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ORIGINAL ARTICLE

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Fiber surface characteristics evaluated by principal component analysis

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Abstract Principal component analysis (PCA) was used to evaluate the results of standard fiber analyses, determinations of charge, electron spectroscopy for chemical analysis (ESCA) measurements, and selective staining of kraft fibers prebleached with oxygen, followed by hydrogen peroxide or ozone. The majority of data variance is explained by the lignin content in fibers and by polarity (hydrophilicity vs hydrophobicity) of functional groups. The lignin determination methods (kappa number, C1 (ESCA), selective staining) gave similar but not equal results, because they measure different parts of lignin. The determination methods of the charged groups (total charge, surface charge, C4 (ESCA), and hexenuronic acids) also gave similar but not equal results. The results of staining by using cationic dyes do not correlate with the quantity of anionic (mainly carboxylic) groups in fibers, regardless of whether the dyes are selective for lignin or hemicellulose. Hydrogen bonding and hydrophobic interactions seem to overrule ionic interactions between dyes and fibers. Therefore, the majority of bonds formed between fibers themselves, as well as between fibers and paper additives, can to a great extent be expected to have the character of hydrogen bonds.

Key words Charge of fibers · Electron spectroscopy for chemical analysis (ESCA) · Principal component analysis (PCA) · Selective staining · VIS – reflectance spectroscopy

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Introduction

In papermaking, the fiber surface is formed mostly during the delignification and bleaching processes. To a certain extent it is reshaped during refining and recycling. All these processes are responsible for the presence of functional groups that characterize the fiber surface.

As a consequence of environmental concerns, several modified cooking and bleaching techniques have been developed. The response of these new pulp grades to paper chemicals is different to that of conventionally produced pulps.[1]

Therefore, a need arose for detailed knowledge of the fiber surface. Different approaches are available. Laine et al.[2] used electron spectroscopy for chemical analysis (ESCA) to discover that, with a different degree of delignification, a different surface coverage of lignin was observed. In addition, delignification took place first of all on the fiber surface. The same technique was used to study whether the redeposition of already dissolved lignin occurs during the delignification process. Also, the lignin might be moving from the middle lamella toward the fiber surface.[3] Residual lignin enrichment in the fiber surface of unbleached kraft pulp was also confirmed by enzymatic hydrolysis. With additional analyses using potentiometric and polyelectrolyte titrations, Laine et al.[4] studied the presence of free carboxylic groups in unbleached sulfate softwoods and hardwoods. These groups probably belong to either every fifth phenylpropane unit of lignin, or to uronic acids attached to the side chains of the hemicellulose type of xylan. A similar study into the effect of refining and charge on elemental chlorine-free and totally chlorine-free bleached kraft pulps was conducted by Laine et al.[2] Peng and Johansson[5] studied the concentration of lignin on fiber surface in relation to their specific surface by measuring the surface charge of high-yield pulp. Recently, the fluorescence of a special dye has been successfully used by Liu et al.[6] and Robinson et al.[7] to observe the uniformity of different delignified fibers. The confocal laser microscopy (CLSM) technique uses fluorescent dyes for studying fiber

surface characteristics.[8] Srebotnik and Messner[9] studied the possibilities of observing the delignification process by using differential staining of wood chips based on the selective staining of lignin and cellulose components. Yu et al.[10] have also used selective staining of different cellulose components to measure the pore sizes of fibers as an important property for water absorption and for specific properties related to it.

Based on all the research mentioned above, Drnovšek and Perdih[11,12] introduced a method of selective staining to the pulp fiber system. It is based on the affinity of dyes for certain parts of fibers. Several dyes were tested and three groups of dyes were formed: the first group has a good affinity for lignin (basic dyes), the second group has a good affinity for hemicellulose (basic phthalocyanine dyes), and the third group is composed of dyes with an affinity for pure cellulose (direct dyes).

The aim of this study was to evaluate the surface of selected fibers after treatment of pulp with chemicals that significantly affect the fiber surface; namely, with oxygen, followed by hydrogen peroxide or ozone. To evaluate the surface of selected fibers, selective staining, polyelectrolyte titration, and ESCA were used. The results of these methods were compared with some standard properties of fibers. To draw relevant conclusions more easily, all data were evaluated using principal component analysis (PCA).

