A Scattering Measurement System to Determine the Optical Characteristics of Industrial Suspensions

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A scattering measurement system to determine the optical characteristics of industrial suspensions in the wavelength range 430-700 nm was realized. The suspensions were mixtures of water and solid matter; the optical characteristics measured were the absorption coefficient, the scattering coefficient and the anisotropy. The measurement system comprised two integrating spheres of 203 mm diameter, a light source and a multichannel optical power meter. Different lasers and a halogen lamp were used as light sources. Optical power was measured with a spectrophotometer or a conventional power meter.

Scattering; absorption; paper fillers; paper pulp

I. INTRODUCTION

The composition of raw materials varies in every field of industry and, in general, cheaper materials tend to have greater variability. The raw materials of paper are a good example in which the cost of pure wood (low variation) compares with recycled paper (high variation). To reduce costs and still produce consistent products it is necessary to develop better measurement devices. By constantly monitoring the composition of raw materials, it is possible to compensate for variation to improve the quality of final product.

In this paper our previous studies with a single wavelength device [1] have been revised and extended to include white light measurements. We also present new ideas for the measurement system. The effect of the surface roughness is evaluated by making polyurethane samples with different roughness. Also the idea to use a cuvette with fixed boundaries is presented.

II. MEASUREMENT SYSTEM

The double integrating sphere system and Inverse Adding-Doubling (IAD) method were chosen to this study. There are also several other techniques available to determine optical properties (absorption coefficient, scattering coefficient and anisotropy of scattering). Optical coherence tomography, photoacoustic techniques and time-of-flight are among the most researched techniques. A comparison between those techniques is presented in [2]. The advantages of the IAD technique are simple measurements using broadband light and relatively deep measurement depths without in-sample probes.

IAD program [3] is used to calculate absorption coefficient and reduced scattering coefficient based on the normalized reflectance and transmittance. Three reflectance and three transmittance measurements are needed to calculate the normalized values. The normalized reflectance is

$$M_{\mathrm{R}} = r_{\mathrm{std}} * \frac{R - R_0}{R_{\mathrm{s}} - R_0}$$

where R is the measured transmittance for the sample, R_0 is the dark measurement, R_{100} is the measurement with the reflectance standard and r_{std} is the reflectance of the reflectance standard. Normalized transmittance can be calculated similarly except T_{100} is measured without sample and the correction factor (r_{std}) is not needed. [4]

The measurement system for total reflectance and total transmittance is presented in Figure 1. If the scattering anisotropy is wanted then an additional unscattered transmission measurements is needed. When using a laser it is hard to distinguish between unscattered transmission and forward scattered light, but with white light sources it is not experimentally feasible.

As light sources Melles Griot 05-LHP-151 He-Ne laser (633 nm), Power Technology PPM25/4969 25 mW diode laser (404 nm) and 150 W halogen lamp were used. Light from the halogen lamp was guided from the lamp through first sphere using an optical fiber. The optical power was measured with a spectrophotometer or a conventional power meter.

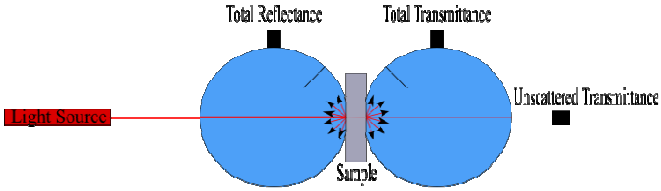

Figure 1. Measurement System

III. MEASUREMENT VARIATION

A. *Sample preparation and placement*

The variation in the sample preparation was estimated by measuring 20 independently prepared samples of Intralipid, TiO_2 and pulp. A single pulp type (GW) was chosen, but it was assumed that variation would be same for other pulps. Intralipid is a liquid and the easiest to measure. The standard deviation in measured reflectance and transmittance between Intralipid samples was 1.3%, TiO_2 samples was 2.8 % and pulp samples 4.8 %. Note that a 5 % variation in reflection and transmission can create a 28 % variation in absorption coefficient, 8.5 % variation in scattering coefficient, and 21 % variation in anisotropy.

The sensitivity of the measurements to sample placement between spheres was estimated by measuring the same sample 20 times. The standard deviation of the reflectance measurement was 1 % for Intralipid and TiO2 but was 2.3 % for pulp sample. Fibers in the pulp aggregate easily and despite careful mixing, the pulp sample was not as homogenous as the Intralipid and TiO_2 samples.

