Determining optical properties of mechanical pulps

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SUMMARY: A method to produce representative sheets for determination of optical properties of mechanical pulps has been developed. It reduces the risk of contamination and discoloration and can be used with small pulp quantities. The deviation from the expected linear behaviour of the light scattering coefficient, s, at wavelengths corresponding to strong light absorption, has been studied using the Kubelka-Munk model and the angular resolved *DORT2002* radiative transfer solution method. This decrease in s could not be explained by errors introduced in the Kubelka-Munk modelling by anisotropic scattering. Linear extrapolation of s can therefore not be justified as a way to obtain a more correct light absorption coefficient, k. For the pulps studied, the decrease in s at short wavelengths had little effect on k at 457 nm.

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The demand for higher brightness and whiteness in newsprint and high quality printing papers, such as LWC (lightweight coated) paper and SC (supercalendered) paper, has increased for several years and the price of these paper grades has been more or less directly related to the brightness/whiteness. This places greater demands on mechanical and chemimechanical pulps, the main components of such papers. Compared to chemical pulps, the advantages of using mechanical and chemimechanical pulps in high-quality paper products are the lower cost of wood due to better wood utilization (high yield) and the possibility of making paper with a combination of strength, stiffness (bulk) and high light scattering, giving high opacity at a low basis weight (Höglund, Wilhelmson 1993; Heikkurinen et al. 2009).

Mechanical and chemimechanical pulps can be bleached to relatively high brightness levels, but discoloration induced by e.g. heat and light is an inherent property of lignin-rich pulps (Gratzl 1985; Heitner 1993;

Leary 1994; Forsskåhl 2000). Transition metal ions such as iron and copper can cause discoloration, either directly (upon ion exchange) or after subsequent ageing or by forming coloured complexes with dissolved or colloidal substances that are retained in the sheet (Gupta 1970; Janson, Forsskåhl 1989; Rundlöf et al. 2000). The standard methods used to characterise the optical properties of mechanical and chemimechanical pulps (e.g. ISO 5263-2; ISO 5269-1; ISO 5269-3) may cause darkening of the pulp due to heat and/or contaminants from the sheet-forming equipment or dilution water. Further, the large amount of pulp material needed and the time-consuming procedures can in some cases be a problem.

The determination of light scattering, s, and light absorption, k, coefficients according to the Kubelka-Munk (K-M) theory (Kubelka, Munk 1931; Kubelka 1948), is important in different unit operations in pulp and paper manufacturing, since it makes it possible to better understand the changes that occur. The light absorption coefficient is an approximate measure of how large a proportion of the light is absorbed by the sample, and as such approximately proportional to the amount of absorbing chemical structures at a given wavelength distribution. The k-value can for instance give the paper-maker information about the need for bleaching. The light scattering coefficient is an approximate measure of how much of the light is scattered in all directions. The s-value is approximately related to the structure of the sample (given by e.g. raw materials and processes), i.e. how the components of the sheet are arranged and their refractive indexes (Pauler 2002). A known shortcoming of the Kubelka-Munk theory is that light scattering is seemingly dependent on light absorption in some cases (Nordman et al. 1966; Moldenius 1983; Rundlöf, Bristow 1997). This means that the assumption that the s-value is related to the structure only and the k-value to the amount of absorbing chemical structures only, does not hold. The light scattering coefficient of chemical and mechanical pulps deviates from a linear behaviour at short wavelengths, where light absorption is strong (Moldenius 1983; Sjöström, Teder 1999). Further, adding dyes to a sheet decreases the light scattering in the wavelength region where the light absorption increases (Rundlöf, Bristow 1997; Neuman, Edström 2010). In the K-M equation, the k-value is calculated from the s-value and the measured reflectivity (Pauler 2002). This means that a deviation in s will also affect k.

The purpose of this investigation was to propose and evaluate an efficient method to produce representative sheets for determining optical properties of mechanical pulps, i.e. a method that reduces the risk of discoloration during preparation of the sheets that is reasonably fast and can be used with small pulp quantities. Different approaches to determine the light absorption coefficient of these sheets when the s- and k-values cannot be regarded as independent of each other were evaluated and discussed.

Optical modelling

Optical modelling is used to relate the measured reflectance to some properties of the sample (sheet) such as the light scattering coefficient, s_λ, and the light absorption coefficient, k_λ. The Kubelka-Munk s- and k-values are determined from two different values of the diffuse reflectance factor at a given wavelength distribution, λ. The reflectance factor of an opaque sample, the reflectivity $R_{\infty\lambda}$ (pad of sheets), and the reflectance factor of a single sheet over a black cavity, $R_{0\lambda}$, are often used (ISO 9416). For paper applications, the grammage, w, is chosen as the variable to relate s_λ and k_λ to the thickness of the sample. The light scattering and absorption coefficients can also be calculated if reflectance factor measurements are made over two different backgrounds, provided that the resulting pair of reflectance factors is sufficiently different.

The Kubelka-Munk model is easy to use, fast and can be used for engineering calculations, since the model allows for calculations of reflectance factors from s and k as well as the other way around. In the K-M model, one assumption is that all light is perfectly diffuse; both illumination of and scattering by the sample. In a standard instrument (ISO 2469), the detection is done in a narrow solid angle around the normal to the sample and assumes the reflected light intensity to be equal in all other angles (isotropic). It has been shown that more light is reflected in large polar angles so the assumption is not correct and the detected intensity will be underestimated in a majority of cases dealt with in paper science (Edström 2004). In strongly absorbing (i.e. "dark") and in optically thin media (i.e. low grammage), the reflected light would be even more anisotropic, with more light reflected in large polar angles (Neuman, Edstöm 2010). It is therefore of interest to model light scattering in more than the two directions used in the K-M model, which can be seen as a simple case of discrete ordinate radiative transfer (DORT) theory. A DORT model adapted to pulp and paper was published by Edström in 2005 and is available as a software tool under the name of *DORT2002* (Edström 2005). The new feature of *DORT2002* compared to K-M is the introduction of angular resolution in the calculation process, taking the anisotropic reflectance into account, and the introduction of a phase function, describing the probability of light being scattered in different directions at each scattering site. The propagation of radiation in a medium with light scattering, $\sigma_{s\lambda}$, and light absorption, $\sigma_{a\lambda}$, properties, also known as cross sections, are considered. The parameters $\sigma_{s\lambda}$ and $\sigma_{a\lambda}$ of the radiative transfer theory are physically objective in the sense that they are directly related to the mean free path of scattering and absorption, respectively, of the medium. They are thereby direct quantifications of physical properties of the medium, independently of any measurements and models. The parameters s_λ and k_λ of the K-M theory are only related to the physical properties via specified measurements and calculations and get their meaning only through the measurements and calculations. Any deviation of this system from reality
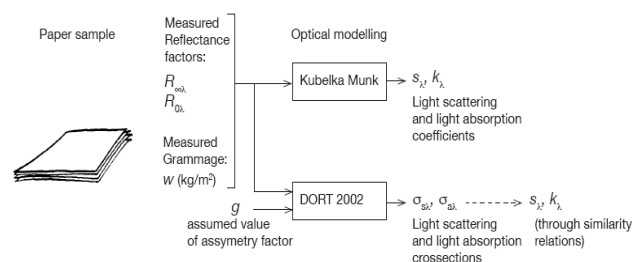