PCA is a multivariate method used for displaying data in cases where each sample (object) is described using several parameters (variables). In such cases, it is hard to extract the relevant information from the data set (typically a table) by investigating one variable at a time. Furthermore, in most cases, the "independent" variables that are measured are not really independent. They usually correlate at least partially to each other, which makes interpretation even more difficult. Graphical presentation of such data sets is also impossible, because we can display only two-dimensional or three-dimensional graphs. The PCA method enables us to present the information contained in the data sets using a small number of graphs. These graphs show us similarities and differences between objects and variables. Similar objects are grouped together, while dissimilar ones are scattered around. The same is true for variables. The graphs in which the grouping of objects is presented are called score plots, while the graphs that present the grouping of variables are called loading plots. From the patterns on the score plots and loading plots one can extract the information contained in the analyzed data set.

From a mathematical point of view, the PCA method is a rotation of the old coordinate system of variables. The coordinate system is rotated in such a way that the relevant information, i.e., the largest portion of the variance in the data set, is presented using only a few variables of the new coordinate system. The new variables are called latent variables or principal components. The other latent variables of the new coordinate system represent noise that is due to errors in measurements. The latent variables are truly independent variables, i.e., they are orthogonal, which means that they do not correlate with each other. Score plots represent objects in the space defined by the latent variables, while the loading plots represent the old (measured) variables in the space of latent variables.

The PCA method is usually done in three steps. In the first step, the data set variables are normalized to variance 1 and the correlation matrix is calculated. The correlation matrix shows how the variables from the data set correlate to each other. In the second step, eigenvalues and eigenvectors of the matrix are calculated, i.e., the matrix is diagonalized. Eigenvectors are the latent variables of the new coordinate system while the eigenvalues show the information content (relevance) of each latent variable. In the third step, the coordinates of samples (objects) in the new coordinate system are calculated. More detailed description about the method can be found in Wold et al.,[13] Massart et al.,[14] Brereton,[15] and Graham.[16] The method is sufficiently simple for one to program it by oneself, as was done in our case.

At the end, one can import the new calculated coordinates of the objects and eigenvectors into one of the spreadsheet programs available on the market to create score plots and loading plots. Due to the normalization of the variables to variance 1, the latent variables are dimensionless. The other consequence of the normalization is that total variance of the data set becomes equal to the number of variables.

Materials and methods

Fibers

Conventional delignification

Unbleached kraft pulp from spruce at kappa number 21 was obtained according to the previously reported laboratory procedure.[11,12] Pulp samples, previously delignified with oxygen, were bleached by peroxide or ozone. Nine fiber samples were prepared. They were labelled according to the pre-bleaching agents used: oxygen (O), sample with kappa number 12.1; peroxide (P), samples with kappa numbers 10.4, 8.5, and 7.1, respectively; and ozone (Z), samples with kappa numbers 10.8, 8.8, 6.7, and 3.2, respectively. All samples were acidified before testing with dilute sulfuric acid to pH 5.

Selective staining of fibers

The whole method was conducted with fibers not previously dried. The preparation of dye solutions, staining procedures, and measuring the color intensity of stained fibers by means of visible reflectance spectroscopy have been described elsewhere.[11,12]

The groups of dyes used in our experiments were:

1. Cationic dyes selective for lignin: methylene blue, C.I. 52015; safranine O, C.I. 50240; crystal violet, C.I. 42555; acridine orange, C.I. 46005; ethyl rhodamine B, C.I. 45175

Table 1. Standard analyses of the fiber samples

Sample	Kappa number	Kappa $number_{corr}$	HxU (μmol/g)	Carbonyl groups (mmol/100 g)	Glucose + mannose (%)	Xylose (%)	Brightness (%)	Brightness stability (%)	Viscosity (ml/g)
Oxygen (12.1)	12.1	11.8	3.37	2.00	15.7	1.78	36.6	0.34	699
Peroxide (10.4)	10.4	10.1	3.87	2.05	17.2	2.72	45.5	0.99	723
Peroxide (8.5)	8.5	8.2	3.99	1.81	13.1	1.80	56.8	1.67	688
Peroxide (7.1)	7.1	6.8	3.82	1.42	15.9	2.69	61.9	1.94	683
Ozone (10.8)	10.8	10.5	3.65	2.18	15.9	2.61	38.2	0.85	715
Ozone (8.8)	8.8	8.6	2.96	2.27	9.36	1.43	41.9	1.05	670
Ozone (6.7)	6.7	6.5	2.63	2.88	21.1	2.90	46.9	1.24	453
Ozone (3.2)	3.2	3.1	1.44	4.79	16.6	2.47	61.5	1.94	354

