The surface charge of regenerated cellulose fibres

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Abstract In this paper the influence of charged species on the sheet strength of viscose fibres was investigated. Four samples of chemical modified viscose fibres, as well as a reference fibre were studied. The swelling of these viscose fibres and the breaking length of hand sheets have been determined. Comparing the results, the influence of both, swelling and surface charge on the bonding force, is evident. The allocation of the charges, induced by cationic starch and Carboxymethylcellulose, has been analyzed by Titration, attenuated total reflection spectroscopy (ATR) and X-ray photoelectron spectroscopy (XPS). Titration was used to make a first estimation of the charge distribution within the fibre. Using ATR and XPS, more detailed information about the surface charge has been achieved. All measurement methods showed a significant amount of charge on the fibre surface.

Keywords Regenerated cellulose · Titration · XPS · ATR · CMC

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Introduction

Paper strength arises from the strength of the single fibre–fibre bonds, as well as from the strength of the fibres themselves. According to Lindström et al. (2005) there are five types of interactions that determine the specific joint strength in the contact zone between the fibres: mechanical interlocking, interdiffusion, coulomb interaction, van der Waals forces and hydrogen bonds. Since wet kraft pulp fibre surfaces are rough and very soft, they adjust towards each other during the drying process. Therefore, an interlocking mechanism occurs. Paper fibres have fibrils which increase the strength of the fibre–fibre joint by mechanical entanglement. Interdiffusion is another mechanism for joint formation between fibres. Thereby, molecules from opposite surfaces migrate across the interface to create linkages between the surfaces. Since there are always charges, as well as OH groups on paper fibres, coulomb interaction and hydrogen bonds contribute to fibre–fibre bonds. Besides these mechanisms, van der Waals forces will

develop between the surfaces. In contrast to kraft pulp fibres, viscose fibres are smooth. Fibrils are arranged in such a way, that no fibrillation occurs by mechanical stress (Götze 1967). Therefore, beating has no effect on the surface roughness of viscose fibres. Thus, there is no mechanical interlocking. In addition, there are no hemicelluloses or lignin in viscose fibres. They are pure cellulose fibres. Viscose fibres typically have only low surface charges which can be changed by chemical modification. Consequently, viscose fibres are a good model for paper fibres. An investigation of specific bonding mechanisms is possible by using viscose fibres.

Since viscose fibres are rigid fibres, they hardly come into close contact during drying (Young 1972). This is the reason why viscose fibres turn out to give a weak and fluffy sheet with little inter-fibre-bonding. Nevertheless, bonding strength can be improved by using additives like carboxymethylcellulose (CMC) which results in an increase in charge density (Duker and Lindström 2008). This was found for CMC grafted softwood pulp. Paper strength was improved, however, only minor effects on the sheet density were seen (Laine et al. 2002). A similar result is achieved by adding cationic starch, a polyelectrolyte, to the fibres. This method is already known for improving the retention and dry strength of paper (Kontturi et al. 2008). In both cases, charges are induced on the fiber surfaces which helps to get the fibres in molecular contact to each other. But charges not only improve the coulomb interaction, they also lead to enhanced swelling. Swelling itself makes the fibres more flexible. The surface hardness decreases with increasing swelling (Persson et al. 2013). This is why improved swelling will result in closer contact between the fibres during the drying process (Persson et al. 2013).

In this paper the influence of coulomb interactions on the sheet strength of viscose laboratory sheets was investigated. The addition of charged species can increase the number of charged species on the surface and swelling of the fibers. Therefore, both, fibre swelling of individual fibers and tensile strength of handsheets, were probed. The four investigated fibre samples only differ in charge. They have the same cross sections (shown in Fig. 1) and dimensions. Viscose fibres without any additives, as well as pure CMC were used as references. Furthermore, the charge allocation was analysed by several
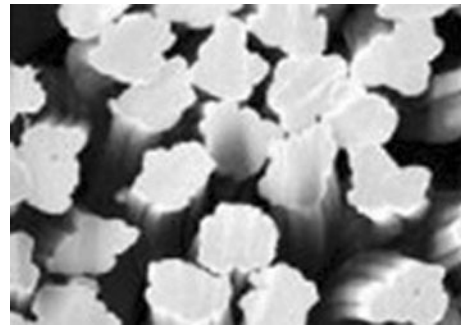

Fig. 1 SEM picture of the investigated fibres. The cross section is seen. (Bernt 2010a)

measurement methods. Titration, attenuated total reflection infrared spectroscopy (ATR), and X-ray photoelectron spectroscopy (XPS) were used to determine the surface charge, and the total charge of all four fibre types.