Fig 1. An overview of the Kubelka-Munk (K-M) and the discrete ordinate radiative transfer (*DORT2002*) optical modelling. $R_{0\lambda}$ =reflectance factor of a single sheet over a black cavity; $R_{\infty\lambda}$=reflectance factor of an opaque sample (reflectivity); w=grammage; g=asymmetry factor; s_λ=K-M light scattering coefficient; k_λ=K-M light absorption coefficient; $\sigma_{s\lambda}$=DORT2002 light scattering cross section; $\sigma_{a\lambda}$=DORT2002 light absorption cross section.

will introduce errors, e.g. parameter dependencies. The parameters s_λ and k_λ will in this sense not be objective, but only retain a correlation to the physical properties.

To describe a single scattering event, the shape of the phase function in *DORT2002* is determined by an asymmetry factor denoted g. The asymmetry factor is specified by a value between -1 to +1. Negative values indicate that backscattering is more likely to occur, while positive values indicate an increased probability for scattering in the forward direction. Isotropic single scattering, as assumed in the K-M model, is modelled with $g = 0$ (Granberg 2001; Edström 2005). A fibre-containing surface from mechanical pulp showed a forward scattering meaning the g value to be positive (Granberg et al. 2003). However, the knowledge concerning the asymmetry factor for paper products is limited. In *DORT2002*, the actual conditions of the measurement device, such as illumination and detection geometry, can be incorporated. *DORT2002* $\sigma_{s\lambda}$ and $\sigma_{a\lambda}$ can be approximately transformed into K-M s_λ and k_λ (Edström 2004). Mudgett and Richards (1971; 1972) and van der Hulst (1980), suggest similarity relations between s_λ and k_λ and $\sigma_{s\lambda}$ and $\sigma_{a\lambda}$ so that $k_\lambda = 2\sigma_{a\lambda}$ and $s_\lambda = 3/4 \cdot \sigma_{s\lambda} \cdot$ (1-g). Such similarity relations are by necessity approximate and objectively correct values of $\sigma_{s\lambda}$ and $\sigma_{a\lambda}$ may well give values of s_λ and k_λ that differ from those given by K-M, which reflects the lower degree of accuracy when using K-M to interpret reflectance measurements. *Fig 1* shows a schematic overview of the K-M and *DORT2002* optical modelling.

Materials and Methods

Pulps

Unbleached and hydrogen peroxide (H_2O_2) bleached commercial mechanical pulps produced from Norway spruce (*Picea abies*) and a totally chlorine free (TCF) bleached softwood kraft pulp were used in the experiments described in this paper. Characteristic pulp data, pulp sampling positions, and experimental parts where the pulps were used are given in *Table 1*.

Table 1. Freeness, sampling position and experimental part where the Norway spruce thermomechanical pulps (TMPs), Norway spruce stone groundwood (SGW) pulp and softwood kraft pulp were used.

Pulp	Denotation	Freeness ml CSF	Sampling position	Pulp used in experimental part
Unbleached TMP	TMP1	70	Blowline, 2nd stage refiner	Dilution Disintegration Sheet forming Heat-induced ageing
Unbleached TMP	TMP2	100	Stand pipe, 2nd stage refiner	Disintegration Sheet forming
H_2O_2 bleached TMP	BTMP1	70	Bleach tower, before dilution	Dilution Sheet forming Heat-induced ageing
H_2O_2 bleached TMP/SGW pulp (93/7) DTPA washed[1]	BTMP2/BSGW	28	Wash press, after bleach tower	Disintegration
TMP 1 fractionated H_2O_2 bleached[2]	BTMPA		Blowline, 2nd stage refiner	Sheet forming
TMP 1 fractionated H_2O_2 bleached[2]	BTMPB		Blowline, 2nd stage refiner	Sheet forming
TMP 1 fractionated H_2O_2 bleached[2]	BTMPC		Blowline, 2nd stage refiner	Sheet forming
TCF bleached kraft pulp	Kraft	450	Baled and dried pulp, laboratory Escher Wyss beaten	Dilution

[1] A washing procedure mainly to reduce the metal content of the pulp. Detailed information is given in Enberg et al. (2009)

[2] Detailed information about the fractionation and hydrogen peroxide bleaching procedures is given in Karlsson and Agnemo (2010).

Preparation of pulps with different amounts of fines

Unbleached Norway spruce TMP (TMP1) was disintegrated in deionised water, diluted to 10 g/l, and fractionated using a Britt dynamic drainage jar (BDDJ) according to SCAN-CM 66:05. A metal wire plate with 76 μm hole diameter (ca. 200 mesh, from PRM Inc., USA) was used to fractionate the pulp suspension. The fibre and fines fractions were mixed in controlled portions to obtain pulps with different fibre/fines ratios. The fines contents of the final remixed pulps were 28, 49 and 75% measured according to SCAN-CM 66:05. The pulps with different fibre/fines ratios were hydrogen peroxide bleached. More detailed information about the fractionation and hydrogen peroxide bleaching procedures can be found in Karlsson and Agnemo (2010).