$Kappa\ number_{corr}$ = kappa number − 0.0863 × HxU (from Gellerstedt and Li[20])
HxU, Hexenuronic acids

Table 2. Absorbances (Kubelka-Munk units) at λ_{max} of all three groups of dyes used for staining selected fibers

Sample (kappa number)	Safranine O	Methylene blue	Crystal violet	Ethyl rhodamine B	Acridine orange	Astra blue (620 nm)	Astra blue (670 nm)	Direct blue 1	Direct red 81	Direct black 75
Oxygen (12.1)	0.95	1.05	3.25	1.30	3.11	2.11	1.91	0.20	0.38	0.21
Peroxide (10.4)	0.58	0.69	2.1	0.99	2.6	1.79	1.57	0.113	0.15	0.048
Peroxide (8.5)	0.41	0.28	2.0	0.42	2.3	1.90	1.69	0.109	0.18	0.040
Peroxide (7.1)	0.25	0.15	1.3	0.34	2.0	1.86	1.58	0.07	0.142	0.032
Ozone (10.8)	0.77	1.02	2.93	1.02	2.8	2.16	1.83	0.23	0.31	0.19
Ozone (8.8)	0.21	0.31	0.88	0.39	1.7	1.59	1.40	0.08	0.13	0.05
Ozone (6.7)	0.14	0.13	0.63	0.20	1.4	1.61	1.44	0.11	0.24	0.09
Ozone (3.2)	0.02	0.020	0.08	0.021	1.1	2.93	2.39	0.17	0.30	0.06

2. Cationic phthalocyanine dye selective for hemicelluloses: astra blue
3. Direct dyes selective for cellulose: direct blue 1, C.I. 24410; direct red 81, C.I. 28160; direct black 75, C.I. 35870

ESCA measurements (XPS X-ray photoelectron spectroscopy)

Hand sheets of fibers with 70 g/m^2 basic weight were formed according to the SCAN-C 26:76 test method, and extractives were removed from the sheets with dichloromethane in a Soxhlet apparatus according to the SCAN-C 7:62 standard. The procedure of the XPS operation is described elsewhere.[17]

Charge of fibers

The method is based on polyelectrolyte titration described by Wågberg et al.[18] The preparation of fiber suspension and all further determination procedures are shown by Laine et al.[2] In this study, a solution of a low molecular weight polyelectrolyte Polybrene (poly 1,5-dimethyl-1,5-diazaundecamethylene bromide), $M_w \approx 8000$ was used to determine the total charge of fibers; to determine the surface charge of fibers, a solution of a high molecular weight polyelectrolyte PDMDAAC (poly-diallyl-dimethylammonium chloride), $M_w \approx 300\,000$ was used.

Standard methods

Standard analytical methods were used for other analyses:

Kappa number: ISO 302-1981
Viscosity: ISO 5351/1-1981
Brightness: ISO 3688-1977 (E)
Carbonyl groups: method described by Browning[19]
Hexenuronic acids: method described by Gellerstedt and Li[20]

PCA software was programmed by one of the authors (M. Perdih). It was tested on the examples presented in the references[13–16] mentioned above.

Results

The results of standard analyses for all fiber samples are shown in Table 1. Selective staining results, namely the absorbances of all three groups of dyes, are listed in Table 2. The results of ESCA measurements and charge determinations are presented in Table 3. All data was evaluated by PCA.

The PCA score plot of the first two principal components is shown in Fig. 1. We have decided to present only the first two principal components due to the high experimental error in some results of fiber charge determination, of C1 and C4 (ESCA), and of selective staining, which ranges from a few percent up to 30% in some cases, because these

Table 3. Results of ESCA measurements and charge determinations

Sample (kappa number)	O/C	C1 (%)	C2 (%)	C3 (%)	C4 (%)	Total charge (μmol/g)	Surface charge (μmol/g)
Oxygen (12.1)	0.71	9.2	71.3	18.2	1.3	78	25
Peroxide (10.4)	0.70	9.6	71.4	17.7	1.3	80	19
Peroxide (8.5)	0.70	8.1	72.5	18.1	1.3	78	21
Peroxide (7.1)	0.72	7.9	72.8	18.1	1.2	80	25
Ozone (10.8)	0.71	8.7	72.3	17.8	1.3	76	27
Ozone (8.8)	0.75	6.4	74.0	18.3	1.3	80	25
Ozone (6.7)	0.74	6.8	73.7	18.3	1.2	84	35
Ozone (3.2)	0.73	7.7	73.0	18.1	1.2	67	19

