

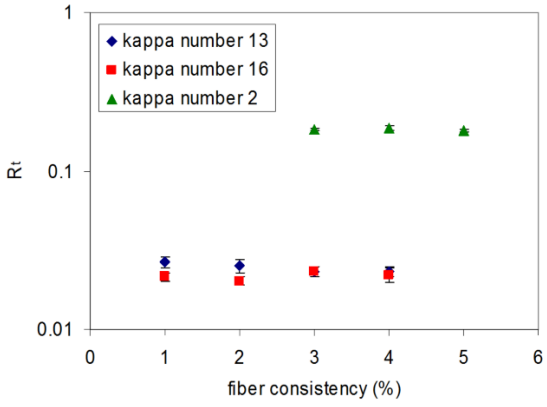

Figure 5. Results of total diffuse reflectance *vs.* fiber consistency measurements of pulp samples with different kappa numbers.

4.3. Deducing absorption and reduced scattering coefficients

When the μ_{eff} and R_t of the samples are measured as in the experiments described above, the samples' absorption and reduced scattering coefficients can be calculated on the basis of Eqs. (1) and (2). The results are listed in Tab. 1 and drawn in Fig. 6 and Fig. 7. Every parameter value was averaged three times, except those corresponding to the samples with 1% consistency.

Fig. 6 shows the relationship between optical parameters and consistency, while Fig. 7 reveals the intercorrelation between optical parameters and kappa number. In the range of the error bars, Fig. 6 indicates that both the optical absorption and the reduced scattering coefficient increase linearly with sample consistency, whereas Fig. 7 shows that the absorption coefficient increases linearly with the kappa number of the samples, but the reduced scattering coefficient is practically unaffected by kappa number.

Table 1. Average optical parameter values measured in pulp samples with different kappa numbers and fiber consistencies.

kappa number	fiber consistency (%)	μ_{eff} (cm^{-1})	R_t	N'	μ_a (cm^{-1})	μ_s' (cm^{-1})
2	3	1.88	0.182	2.92	0.54	1.57
	4	2.89	0.186	3.01	0.83	2.51
	5	3.58	0.179	2.84	1.05	3.00
13	1	3.50	0.026	0.33	1.76	0.57
	2	7.30	0.025	0.35	3.62	1.25
	3	10.00	0.023	0.31	5.02	1.56
	4	14.80	0.023	0.31	7.48	2.31
16	1	3.20	0.021	0.29	1.63	0.47
	2	6.00	0.020	0.28	3.07	0.87
	3	10.60	0.023	0.31	5.38	1.65
	4	15.70	0.022	0.28	8.04	2.23

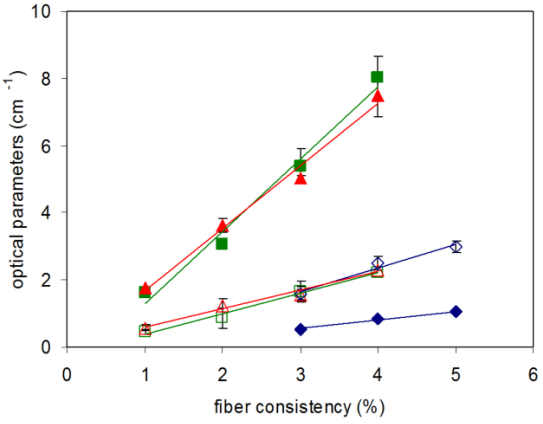

Figure 6. Relationship between optical parameters and consistency (the diamond, triangle and square marks correspond to samples with a kappa number of 2, 13, and 16, respectively; the solid marks represent absorption coefficients, and the empty marks reduced scattering coefficients. The lines show a linear relationship).

5. Discussion

In sample preparation, some of the stock pulp suspensions were sampled and diluted. Due to the inhomogeneity of stock suspensions, the sampled suspensions may have consistencies differed from those of the original ones.

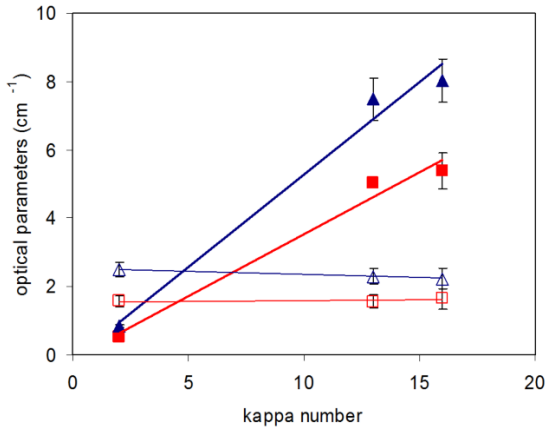

Figure 7. Relationship between optical parameters and kappa number (the triangle and square marks correspond to samples with a fiber consistency of 4 % and 3 %, respectively; the solid marks represent absorption coefficients and the empty marks reduced scattering coefficients. The lines show a linear relationship).