Pulp disintegration

Two methods for pulp disintegration have been used; the ISO standard method 5263-3 and a new method developed for small pulp quantities. In the ISO method, 50 g of oven-dry pulp is disintegrated in a standard disintegrator at 2% pulp consistency, 85°C for 30000 revolutions (approximately 10 minutes). In the new method, ~1.9 g of oven-dry pulp is disintegrated in deionised water at a pulp consistency of 1% using a kitchen hand blender (Braun, 300 W). The hand blender has a stainless steel mixing blade (~30 mm Ø) mounted on a long shaft fitted with a plastic enclosing. The motor has an effect of 300 W according to the manufacture,

resulting in about 10500 rpm. The mixing blade was blunted to reduce possible cutting of the fibres. The disintegration temperature was 85°C and the disintegration time 1, 2 or 5 minutes.

Preparation of laboratory sheets using standard methods (A and B)

Laboratory sheets (60 g/m^2, oven-dry) for determination of optical properties were prepared in a conventional sheet former without (method A) and with a closed water system (method B) according to the ISO standard methods 5269-1 and 5269-3, respectively. Prior to sheet forming, the pulps were disintegrated using the ISO standard method 5263-3. The wire screen in the sheet former has a nominal size of aperture of 125 μm (ca. 120 mesh). Deionised water or tap water was used in disintegration and sheet forming procedures. Laboratory sheets produced with tap water are denoted tap water hereafter. Sheets for brightness determination (approximately 200 g/m^2, oven-dry) were prepared according to ISO standard method 3688 and these sheets are henceforth referred to as brightness pads.

Preparation of laboratory sheets using the new method (C)

A new sheet former was developed to produce laboratory sheets (method C). A schematic picture of the sheet former is shown in *Fig 2*. The circular sheet former is made of poly methyl methacrylate, PMMA, and has a
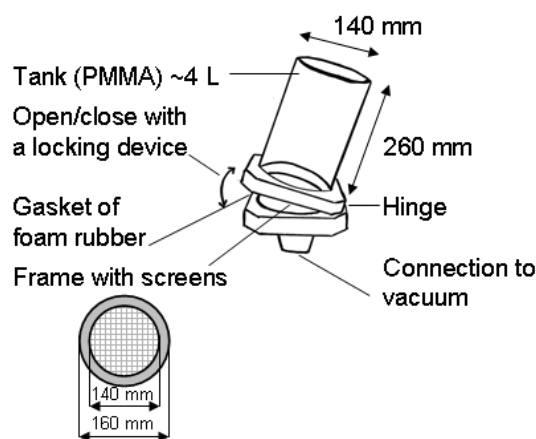
Fig 2. Schematic picture of the new sheet former.

polyamide, PA, wire screen (from Derma, Sweden) with a diameter of 140 mm and a size of aperture of 76 µm (ca. 200 mesh). The wire screen is backed by a coarser wire screen (ca. 30 mesh) made of stainless steel and the sheet former is connected to vacuum for drainage. The sheet former may easily be equipped with a draining pipe as described in ISO standard method 5269-1 if the laboratory sheets are to be used for testing of physical properties.

Pulp sufficient for two laboratory sheets (~1.9 g oven-dry) was disintegrated in deionised water (~0.2 l) using the modified method described above. The pulp suspension was then diluted with deionised water to 0.2% pulp consistency. The pH was adjusted to 5 prior to sheet forming using acetate buffer, 0.05 mol/L H_2SO_4 (p.a.) or 0.1 mol/l NaOH (p.a.). An amount of stock which contained an accurate mass of the pulp to produce a laboratory sheet with a grammage of 62 g/m² (oven-dry) was added to the sheet former, pre-filled with deionised water (~2 l), to a final pulp consistency of approximately 0.05%. The pulp suspension was gently mixed with a plastic stirrer before draining. The laboratory sheets were then transferred pressed and dried according to ISO standard method 5269-1.

Heat-induced ageing

Unbleached (TMP1) and hydrogen peroxide bleached (BTMP1) Norway spruce pulps were used to produce laboratory sheets on the new sheet former (method C). These sheets were heated at 80°C and 65% relative humidity in a climatised cabinet according to ISO standard method 5630-3 for up to 500 hours. The optical properties, grammage and density were evaluated on the same sheet and in the same position on the sheet each time. The sheets were conditioned for 15 min at 23°C and 50% relative humidity before measuring and then immediately put back into the cabinet.

Optical measurements and calculations

The spectrophotometer Datacolor Elrepho 2000 was used for the reflectance factor measurements. ISO brightness (brightness pads) was determined according to ISO standard method 2470. In this paper, the light scattering and light absorption coefficients were determined for different wavelengths in the region 400-700 nm or with the brightness function, R_{457}. All samples were conditioned at 23°C and 50% relative humidity according

to ISO standard method 187 before the optical (and physical) properties were determined.

Laboratory sheets were produced using method C and the *s*- and *k*-values were then determined in four different ways:

1. Calculations from reflectance factors measured on sheets made of pure mechanical pulps (*standard approach*). Diffuse reflectance factors $R_{0\lambda}$ and $R_{\infty\lambda}$ were used to calculate *s*- and *k*-values using the K-M equations (ISO standard method 9416).

2. Calculations from reflectance factors measured on sheets made of mixtures of mechanical pulp and a fully bleached chemical pulp (*dilution approach* see e.g. Sjöström, Teder (1999) and references therein). A bleached softwood kraft pulp (Kraft), with a low k_{457}-value (0.3 m²/kg) was used to dilute the mechanical pulp. The kraft pulp was mixed with an unbleached Norway spruce TMP (TMP1) in different ratios. Diffuse reflectance factors $R_{0\lambda}$ and $R_{\infty\lambda}$ were measured and *s*- and *k*-values were calculated using the K-M equations. The *k*-values for the pulps mixed with the dilution pulp were calculated according to:

$$k_{mixture} = x_{sample} \cdot k_{sample} + x_{Kraft\ pulp} \cdot k_{Kraft\ pulp}$$

where the two *x* are the proportions of the different pulp samples in the mixture.

3. Calculations from reflectance factors measured on sheets made of pure mechanical pulps with linear extrapolation of *s*-values in the region 500-700 nm to obtain new *s*-values (and *k*-values) for the wavelength region 400-490 nm (*linear extrapolation approach*). Diffuse reflectance factors $R_{0\lambda}$ and $R_{\infty\lambda}$ were measured and *s*- and *k*-values were calculated using the K-M equations for every 10th nanometre in the wavelength region 500-700 nm. The *s*-values for 500-700 nm were used for linear extrapolation to obtain new *s*-values for the wavelength region 400-490 nm. From the extrapolated *s*-values and the measured R_∞ at 400-490 nm, new *k*-values were calculated using the K-M equation.