B. *Absolute error*

Intralipid-10%, Fresenius Kabi AB was used as a reference to verify that the calculated absorption and scattering coefficients agreed with previous studies. Measurements were done with a 632.8 nm HeNe-laser. Intralipid was diluted with water to 18 different concentrations between 1% and 24%. The measured scattering coefficient was then corrected using the sample concentration to get an equivalent 100% Intralipid coefficient. The resulting scattering coefficient of 36.6±1.24 mm^{-1} was in agreement with [5] (34 mm^{-1}) and with [6] (47.6 mm^{-1}). The measured anisotropy 0.661±0.006 did not agree with either [5] (0.825) or [6] (0.796). This may be due the differences between Intralipid batches (e.g., our sample may have had smaller fat globules). The measured absorption coefficient was higher 0.0050±0.0008 mm^{-1} in this study compared to 0.0027 mm^{-1} in [5] and 0.00169 mm^{-1} in [6].

C. *Thick Sample Problem*

In this study a sample thickness of 5 mm was used. According to [3] the variation in optical coefficients between measurements with different sample port sizes is less than 6 % when the sample is a few millimeters thick. Measurements should be reliable with this thickness and thinner samples are commonly used. Unfortunately injecting pulp into a cuvette this small becomes impossible when the pulp concentration exceeds 1 %. To apply the measurement system in on-line measurements a higher pulp concentration must be measured. This means a thicker cuvette. When using thicker samples (say 15 mm), the Monte Carlo simulation of lost light (light not absorbed or collected by the integrating spheres) becomes very sensitive to boundary conditions. To simplify simulations two different boundary conditions were tried with polyurethane phantoms. Fixed boundaries were used instead of the usual infinite-extent, finite-thickness sample assumption.

A set of polyurethane samples was made as described in [8]. Titanium oxide was used as a scatterer and Epolin 5532 (Epolin Inc., Newark, NJ) was used as an absorber. For each sample size two cylindrical molds with black and white inside walls were made and polyurethane was poured into molds as presented in Figure 2. All the samples were made from the same mixing patch and two 4 mm thick large reference samples were made to compare results. The samples were cured on very smooth plastic to make glossy surface. The reflectance of black paint was 0.2 and the reflectance of white paint was 0.8. The thicknesses of the samples were 13 mm, 19 mm and 25 mm and the inside diameters were 19 mm, 25 mm and 38 mm.

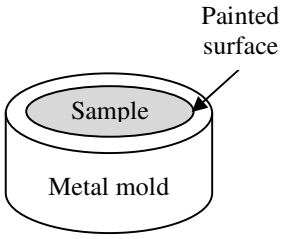

Figure 2. The sample with fixed boundaries

The sample port size was chosen to match inside diameter of the mold. The assumption was that the results measured with white cuvette would match the case of the usual infinite-extent, finite-thickness sample assumption and the black cuvette would present the case where all the light going sideways would be lost. All the effects exist for all the sample cases but can be obviously seen most clearly when the diameter is the smallest. The measured absorption coefficient for the samples of diameter 13 mm is presented in Figure 3. All the samples with white boundaries match the disc measurement closely. Also the thinnest sample with black boundaries matches the other measurements. When the thickness is increased the samples with black boundaries deviate from others.

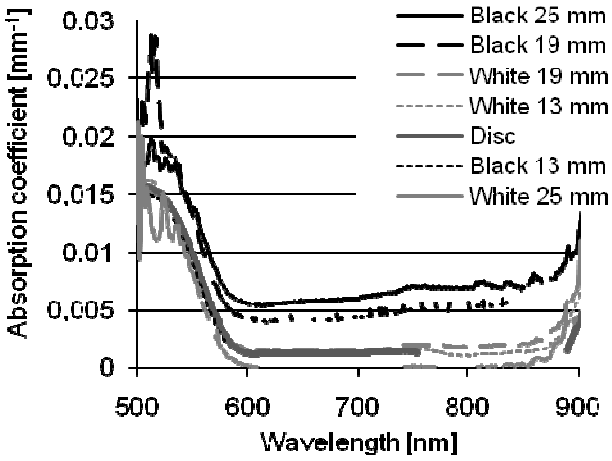

Figure 3. Absorption coeffient comparison of painted cuvettes (inside diameter 13 mm)

It was assumed that changing the boundaries of the sample would affect only to the absorption coefficient. For some so far unknown reason scattering coefficient results were affected as well. Scattering coefficient comparison for the same samples is presented in Figure 4. The most surprising difference is that the shortest samples are close to each other but are different from the discs.