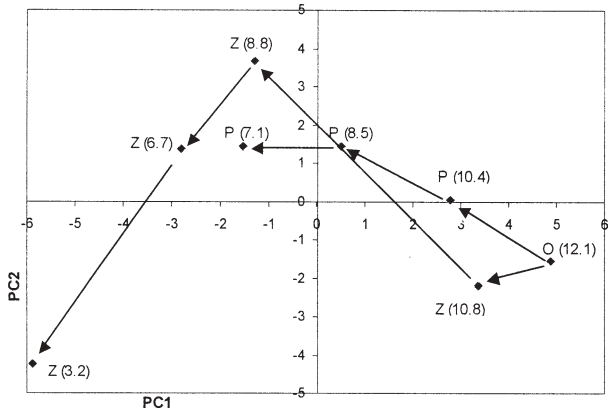

Fig. 1. The score plot of the fibers under the influence of their properties in the plane of the first two principal components. *O*, Oxygen-bleached fibers; *P*, peroxide-bleached fibers; *Z*, ozone-bleached fibers; *data in parentheses*, kappa numbers

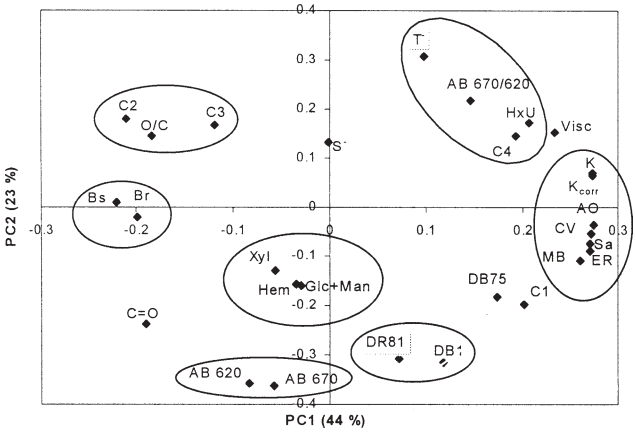

Fig. 2. The loading plot for the first two principal components of the fiber properties. Absorbances of cationic dyes at λ_{max} are shown by *CV*, Crystal violet; *ER*, ethyl rhodamine; *AO*, acridine orange; *Sa*, safranine O; and *MB*, methylene blue. *AB620*, *AB670*, *AB670/AB620*: absorbances of cationic phthalocyanine dye astra blue at 620 nm, 670 nm, and the ratio of these absorbances, respectively. *DR81* (Direct red 81), *DB1* (direct blue 1), and *DB75* (direct black 75): absorbances of direct dyes at λ_{max}. *O/C*, *C1*, *C2*, *C3*, *C4*: electron spectroscopy for chemical analysis (ESCA) values. S^-, T^-: surface charge and total charge of fibers; *Hem*, hemicelluloses; *Glc+Man*, glucose and mannose; *Xyl*, xylose; *K*, kappa number; K_{corr}, kappa number corrected for hexenuronic acids (*HxU*); *C=O*, carbonyl groups; *Br*, brightness; *Bs*, brightness stability; *Visc*, viscosity

errors may lead to misinterpretation of the other principal components due to the high noise content in the data mentioned. The first principal component (PC1) explains 44% of data set variance, while the second principal component explains 23% of the data set variance. The score plot (Fig. 1) therefore presents 67% of all the information contained in the whole data set consisting of 26 variables. In the rest of variance (33%), there predominates the noise due to experimental errors. The sample bleached by oxygen (O) is on the right side of the figure. All other samples are to the left of the sample bleached by oxygen. The numbers in brackets are the kappa numbers of the samples. It is clear that the samples are ordered along the first principal axis according to the kappa number. One can also notice that the samples bleached by hydrogen peroxide (P) show a monotonous tendency, while this is not the case with the samples bleached by ozone (Z). The corresponding loading plot is presented in Fig. 2. There are several groups of variables scattered around the plot. The variables that are far from the center of origin are important for interpretation of the results. The variables close to the origin (like xylose, glucose + mannose, and hemicellulose content) are not relevant in this case. On the right side of Fig. 2, close to the axis (PC1) is a group of variables containing the kappa number and cationic dyes. On the left side, close to the axis, are brightness and brightness stability. This is not surprising, because a higher kappa number for a pulp sample means lower brightness and brightness stability, and vice versa. The first principal component is obviously related to the presence of lignin (kappa number, brightness, brightness stability, cationic dyes selective for lignin) on the fiber surface. This is in agreement with the pattern in Fig. 1 described above. Such a result is not surprising, because one of the purposes of bleaching is to obtain higher brightness in the pulp, which is achieved by the removal of lignin.