4. Calculations from reflectance factors measured on sheets made of the pure pulps taking into account the non-isotropic light reflectance (*DORT2002 approach*). *DORT2002* was used with diffuse reflectance measurements of $R_{0\lambda}$ and $R_{\infty\lambda}$ to calculate the scattering- and absorption cross sections $\sigma_{s\lambda}$ and $\sigma_{a\lambda}$ for wavelengths 400-700 nm. The asymmetry factor, *g*, was set to 0, 0.5 or 0.7, the number of channels, N, were 30. The $\sigma_{s\lambda}$ and $\sigma_{a\lambda}$ were translated into K-M s_λ and k_λ according to the following equations (Mudgett, Richards 1971; Mudgett, Richards 1972; van de Hulst 1980):

$$k_\lambda = 2\sigma_{a\lambda}$$

$$s_\lambda = 3/4 \cdot \sigma_{s\lambda} \cdot (1\text{-}g)$$

Other analyses

Analyses and methods not mentioned elsewhere in the experimental section are: density and grammage (ISO standard method 5270), freeness (ISO standard method 5267-2), and metal ion content (SCAN standard method CM 38:96). Fibre length and width were measured with

the optical fibre analyser PQM 1000 (Sunds Defibrator, Sweden).

Results

The results presented in this paper are divided into the following sections. The first part, *pulp disintegration*, compares the standard disintegration method with the new disintegration method. The second part, *preparation of laboratory sheets using conventional and new sheet formers*, presents a comparison between different sheet forming procedures. The third part, *spectral evaluation of sheets with strong light absorption*, discusses the problem with determination of Kubelka-Munk (K-M) *s*- and *k*-values at wavelengths corresponding to strong light absorption. Different unbleached and hydrogen peroxide bleached Norway spruce mechanical pulps have been used in the different parts of the study (see *Table 1* for explanation).

Pulp disintegration

Latency, defined as the changes in pulp properties resulting from a hot disintegration treatment, may be found in pulps with high lignin content e.g. pulps produced in stone grinding and refining processes where the fibres are separated at a temperature exceeding the softening temperature of lignin. To remove latency from a pulp, it is necessary to disintegrate the fibres in a water suspension of about 1-2% at a temperature exceeding the softening temperature of lignin (Beath et al. 1966; Mohlin 1980). The latency removal is faster at higher suspension temperatures, but pulp brightness can be adversely affected by increased disintegration temperature (Htun et al. 1988).

In order to reduce the heat-induced discoloration and the risk of contamination of the pulp sample during latency removal, a new disintegration procedure was developed and evaluated against the standard ISO method 5263-3. A further advantage with the new disintegration method is that smaller quantities of pulp can be used. Unbleached and hydrogen peroxide bleached mechanical pulps were disintegrated and laboratory sheets were formed on the new sheet former (method C, see *Experimental* section). The freeness value, fibre length and fibre width of the pulps and the optical properties of the laboratory sheets are presented in *Table 2*. For the pulps investigated, the differences in optical properties between the two disintegration methods were generally small and within the experimental variation. The freeness value did, however, decrease with increasing disintegration time (*Table 2*), indicating that too short treatment time possibly did not remove latency sufficiently well. Further, the fibre length and width were more or less the same for both disintegration methods. A disintegration time of two minutes was considered to be sufficient for the pulps used in this work. For other pulps, a longer disintegration time may be needed.

Preparation of laboratory sheets using conventional and new sheet formers

Retention of the fine material is important in the preparation of laboratory sheets, i.e., that the sheets contain a representative amount of fibres and fines. As is well known, an increased amount of fine material in the

pulps increases both the light scattering and the light absorption coefficients (Mohlin 1977; Rundlöf et al. 2000; Karlsson, Agnemo 2010). In the standard laboratory sheet forming procedures, the loss of material through the wire screen is compensated for either by charging an excess of the pulp suspension for a certain grammage (ISO 5269-1, method A) or by using a closed white water system which is brought to retention equilibrium (ISO 5269-3, method B). Method A gives laboratory sheets which are richer in larger particles than the original pulp, since the loss of fines is compensated for by addition of the whole pulp suspension. Method B builds up fractions in the white water system that is not so easily retained and once equilibrium in the mass balance is reached it does not necessarily imply that the resulting sheets are representative for the original pulp. There is also a risk that the laboratory sheets produced contain an unrepresentative amount of dissolved and colloidal material due to the large amounts of white water used. The recirculation of white water is time-consuming since many sheets need to be formed to build up the concentration in the white water. This also demands large amounts of pulp and water. A new sheet former was therefore constructed with the aim of having a fast sheet forming procedure using small amounts of material, reducing possible sources of contaminants and that produces a laboratory sheet with a representative fibre and fines composition. The new sheet forming method is denoted method C.

The amount of material that is lost in the new sheet former was evaluated using an unbleached thermo-mechanical pulp, a hydrogen peroxide bleached thermo-mechanical pulp, and blends of a hydrogen peroxide bleached thermomechanical pulp with different fibre/fines ratios. The loss of fines was found to be rather constant and about 8% of the *total amount* of fines (*Table 3*), independent of the fines content of the pulp within the wide range examined (28 – 75%). The total material losses for the unbleached and the hydrogen peroxide bleached thermo-mechanical pulps were about 3%, which was considered to be acceptable. Laboratory experience estimates the material loss for 90 ml freeness TMP to be about 6-7% in a conventional sheet former without white water recirculation (method A).

Table 4 presents the optical properties and the iron and copper contents of laboratory sheets produced using the different laboratory sheet forming methods A-C. The pulps were disintegrated according to ISO 5263-3 prior to sheet forming using conventional methods (A and B), whereas the hand blender was used to disintegrate the pulp prior to forming sheets in the new sheet former (method C). The brightness value of laboratory sheets produced in the new sheet former was in good agreement with the brightness value obtained from brightness pads. Laboratory sheets formed in a conventional sheet former, with or without white water recirculation (deionised water), had a lower brightness mainly due to a higher light absorption coefficient. Method A had lower light scattering coefficient probably due to loss of fines. The loss of fines also means that the *k*-value is likely to be underestimated since the fines fraction in most cases contains more colour than the fibres. Using tap water in disintegration and sheet forming caused pronounced

Table 2. Freeness, optical and fibre properties after disintegration of unbleached and hydrogen peroxide bleached Norway spruce mechanical pulps using standard (ISO 5263-3) and new disintegration methods. More information about the pulps is given in Table 1. The optical properties are given with 95% confidence interval.