Experimental

Materials

Viscose fibres without any additives were used as reference (RF). Two anionic rayon fibres (AF1 and AF2), blended with different amounts of CMC were investigated, to verify the influence of anionic charge to the bond strength. In addition to these anionic fibres, two cationic rayon fibres (CF1 and CF2) were analyzed. All viscose fibres used have the same cross section (Fig. 1) with an approximate diameter of 20 μm and a length of 6 mm. The fibre samples where provided by Kelheim Fibres GmbH, Germany. Information about the incorporation of CMC is given by Bernt (2010b). Detailed specification about the formula of the cationic starch, as well as the incorporation of the starch to the used fibres are a company secret of Kelheim Fibres GmbH. A scanning electron microscope (SEM) picture of the used fibre cross section is shown in Fig. 1. The specific parameters of the fibres are given in Table 1.

Handsheets of the fibre samples were formed for ATR, and XPS measurements, and breaking length determination. The handsheets were made using a Rapid-Köthen sheet former (DIN EN ISO 5629-2:2004).

Table 1 Fibre parameters of the viscose samples used

Fibre	Titer [dtex]	Fibre length [mm]	Fibre strength [cN/tex]	Amount COOH [% w/w] Amount N [% w/w]– cationic fibre
Reference (RF)	2.34	6	22.85	0.77
Anionic fibre 1 (AF1)	2.55	6	21.58	2.60
Anionic fibre 2 (AF2)	2.56	6	20.20	3.78
Cationic fibre 1 (CF1)	1.62	6	21.50	0.26
Cationic fibre 2 (CF2)	1.70	6	20.90	0.13
CMC	–	–	–	16 (calculated value)

Methods

Swelling & breaking length

Swelling was investigated on single fibres. One end was fixed on a glass-slide with super glue. The fibres were wetted with deionised water. Using a digital microscope camera (Leica DFC 290) mounted on a light microscope (Leica Microsystem, Type 301-371.010) the fibre width was measured in dry and wet state. First the microscope had to be calibrated by using a stage micrometer. A picture of the micrometer at a given magnification was made. Then the number of pixels within 1 μm was counted. Thus, the length of 1 μm within a picture at this magnification is obtained. The fibre width was determined by counting the pixels and converting the number to μm.

Additionally, tensile strength of handsheets was measured (ISO 1924-2:2008) after sample conditioning (DIN EN 20187:1993).

Titration

The determination of the total fibre charge, as well as the amount of COOH- and N-groups was done in the following way. The pulp was transformed into the acidic protonated form and titrated with 0.1 M NaOH. A COOH amount of 0.77 % is obtained for RF (typical values are 0.3–0.5 %). According to Bernt, [1] pure

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[1] Private communication.

CMC cannot be titrated. For this reason the data for CMC was calculated. Based on a degree of substitution of DS = 0.77 a COOH amount of 16 % is obtained. Quantitative analysis of the amount of nitrogen was done according to Kjeldahl (1883).

The determination of the surface charge was done at Mondi Frantschach GmbH by adsorption of a cationic polyelectrolyte, polydiallyldimethylammonium chloride (poly-DADMAC) on pulp in sodium form. Afterwards the filtrate was titrated with a colour indicator and 0.001 N potassium polyvinyl sulfate (KPVS). Further description of the surface charge determination is given by Horvath et al. (2006), Horvath and Lindström (2007), Katz et al. (1984). This method was unapplicable for the cationic fibres. Adsorption of a cationic polyelectrolyte on a cationic fibre is not possible. Nevertheless, the total charge of the cationic fibres is obtained via the amount of N blended to the viscose suspension, as cellulose does not contain any nitrogen. Since the nitrogen atoms are added in the form of quaternary ammonium ions, one nitrogen ion corresponds to one positive charge.

ATR

Attenuated total reflection (ATR) infrared spectroscopy was done according to Gilli et al. (2009). This measurement technique was first introduced by Harrick (1960). The main advantage of ATR is that any sample without preparation can be measured. ATR uses an optical near field effect which occurs at total internal reflection. This reflection results in an evanescent wave which interacts with the sample. The penetration depth of the ATR is given by Eq. 1 (Griffiths and de Haseth 1986). The parameters in Eq. 1 needed are the refractive index n_1 of the hemispherical diamond which is the ATR crystal and of regenerated cellulose n_2; the incidence angle γ of the IR beam and the wavelength λ. The spectrum of the empty ATR unit is used as background for IR spectra of the reference and the anionic fibres. In case of cationic fibres the reference viscose fibres were used as background.

$$d = \frac{\lambda}{2\pi\sqrt{n_1^2 \sin^2 \gamma - n_2^2}} \tag{1}$$

The measurements were done on 2×2 cm sections of handsheets using a Bruker IFS 66 v/S FT-IR spectrometer. ATR measurements were done using a

single reflection unit from Specac (MKII Golden Gate). A diamond was used as ATR crystal and the incident angle was 45°. For the investigations of pure CMC, CMC was dissolved in deionized water. The received solution was dried at 50 °C for one day to gain a film which was analyzed. The spectra were evaluated using the *OPUS* software from Bruker.