The meaning of the axis PC2 can be elucidated in a similar way. At the bottom of Fig. 2, close to the axis, are astra blue absorbances, while direct red and direct blue are also not far away. On the opposite side, at the top of the figure, is the total charge of the fibers (T^-). This means that a higher total negative charge in fibers generally decreases the ability of the dyes mentioned above to bind to the fibers.

Based on this information, we can conclude that the second principal component is related to a property or properties that enable these dyes to bind to the fiber sur-

face, or better, inhibit them from doing so. Because these dyes bind to hemicellulose and cellulose respectively, the position of a sample along PC2 indicates the presence or absence of cellulose and hemicellulose on the fiber surface and its charge. The curve of the peroxide-bleached samples in Fig. 1 indicates that the number of binding places for these dyes on the fiber surface is decreased by a higher degree of bleaching. On the other hand, the curve of the ozone-bleached samples shows first a decrease in the number of binding places, while at higher levels of bleaching the number of binding places is increased again. This may indicate that at a certain degree of bleaching another process is started that makes more cellulose and hemicellulose available to the dyes.

Figure 2 also represents some other relations between fiber characteristics. For example, the kappa number which contributes most to the first principal component in the PCA plot in Fig. 2 only slightly affects the second principal component followed by viscosity of fiber carbohydrates, the contents of hexenuronic acids, and the C4 (ESCA) data that represent the content of carboxylic carbon in acids, esters, and lactones in the 10-nm-thick surface layer of the fiber sheet. A number of characteristics are negatively related to the lignin content of fibers: the brightness of fibers, their brightness stability, their content of carbonyl groups, the C2 (ESCA) data representing C-O structures in alcohol, phenol, ether, ester, and lactone groups in the 10-nm-thick surface layer of the fiber sheet, the C3 (ESCA) data representing the carbonyl and acetal groups in the 10-nm-thick surface layer of the fiber sheet, as well as the O/C ratio, which is the ratio of oxygen to carbon contents in the 10-nm-thick surface layer of the fiber sheet. The content of hemicellulose, expressed as glucose + mannose or as xylose content of the fibers, as well as the fiber charge, correlate with the lignin content only to a small extent. Cationic dyes that were earlier proved to be selective for lignin[12] are grouped near positions representing the kappa number and the C1 (ESCA) data.

Discussion

In Fig. 2, it is obvious that kappa number, lignin-selective staining, and C1 (ESCA) data do not coincide. The main reason is that they measure different features. The kappa number measures the bulk content of lignin, i.e., of all aromatic structures and double bonds in fibers.[21,22] On the contrary, C1 $(ESCA)^2$ measures the content of oxygen-free carbons in the 10-nm-thick surface layer of the fiber sheet. These are, e.g., the C_1, C_2, and C_6 atoms in the aromatic moiety of the lignin structure (in guaiacyl groups also the C_5 atom); plus some minor oxygen-free structural features observed in cinammyl, phenylcoumarone stilbene, and pinoresinol groups, carbon atoms involved in β-1, β-5′, β-β′, 5-5′ and similar oxygen-free bonds in lignin (cf. Fig. 3), as well as the methyl carbon in rhamnose residues and the C_4 carbon in hexenuronic acids in hemicellulose. Thus, kappa number measures all aromatic lignin structures,[21,22] i.e., both