Properties	TMP1		BTMP2/BSGW			
	ISO 5263-3 10 min.	New 2 min.	ISO 5263-3 10 min.	New 1 min.	New 2 min.	New 5 min.
Freeness, ml	70	72	28	34	32	26
Brightness, % ISO	61.3±0.5	61.3±0.2	72.0±0.3	72.6±0.1	72.4±0.1	72.0±0.7
s_{457nm}, m2/kg	60±1	60±1	64±3	65±1	59±1	61±3
k_{457nm}, m2/kg	7.3±0.2	7.3±0.2	3.5±0.2	3.4±0.1	3.1±0.1	3.3±0.3
Fibre length, mm			1.10	1.08	1.07	1.09
Fibre width, µm			36.1	36.0	36.5	36.2

Table 3. The material lost in the new sheet former (method C) for unbleached and hydrogen peroxide bleached Norway spruce thermomechanical pulps with various fibre/fines ratios. The total material loss is given as max. and min. values. More information about the pulps is given in *Table 1*.

Pulp	Fines content, %	Loss of fines, %	Total material loss, %
TMP1	29		3.3±0.2
BTMP1	28		3.2±0.2
BTMPA[1]	28	7.9	2.2
BTMPB[1]	49	8.9	4.4
BTMPC[1]	75	7.3	5.4

[1]Fines re-added, see experimental section and Karlsson and Agnemo (2010).

brightness losses (methods A and B), in this case probably due to metal impurities present in the tap water. The copper content increased significantly (cf. *Table 4*), and copper has been reported to cause discoloration by forming coloured metal complexes with wood constituents (Gosh, Ni 1998; Ni et al. 1999). The accuracy in the measurement of optical properties on the sheets produced according to the new method was similar compared to the other methods. The method chosen for producing laboratory sheets will have a large impact on the optical properties, and for the unbleached pulps in this study, the difference in brightness was up to 6% ISO.

Spectral evaluation of sheets with strong light absorption

It is normally assumed that the Kubelka-Munk (K-M) light scattering coefficient, s_λ, can be used as a measure of the ability of a sheet structure to scatter light, independently of the light absorption properties of this structure (Pauler 2002). It is also well known that this assumption does not hold in regions of the spectrum corresponding to strong light absorption (Nordman 1966; Rundlöf, Bristow 1997; Granberg, Edström 2003). In the K-M equations, the k-value is calculated from the s-value and the measured reflectivity which means that a deviation in the s-value will also affect the k-value.

Laboratory sheets of an unbleached and a hydrogen peroxide bleached spruce thermomechanical pulp were produced in the new sheet former and then subjected to an elevated temperature (80°C, 65% relative humidity) for 500 hours in order to increase the light absorption without changing the sheet structure. The unbleached pulp had a brightness of 62.7% ISO before ageing and 56.0% ISO after an ageing time of 500 hours, the corresponding light absorption coefficients (k_{457}) were 7.1 and 11.1 m^2/kg. The hydrogen peroxide bleached pulp had a brightness of 77.9% ISO before ageing and 57.7% ISO after an ageing time of 500 hours and the corresponding light absorption coefficients k_{457nm}-values were 2.1 and 9.3 m^2/kg. *Fig 3* and *Fig 4* shows the K-M s and k as a function of wavelength after heat-induced ageing for 4 and 500 hours. It is obvious that the light scattering coefficient deviates from a linear behaviour; the decrease in K-M s was present for both pulps and for both ageing times as expected. The decrease was more pronounced and began at longer wavelengths for the sheets aged for 500 hours (*Fig 3*), where the light absorption also was stronger (*Fig 4*). The sheet density and grammage were not changed and the light scattering coefficient at longer wavelengths was to a large extent unaffected by the heat-induced ageing procedure (*Fig 3*). The slope of the light scattering versus wavelength curves were approximately the same up to a wavelength of 490 nm for both pulps, which may be taken as a further indication that the pore structure of the sheet was not affected by the heat-induced ageing procedure (Gate 1972; Lindblad et al. 1989).

Different ways of determining the K-M s- and k-values are discussed in the following. Firstly the *standard approach*, to measure $R_{0\lambda}$ and $R_{\infty\lambda}$ on sheets made of the pulp to be studied, and then calculate s- and k-values using the K-M equations (Kubelka 1931; Kubelka 1948). Secondly, *dilution* with a pulp of low light absorption (Polcin, Rapson 1969; Moldenius 1983), then measurement and calculations as above with k-values of the pure pulp obtained using "additively rule". Thirdly, *linear extrapolation* where the s-values were discarded in areas where s deviates from the expected line and replaced by s-values obtained by linear extrapolation of s

Table 4. The optical properties and the iron and copper contents of laboratory sheets produced from an unbleached Norway spruce TMPs using different sheet forming procedures. The optical properties are given with 95% confidence interval. Methods A and B are sheets formed in a conventional sheet former without or with white water circulation, whereas method C is the new sheet forming procedure that is described in this paper.