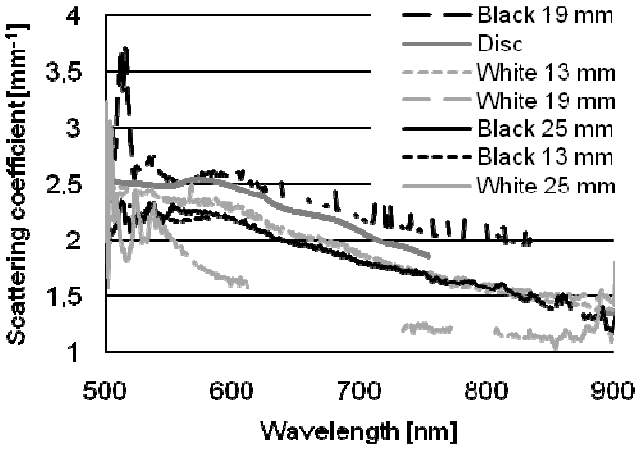

Figure 4. Scattering coefficient comparison of painted cuvettes (inside diameter 13 mm)

D. *The effect of surface roughness*

When the polyurethane is cured on a weigh boat the top surface looks different than the surface towards the weigh boat. Four samples were cured on different surfaces to find out if the difference is significant. The samples were made from same patch and same weights of polyurethane were cured on Nalgene container (4 oz PP Jar), Berry plastic container, over head sheet and several sand papers. Each sample was measured and the measured scattering coefficients are presented in Figure 3. It can be seen that difference is measurable and should be taken into account. Only one sandpaper measurement is presented because all of them were close to each other. The measured absorption coefficient is not presented because results vary a lot less than the measurement accuracy.

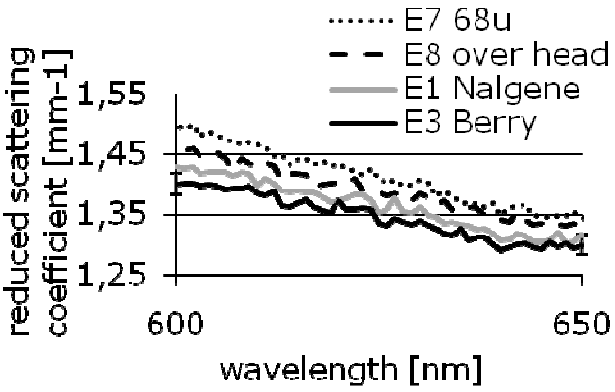

Figure 5. Comparison of scattering coefficients

IV. MEASUREMENTS

A variety of fundamental raw materials of paper industry were characterized. Optical properties of three different fillers (Kaolin, TiO_2 and $CaCO_3$) and three different types of pulp (SW, GW and BGW) were measured. SW stands for Softwood; GW stands for Ground Wood and BGW for Bleached Ground Wood. Samples were prepared by separately diluting different substances with water. Spectral measurements were done to compare results with different set-ups. With spectral measurements it could be possible to find peaks in scattering or absorption spectra.

Measured anisotropies of all samples are presented in Figure 6. The anisotropies were calculated from four different concentrations for each substance. Differences between pulps were so small that results are presented with one line. It can be seen that the anisotropies of Kaolin and different pulps are similar. For clarity only single error bars are drawn for those. The scattering of $CaCO_3$ and TiO_2 is more isotropic which is due the smaller particle size. The anisotropy does not decrease with wavelength as it does for Intralipid.

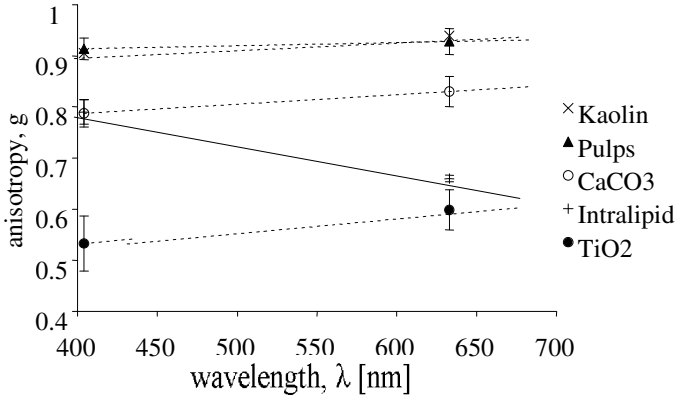

Figure 6. Measured Anisotropies for All Samples

A. *Filler Measurements*

For each filler a series of concentrations between 0.2 % and 4 % was made. For concentrations below 0.6 % the measurement noise was too high to get any reliable results. Absorption and scattering coefficients and anisotropy calculated from laser measurements are presented in TABLE I.