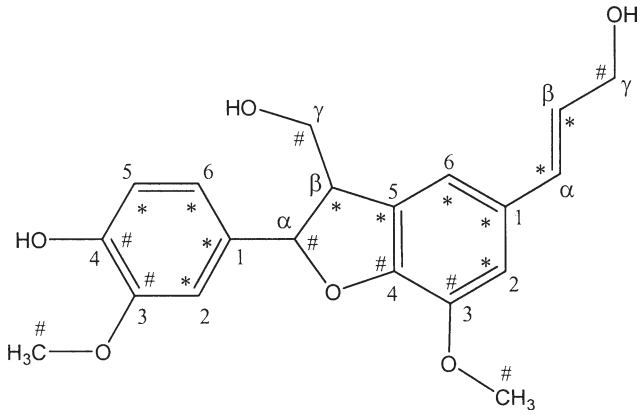

Fig. 3. Illustration of C1 (*) and C2 (#) carbons in the structure of dehydroconiferyl alcohol. C1 and C2 carbons appear in the carbon spectra of ESCA

the nonpolar and polar (hydrophobic and hydrophilic) moieties of the lignin structure in bulk fiber, whereas C1 (ESCA) measures only the nonpolar (hydrophobic) part of the lignin structure in the 10-nm-thick surface layer of the fiber sheet. However, that does not mean that C1 (ESCA) is an aromatic marker, but rather it reflects the fact that most carbons in fiber that are not bound to oxygen belong to the aromatic moiety of the lignin structure contained in that fiber.

These differences enable us to understand some other features related to the PCA axis PC2 in Fig. 2. The position of C1 (ESCA) in Fig. 2 indicates that the results related to nonpolar (hydrophobic) groups in tested fibers are positioned on the negative section of the PC2 axis. The results related to polar (hydrophilic) groups in the tested fibers – i.e., oxygen-containing functional groups represented by the O/C ratio, or the C2, C3, and C4 (ESCA) data, the content of hexenuronic acids, the content of total or surface charge – all of them are positioned on the positive part of the PC2 axis, more distant from the C1 (ESCA) data than the kappa number, which measures both the polar and the nonpolar components of lignin. In our case, the PC2 axis in Fig. 2 thus represents some measure of polarity (i.e., hydrophilicity and/or hydrophobicity) of functional groups in fibers.

The position of data for the contents of hemicellulose and for (hydrazine-reactive) carbonyl groups in tested fibers is rather surprising. For the carbonyl groups the reason could be their involvement in intramolecular hydrogen bonds leading to the less polar cyclic structures. But what about hemicellulose? According to its position in Fig. 2, its quantity as such does not seem important. In its surface accessible to the dyes, however, its hydrophobic regions are of some importance for selective dyeing. The curves of the peroxide-bleached and/or ozone-bleached samples in Fig. 1 might thus reflect the hemicellulose substructures that are modified or removed under the influence of these oxidants.

If kappa number is corrected for the content of hexenuronic acids, then its position in Fig. 2 is moved

slightly toward the position of the C1 (ESCA) data, indicating on the one hand that the information about hexenuronic acids in the kappa number represents only a minor amount of information in the present case. On the other hand, the direction of this movement is in line with the more polar character of hexenuronic acids than that of lignin.

In view of the above conclusions, the PCA loading plot in Fig. 2 helps us rationalize the position of dyes used for selective staining of fibers. Cationic dyes, staining selectively the lignin component of the fibers, are positioned with respect to the PC2 axis between the positions of kappa number and C1 (ESCA) data, somewhat closer to the position of kappa number. This indicates that the tested cationic dyes do not interact preferentially with the nonpolar moiety of the aromatic structure of lignin, but rather with some of its polar moieties. These could be either the aliphatic hydroxyl groups of the phenylpropane lignin structure, or the phenolic OH groups in it. If the former were the case, then these dyes should also interact well with carbohydrates, which is not the case. These and other considerations[12,13] enabled us to draw the conclusion that the tested cationic dyes most probably interact with the phenolic groups of lignin. Their position with respect to the PC2 axis *between* the positions of kappa number and C1 (ESCA) data and *not* on the other side of the position of kappa number suggests that the hydrophobic component of the aromatic system is involved in this interaction to some degree as well.

Surprisingly and contrary to general opinion,[23] according to Fig. 2, these positively charged cationic dyes as well as the astra blue dye do not bind appreciably to the negatively charged carboxylic groups at pH 5, although the dyes as well as the carboxylic groups of uronic acids are largely (to >90%) charged at this pH level. The only staining result that correlates well with the content of anionic groups in fibers is the ratio of absorbance of the astra blue dye at 670 and 620 nm.