Sheet forming method	Brightness[1], % ISO	s_{457nm}, m²/kg	k_{457nm}, m²/kg	Fe, mg/kg	Cu, mg/kg
TMP1, 70 mlCSF					
Brightness pads (ISO 3688)	63.4±0.2			2	<0.01
Method C (this paper)	63.4±0.2	62±3	6.5±0.3	3	<0.01
Method A (ISO 5269-1)	60.8±0.1	56±1	7.0±0.1	2	3
Method B (ISO 5269-3)	61.0±0.1	59±2	7.3±0.3	3	6
Method A (ISO 5269-1), tap water	59.4±0.1	58±2	8.1±0.3	4	139
Method B (ISO 5269-3), tap water	57.4±0.1	57±2	9.1±0.4	5	104
TMP2, 100 ml CSF					
Brightness pads (ISO 3688)	62.8±0.1				
Method C (this paper)	62.7±0.2	58±2	6.5±0.3		
Method A (ISO 5269-1)	61.1±0.2	52±3	6.5±0.3		
Method B (ISO 5269-3)	60.7±0.1	60±4	7.6±0.5		
Method A (ISO 5269-1), tap water	56.8±0.1	58±4	9.6±0.6		
Method B (ISO 5269-3), tap water	58.3±0.1	61±2	9.1±0.2		

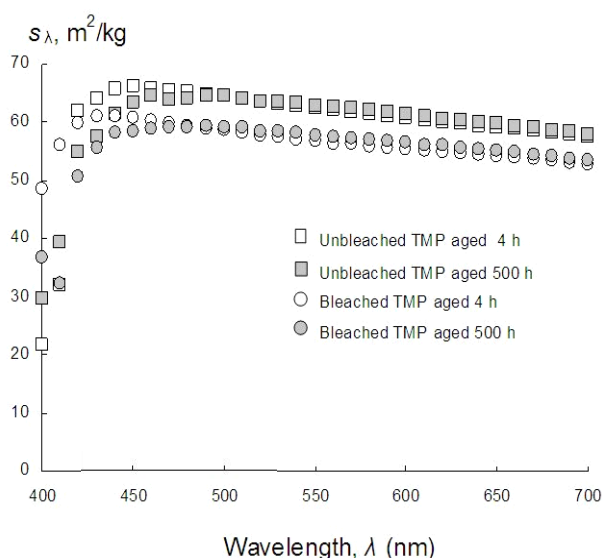[1]Brightness measured according to ISO 2470.

Fig 3. The Kubelka-Munk light scattering coefficient (*s*) as a function of wavelength for unbleached and hydrogen peroxide bleached Norway spruce thermomechanical pulps after accelerated heat-induced ageing for 4 and 500 hours.

Fig 4. The Kubelka-Munk light absorption coefficient (*k*) as a function of wavelength for unbleached and hydrogen peroxide bleached Norway spruce termomechanical pulps after accelerated heat-induced ageing for 4 and 500 hours.

versus wavelength at longer wavelengths as proposed but not evaluated by Haugan (2006). And finally, using a recently published model, *DORT2002* (Edström 2005), which takes anisotropic scattering into account. Further, making sheets of low grammage has been suggested as a way of lowering the actual amount of light absorbing material, and hence to coming closer to the region where s_λ is less affected by strong absorption (Schmidt, Heitner 1993; Johansson 2000). This approach was not included here for two reasons: *i)* it is unlikely that a sheet of extremely low grammage, around 10 g/m², is representative for the whole pulp sample, losses of fine material and formation problems may be quite significant and *ii)* it has been shown that anisotropy of the light scattering
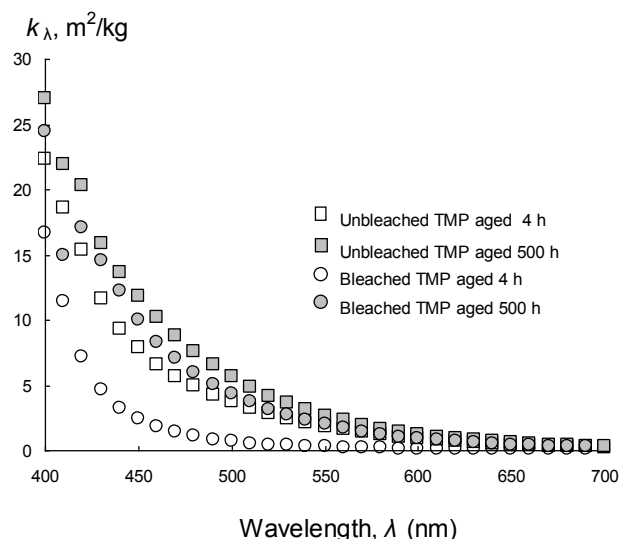
least in some cases (Neuman, Edström 2010), and consequently the assumption of isotropic scattering in the K-M equations becomes less applicable.

Fig 5 shows the light scattering coefficient as a function of wavelength for unbleached spruce TMP aged for 500 hours. The *s*-values were calculated from the same set of reflectance factor data using both the Kubelka-Munk model (*standard approach*) and the angular resolved model *DORT2002*. *DORT2002* gave *s*-values on a different level, which is to be expected since the similarity relations are not exact. The difference in *s*-values reflects the lower degree of accuracy when using K-M to interpret reflectance measurements (the interested reader is referred to Neuman and Edström (2010) for a
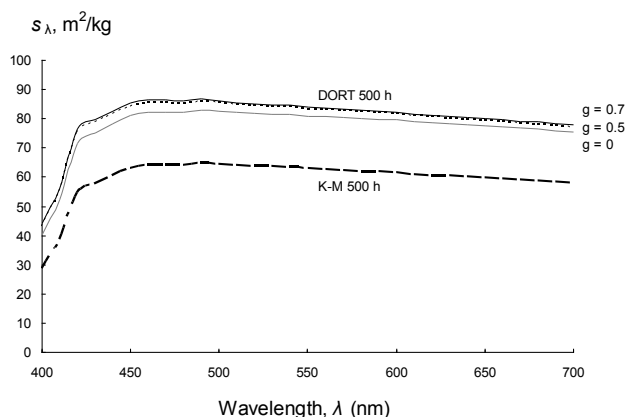
Fig 5. The light scattering coefficient (*s*) as a function of wavelength for an unbleached Norway spruce thermo-mechanical pulp subjected to accelerated heat-induced ageing for 500 hours. The light scattering coefficient was calculated from reflectance factor data using the Kubelka-Munk (K-M) equations or the *DORT2002* model. *g* = asymmetry factor.

deeper theoretical reasoning). It is obvious when comparing the shape of the curves that the deviation of *s* from a linear behaviour is still present (though to a somewhat lower degree) when possible errors introduced by anisotropic scattering are eliminated or nearly eliminated. The value used for the asymmetry factor *g* (0, 0.5 or 0.7, see *Optical modelling* for explanation) did not change the shape of the *s*/wavelength curves. The decrease in *s* is therefore not due to errors introduced by the assumption of isotropic scattering in the Kubelka-Munk model. Whether or not these lower *s*-values really represent the light scattering of the sample remains to be answered. However, the *s*-values obtained in regions where *s* deviates from the expected linear behaviour cannot be used as a measure of sheet structure independent of light absorption, as normally assumed in pulp and paper technology. This also means that the method of linear extrapolation of s_λ cannot be justified as a useful way of obtaining k_λ-values which better describe the optical properties of the sample. Further, the new pairs of s_λ and k_λ obtained from linear extrapolation will only fit the measured $R_{\infty\lambda}$ data, not the $R_{0\lambda}$.