As a result, the diluted samples used in the experiments suffer from a consistency error. During the actual measurements, all pulp samples, high consistency samples in particular, were not exactly homogeneous. Consequently, the optical absorption distribution in these suspensions deviated from the exponential rule along the laser beam's incident direction. Fortunately, the former problem can be avoided and the latter can be reduced in online measurements, because the suspensions are not sampled and they are flowing.

In time-resolved stress detection, the experimental setup was used in the transmission mode. It is known that acoustic waves are strongly attenuated in pulp suspensions. Moreover, if the suspension also contains micro-air bubbles, the transmitted acoustic waves will be further attenuated and scattered. As a result, although the thickness of the cuvette was only 2.4 cm, the profile of the waves received by the transducer may differ from the initial stress distribution in the photoacoustic source. To avoid potential errors due to these factors, it is better to use the backward mode, in which the transducer is located on the same side as the laser source.

Most pulp suspensions used in this study were locally inhomogeneous, for wood cellulose varies from a few submillimetres to 1 $\sim$ 2 mm in length and measures a few tens of micrometers in cross-section width. However, the irradiated area of the laser beam on the incident window of the cuvette had a diameter of 12 mm, which is much larger than the size of cellulose fibers. Therefore, the samples are macro-homogeneous, at least to a laser beam with a large diameter.

In addition, the transducer bandwidth is extremely important in detection of the wideband PA signals, because the detected signal is a convolution of the generated OA pulse in the sample and the transient response of the transducer. Therefore, in order to detect the OA signal accurately it is required that the frequency bandwidth of the transducer must be wider than the frequency bandwidth of the signal being detected. In studied samples, the minimal value of μ_{eff} is 1.88 cm^{-1} (seen Tab. 1). The calculation shows that the PA waveform (the exponential decay of signal front), generated in a medium with such value, has a signal frequency band lower than 48 kHz at a half-maximal level. It can be seen, from Fig. 2, that the transducer response in this frequency band is about 10 times lower than the maximal response. In this case, the signal amplitude is therefore very low and the PA profile is probably distorted (seen in Fig. 3b), and the deduced μ_{eff} has a large relative error ($\sim$ 30% for the samples with kappa number 2, as shown in Fig. 4). To improve measurement accuracy, it requires using a transducer with a lower frequency response (of course, cuvette size should also be bigger). However, for the other samples with kappa numbers of 13 or 16, the PA profiles are less distorted such that the exponential fittings are satisfied very well, as seen in Fig. 3. The deduced μ_{eff} has a relative error not larger than 17%. This error is accepted in practice, considering the random property of pulp suspension. Moreover, the error would be further decreased in online measurement because a flowing suspension will improve its homogeneity.

In the total diffuse reflectance measurement, we used a simple method in which a photodiode was located at some distance from the cuvette's incident window to receive part of the diffuse light. Although this method was effectively used in homogeneous suspensions, it may cause a large error in pulp suspensions with poor homogeneity. To decrease this error, it is better to let the suspension flow and (if necessary) apply an integrating sphere to measure total diffuse reflectance.

Deduced effective attenuation coefficient and total diffuse reflectance from experimental data allow the absorption and reduced scattering coefficients of pulp suspensions to be determined. As shown in Figs. 6 and 7, a sample's consistency has a linear relationship with its absorption and reduced scattering coefficients, while its kappa number is unaffected by the reduced scattering coefficient. Therefore, we can determine an unknown sample as follows. When the reduced scattering coefficient of the sample is known, its consistency can be determined from Fig. 6. Based on the known consistency and absorption coefficient, we can further determine the sample's kappa number from Fig. 7.

Finally, our results are based on measurements conducted

on three kinds of pulp suspensions with a kappa number of 2, 13, and 16, respectively. To make the results more reliable requires studying a range of pulp suspensions with different kappa numbers. For online measurements, both setups shown in Fig. 1 can be combined simply by splitting the laser output into two beams and projecting them into different measurement points. This serves to reduce cost of the measurement system, while boosting its efficiency.

6. Conclusions

Pulp suspensions' absorption and reduced scattering coefficients were determined simultaneously based on detecting the time-resolved stress profile and the total diffuse reflection from the samples' surface. It was shown that an approximately linear relationship exists between optical coefficients and pulp consistency within the study range. Moreover, a linear relationship was also found between a suspension's absorption coefficient and its kappa number. However, the kappa number had no effect on the reduced scattering coefficient. Hence, by measuring the absorption and reduced scattering coefficient of an unknown pulp suspension, we may determine its consistency and kappa number. This measurement method has obvious potential for online applications if air bubbles in pulp suspensions were removed.

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