TABLE I. OPTICAL PROPERTIES OF FILLERS

	μ_a [1/mm/w%]	μ_s' [1/mm/w%]	g
	633 nm		
Kaolin	0.013±0.006	0.38±0.03	0.94±0.04
$CaCO_3$	-	0.23±0.03	0.83±0.03
TiO_2	-	1.05±0.14	0.60±0.04
	404 nm		
Kaolin	0.026±0.006	0.54±0.04	0.91±0.02
$CaCO_3$	-	0.25±0.02	0.79±0.03
TiO_2	0.007±0.003	1.20±0.11	0.53±0.05

Absorption and scattering results for different concentrations are corrected by the concentration before

calculating the average and standard deviation. Absorption by fillers is small. Only absorption of kaolin at 404 nm differs significantly from zero. Kaolin at 633 nm and TiO_2 at 404 nm have weak absorption, which is just above measurement error.

B. *Pulp Measurements*

For different pulp types dilution series between 0.4 % and 1 % was made. At the highest concentrations measurements couldn't be done because pulp was so thick it was impossible to inject into 5 mm cuvette and at the lowest concentrations pulp was too clear to make good measurements. At 633 nm the absorption of the pulp samples were below the detection limit. At 404 nm SW didn't absorb enough light to be measured. The absorption coefficient of GW was measured and found to be higher than the absorption coefficient of BGW. This is consistent with the expected result that bleaching should decrease absorption. All measurement results are presented in TABLE II.

TABLE II. OPTICAL PROPERTIES OF PULPS

	μ_a [1/mm/w%]	μ_s' [1/mm/w%]	g
		633 nm	
GW	-	0.27±0.02	0.91±0.03
BGW	-	0.20±0.02	0.93±0.03
SW	-	0.11±0.01	0.95±0.01
		404 nm	
	μ_a [1/mm/w%]	**μ_s' [1/mm/w%]**	**g**
GW	0.097±0.005	0.28±0.01	0.90±0.03
BGW	0.038±0.005	0.27±0.01	0.91±0.03
SW	-	0.16±0.03	0.93±0.01

C. *Spectral Measurements*

The white light measurements of fillers agreed with measurements made with the laser. In the pulp measurements the variation was more pronounced. It can be seen in Figure 7. that there were no peaks in scattering coefficient over the measured spectrum. Similar monotonic behavior was observed in all scattering measurements. One possible reason for the difference between measured values of TiO_2 scattering is that increased scattering decreases transmitted light, which in turn increases the measurement error.

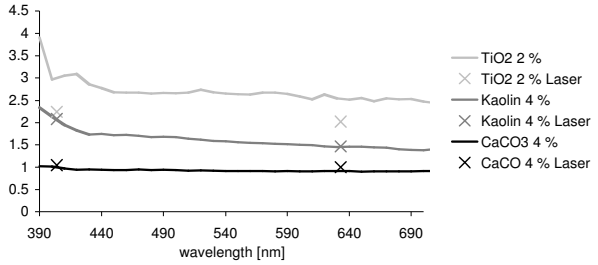

Figure 7. Measured reduced scattering coefficient of different paper fillers.

V. CONCLUSION

A double integrating sphere apparatus and inverse adding-doubling calculations were successfully used to measure the optical properties of dilute pulp suspensions. Due the lack of an absolute scattering and absorption standard it's impossible to completely verify accuracy but measurements with Intralipid show that absolute values are similar to measured in other studies.

It was shown that surface roughness affects the scattering coefficient but not the absorption coefficient. The change in scattering coefficient results is highest between glossy and almost glossy surface. Significant difference can be seen between different plastics but almost no difference can be seen between different sand papers.

Also a possible solution to the critical problem, of accurately measuring thick samples was presented. It was shown that the fixed boundaries of the cuvette can help to solve the problem of the lost light. Unfortunately an unexpected problem to measure scattering arose. Technique seems promising but further investigations are needed to find out why measured scattering coefficients differed significantly between different cuvettes. Also another problem with this kind of cuvettes needs to be solved before applying it to on-line measurements. The cuvette of ideal shape based on flow simulations needs to be designed and tested if fixed boundaries can be used with different shapes.

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