A decrease in s_λ will also affect k_λ, since k_λ is calculated from s_λ and $R_{\infty\lambda}$ in the K-M equations. *Fig 6* shows K-M k_λ for an unbleached spruce thermomechanical pulp obtained by the *standard approach* (direct measurement), *linear extrapolation approach*, *dilution approach* (diluted with a low-absorbing kraft pulp) and *DORT2002*. It can be seen that all approaches gave values that were fairly close. The *k*-values at the shortest wavelengths can, however, sometimes not be determined using the *standard approach,* since the samples are nearly opaque. Then, the difference between the two reflectance factors is too small and in some cases the R_0-value incorrectly exceeds the R_∞-value due to experimental variation of the same magnitude as ΔR.

Table 5 shows the *k*-values calculated with the brightness function, R_{457}, for an unbleached spruce thermomechanical pulp. The *standard* and *dilution* approaches gave k_{457}-values that were identical (within the experimental variation) independent of the degree of
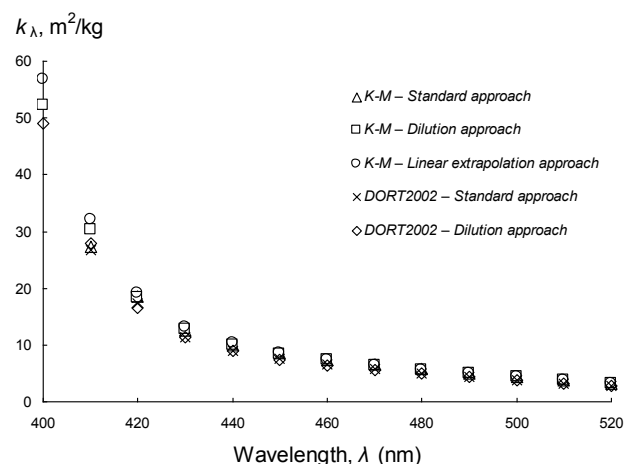

Fig 6. Kubelka-Munk (K-M) *k* for an unbleached spruce thermomechanical pulp (TMP) calculated in various ways; *standard approach* (100% TMP), *dilution approach* (95% kraft, 5% TMP), *linear extrapolation approach* (100% TMP) and *DORT2002 approach* (100% TMP and 95% kraft, 5% TMP). The light absorption coefficient was calculated from reflectance factor data using *DORT2002* with the asymmetry factor *g* = 0.

Table 5. The light absorption coefficient (k_{457}) for an unbleached Norway spruce thermomechanical pulp. Sheet forming method C was used for producing the sheets. For more details, see *Optical modelling* and *Experimental* section.

Ratio Kraft/TMP[1]	Procedure	K-M k_{457}, m²/kg	K-M k_{457} via DORT2002 g^1=0
0/100	Standard	8.5	7.7
75/25	Dilution	8.6	7.7
80/20	Dilution	8.5	7.6
85/15	Dilution	8.5	7.6
90/10	Dilution	8.5	7.6
95/5	Dilution	8.6	7.6
0/100	Linear extrapolation	8.9	

[1]Assymetry factor.

dilution or optical model used, even though the k_{457}-values were on a different level depending on the optical model used (cf. the discussion regarding *s* above, *Fig 5*). The *linear extrapolation approach* gave a k_{457}-value that was 0.4 m²/kg higher compared to the K-M k_{457} determined with *the standard approach* (corresponds to a reduced brightness by about 0.5% ISO for this pulp). Though, in general there were small differences between the procedures when *k* was calculated with the brightness function, R_{457}. The effect of using different methods may, however, be larger at shorter wavelengths, where light absorption is much stronger, as when studying chromophore formation by measurements also in the ultra violet region.

Discussion

There is since long an outstanding issue in the literature regarding unexpected dependencies between the K-M *s* and *k* parameters for strongly absorbing media. Foote (1939) describes the decrease in K-M *s* at a fixed

wavelength as K-M k is increased by adding dye. Nordman et al. (1966) describe the decrease in K-M s along a wavelength range, for a dyed pulp as compared to the same pulp without dye, in the absorption region of the dye. Later, the decrease in K-M s for mechanical pulp when moving towards shorter wavelengths has been seen as anomalous, since K-M k simultaneously increases (Moldenius 1983). But the (not explicitly stated) analogy with the NAM anomaly does not hold completely, since there is no 'original' sample without decrease in K-M s for shorter wavelengths. The results of Foote and Nordman et al. are fully compatible, and have later been referred to as the "Foote effect" and the "NAM anomaly" (Olf 1989; van den Akker 1990; Olf 1990). Complementing studies and comments have been made both earlier (van den Akker 1966; van den Akker 1968) and later (Rundlöf, Bristow 1997; Neuman, Edström 2010; Granberg, Edström 2003; Koukoulas, Jordan 1997).

Is it reasonable to expect that s_λ should increase towards shorter wavelengths? The increase is observed in plots of K-M s_λ for materials of weak light absorption, such as coating layers (Lindblad et al. 1989) copy paper (Rundlöf, Bristow 1997) and fully bleached chemical pulp (Sjöström, Teder 1999). Johansson (2000) observed that sheets made of dissolving pulp also extend the linear behaviour into the ultra violet region of the spectrum. The gradual increase in light scattering when moving towards shorter wavelengths may be qualitatively described in the following way: A paper sample contains a number of scattering sites of different sizes. It is well known that light scattering becomes more efficient with decreasing size of scattering sites, e.g. particles, until they reach a limiting size (approximately half the wavelength of light, as a rule of thumb); particles or scattering sites smaller than that will not scatter light efficiently (Alince 1986; Fineman et al. 1990). According to this approximate rule, scattering sites about 350 nm would be most efficient in red light, at the other end of the spectrum (blue) the limiting size would be about 200 nm, smaller scattering sites would be less efficient. In a plot such as *Fig 3*, when moving towards shorter wavelengths this means that smaller structures will begin to scatter light and give an additional contribution to the *s*-value. This resembles a situation where we gradually reveal more and more of the scattering sites, without taking away the ones already present, i.e. the light scattering should increase when moving from longer wavelengths towards shorter wavelengths (provided that there are scattering sites available in the size range, if not, the *s*-value would remain constant without further increase). When colour is added to a given sheet structure without changing it, as when adding a dye (Rundlöf, Bristow 1997) or by thermal ageing (present work), a decrease in s_λ is observed in a region of the spectrum corresponding to the increase in light absorption. In such cases, s_λ cannot be considered to be dependent on the structure and independent of light absorption, which it is assumed to be, at least when used in pulp and papermaking applications. Provided that it can be shown that a linear increase in *s* when going towards shorter wavelengths is correct and thereby represents the sheet structure