In the PCA loading plot in Fig. 2, the direct dyes are positioned away from other data. This is not surprising, because any other measure of accessible pure cellulose surface in fibers is lacking here. The observations and conclusions that can be drawn from the PCA loading plot in Fig. 2 enable us to arrive at some additional conclusions. Taking into account the simple fact that neither cationic dyes, selective for lignin, nor cationic phthalocyanine dye, selective for hemicellulose, correlate well with the charge of fibers, we can conclude that the great majority of interactions between fibers and dyes are not realized through ionic interactions but primarily through hydrogen bonds, and, to a lesser extent, through other interactions, including hydrophobic ones. Here, the dyes can be divided into two groups:

1. Weak bases, which can be bound only to strongly acidic groups on fiber surfaces. That means that cationic dyes (crystal violet, acridine orange, ethyl rhodamine, safranine O, and methylene blue), having a delocalized positive charge in their molecular structure and electron-rich substituted amino groups at the periphery, can be primarily bound to phenol groups of lignin, together with some interaction with other components of the aromatic system of lignin, which is why they are selective to lignin.
2. Stronger bases, which can be bound to strong as well as to weak nonionized acidic groups on the fiber surface. The substituted amino groups of the phthalocyanine astra blue dye, as well as sulfonic and amido groups of direct dyes, have such a basic character. They can be bound to hydroxyl groups of hemicellulose and cellulose. In these cases, the structure of dye molecules is important: long, ribbon-like molecules of direct dyes suit cellulose more than hemicellulose; round and flat phthalocyanine dye obviously suits hemicellulose to a greater extent. In this respect, the shape of the hydrophilic as well as of the hydrophobic domains in these polysaccharides seems to be important and the dyes that should be selective for them have to fit their shape.

Kappa number, the C1 (ESCA), and selective staining with tested cationic dyes do not all measure the same characteristics. During kappa number determination, the permanganate reacts with all aromatic structures and double bonds throughout the fibers.[21,22] C1 $(ESCA)^2$ measures only the oxygen-free carbons of a very thin surface layer in the fiber sheet that is approximately 10 nm thick,[2] which is approximately 16 molecular layers from the surface of the sheet. The method of selective staining, on the other hand, provides only data about the actual fiber surface accessible to a dye in water solution.

Conclusions

Principal component analysis (PCA) simplifies the understanding of the relationships between fiber characteristics, especially when measured by different methods. In our case, the PC1 principal component reflects the lignin content in fibers and its consequences for fiber characteristics and interactions with dyes. The PC2 principal component reflects the differences in polarity (hydrophilicity vs hydrophobicity) of functional groups and its importance for the interaction with dyes.

The tested methods of measuring the lignin contents of fibers (kappa number, C1 (ESCA), selective staining), provide similar but not equal results, because they measure different parts of lignin [kappa number: all aromatic and double bonds in the bulk of the fibers; C1 (ESCA): carbons not bound to oxygen in the 10-nm-thick surface layer of fiber sheet; selective staining: phenolic groups accessible for the water solution of the dye].

The tested methods of measuring the quantity of anionic groups in fibers (total charge, surface charge, C4 (ESCA), and hexenuronic acids) also provide similar but not equal results. The observed differences were expected, because we know the mechanisms by which the methods act.

Contrary to expectations, staining results using tested cationic dyes did not correlate with the quantity of anionic (mainly carboxylic) groups in fibers, regardless of whether the dyes are selective for lignin or hemicellulose. Hydrogen

bonding and hydrophobic interactions seem to overrule ionic interactions between dyes and fibers. The only exception is the ratio of peak heights at 670 and 620 nm of the astra blue dye.

The PCA loading plot confirms that the dyes found previously to be selective for lignin are indeed selective for lignin and the dyes found previously to be selective for hemicellulose are also selective for hemicellulose. To assess the results of staining of tested fibers with direct dyes, an independent measure of accessible pure cellulose surface is needed.

The method of selective staining offers reagents that can measure a series of interactions that cannot be otherwise directly determined. It provides an insight into the activities on fiber surfaces during different processes, e.g., fiber delignification and bleaching processes, refining, paper sheet formation, as well as recycling processes; all of them are important for developing fiber surface activity. With additional evaluation of this method, e.g., comparison with the physical properties of fibers, the method of selective staining could be used as a direct method for testing fiber surface characteristics.

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