independent of light absorption, the *linear extrapolation* approach could tentatively be used to obtain a better description of the sheet structure compared with the *standard approach,* giving *s* that decreases towards shorter wavelengths. However, when making the extrapolation, there is no way of knowing if the s_λ-line will continue or change its slope, perhaps several times (Lindblad et al. 1989).

As light absorption increases, the samples become nearly opaque regardless of the model used and the difference between $R_{0\lambda}$ and $R_{\infty\lambda}$, becomes small. In some cases, the variations in the measurement are of greater magnitude than the difference between $R_{0\lambda}$ and $R_{\infty\lambda}$. The variation of s_λ would in this case be randomly distributed, and when the obtained value of $R_{0\lambda}$ incorrectly exceeds $R_{\infty\lambda}$, it is not possible to calculate s_λ and k_λ. Before this occurs, still close to complete opacity, the observed decrease in s_λ is continuous. As pointed out by Granberg and Edström (2003), any systematic error will have a stronger effect as the difference between the two values of R becomes smaller. If, for the sake of discussion, small artificial differences are introduced in a typical pair of measured data well into the region where s_λ decrease, the following results: A small artificial increase in $R_{0\lambda}$ makes the decrease in s_λ smaller, whereas a small artificial decrease in $R_{0\lambda}$ makes the decrease in s_λ larger. This could possibly indicate, but not prove, that the difference between measured values of R_λ may be somewhat too low when measuring material with strong absorption, and may in that case be a cause behind the observed decrease in s_λ. It is clear that a small systematic error could have a large effect (Edström 2008). According to the ISO standard 2469, annex A2: "The photometric accuracy of the instrument shall be such that the residual departure from photometric linearity after calibration does not give rise to systematic errors exceeding 0.3% radiance factor". A typical pair of R_0 and R_∞ was chosen from the region where s_λ decrease in one set of data, 53.0% and 53.3%. Using the *linear extrapolation approach, s* was increased with 4.7 units. An artificial increase of R_0 with 0.3% increased the *s* with 8.5 units, 0.1% increase of R_0 increased *s* with 2.2 units and 0.05% increase of $R_{0\lambda}$ increased *s* with 1 unit. Normally, calibration is done using two points, completely black and white. A small deviation from a perfect line between these two points may be of little significance in most cases and go unnoticed, whereas it can have a large influence near total opacity. Further, the variation in s_λ and k_λ increases when the sample approaches total opacity, since the effect of the experimental variation increases.

The *dilution approach* eliminates the problem of nearly opaque samples, and probably yields a sample that lies within the area where the K-M equations give sufficiently correct values. The concentration of the material to be studied is low in the sample, however. The "rule of additivity" used to calculate s_λ and k_λ may therefore not hold, especially not at the extreme ends of the curve, and a small error in the amount of dilution pulp added may have a large effect on the result. The Kubelka-Munk and the *DORT2002* models both gave a decreasing s_λ at short wavelengths when applied to the same set of data. The

decrease in s_λ can therefore not be explained as an error introduced by anisotropic scattering, because most of the decrease remained when the angular resolved model *DORT2002* was used, nearly eliminating the effects of anisotropy. The *dilution approach* and the use of the angular resolved model (*DORT2002*) seem, however, to be the two ways to determine k_λ that are likely to come closest to the true light absorption, since both approaches reduce or eliminate known errors in the K-M model.

The problem discussed above is of importance in pulp and papermaking applications, where the s_λ-value can no longer be regarded as a measure of "structure", regardless of the colour or light absorbing properties of this structure, and the k_λ-values obtained at the same time also become dependent on these s_λ-values. The question remains; Should we expect to find a measure of light scattering which can be related only to the structure (and refractive indexes) of a paper regardless of the colour of this paper and, at the same time, a good measure of the amount of chromophores? The measured data needed and how data should be treated to possibly achieve this when complete opacity is approached, remains to be further discussed.

Anisotropic light scattering was not a major cause of the deviation in s_λ from a linear behaviour, as evaluated using *DORT2002*. *Linear extrapolation* of K-M s into shorter wavelengths can therefore not be justified as a useful way of obtaining k-values which better describe the optical properties of the sample and is not recommended. Also, the present study does not contradict the possibility that the simultaneous decrease in K-M s and increase in K-M k in mechanical pulp at shorter wavelengths could be a physically correct and independent wavelength variation of these parameters.

Conclusions

The efficient laboratory procedure which was developed, can be used with small pulp quantities and reduces the risk of darkening and was found to produce representative sheets suitable for determining optical properties.

The decrease in the light scattering coefficient, s, at short wavelengths which coincided with strong light absorption, could not be explained by errors introduced in the Kubelka-Munk modelling by anisotropic scattering as evaluated using the *DORT2002* radiative transfer solution method. It cannot be excluded that the decrease in s could be correct and represents the light scattering of the sample. Even if this is the case, the s-value cannot be used as an independent measure of the sheet structure as is normally assumed in pulp and paper technology. Linear extrapolation of s to avoid this decrease cannot be justified as a way to obtain more correct values of the light absorption coefficient, k. Other possible reasons for the decrease in s should also be considered.

For the pulps studied, the decrease in s at short wavelengths had little effect on the k-value at 457 nm, as judged by a comparison based on reflectance values measured on a sheet of 100% mechanical pulp and on sheets containing small amounts of a mechanical pulp mixed with a pulp of low absorption.

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