XPS

The XPS data were obtained using a SPECS Phoibus 150 electron energy analyser and a non-monochromated Mg $K\alpha$ (1,253.4 eV) X-ray source. The overall energy resolution obtained was 0.8 eV. The samples (10 × 10 mm) were mounted on standard SPECS sample plates using conductive carbon tape. The samples were typically stored under vacuum for 12 h before the measurement. The pressure in the XPS analysis chamber during measurement was better than 3×10^{-9} mbar. Evaluation of the peaks was done by the CasaXPS software (Version 2.3.14dv38). Components were created and modified to achieve the best fit of the dataset considering physical correctness. The knowledge of the sample chemistry is used to limit the number of possible solutions. The total number of peaks present was limited to three for the reference and the anionic fibres. The number of peaks for the cationic fibres and for pure CMC was set to four. Additionally, the binding energy of all peaks was calibrated according to Conners and Banerjee (1995). The calibration puts the energy of the carbon C 1s peak (C1 (C–C bond)) exactly at 285 eV (see Figs. 7, 8, 9; Table 3).

Results and discussion

Swelling & breaking length

Swelling and breaking length were investigated, to verify the influence of the bonded area and the surface charge on the mechanical properties of the paper. Anionic charges can be increased by attaching CMC on to the fibres (Laine et al. 2003b). These charges turned out to be important for fibre swelling (Lindström 1980). Especially surface charges play an important role. At a given charge level, swelling is mainly influenced by the surface charge which was shown by Laine et al. (2003a). Hence, swelling of RF, AF1 and AF2 were investigated. To verify in which
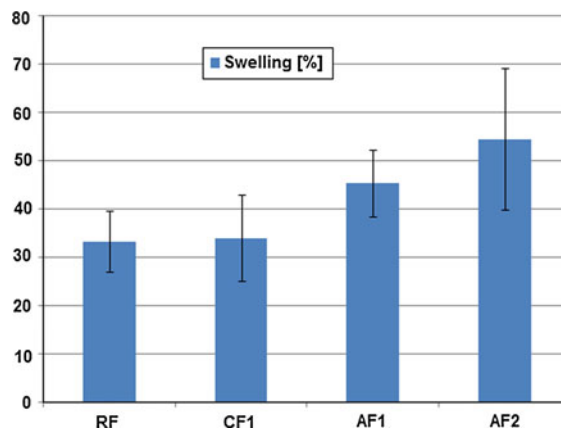

Fig. 2 Swelling of each fibre-type. The mean values of ten fibres of each fibre-type are shown
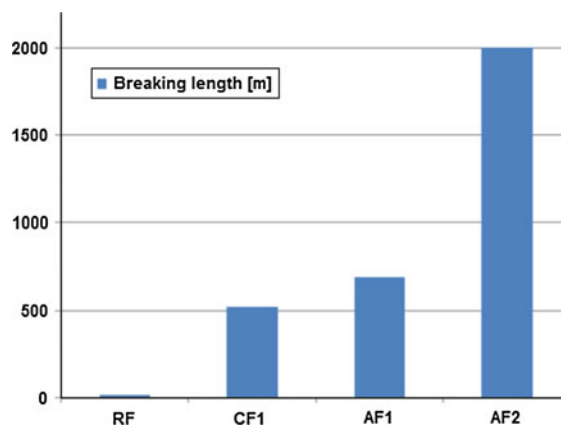

Fig. 3 Breaking length of the investigated hand sheets. No measurable value for handsheets made of RF

way cationic charges contribute to improved paper properties, the swelling of CF1 was measured as well. The swelling of ten fibres of each fibre type was investigated. The average values are shown in Fig. 2. The fibre width of RF increases in water by 33.32 %. CF1 shows a swelling of 34.08 %. There is almost no difference between RF and CF1. Apparently, cationic starch has no influence on the swelling behaviour. As expected, by adding CMC fibre swelling is enhanced. The moisture expansion of AF1 is 45.43 %. For the largest amount of CMC (AF2), swelling is 54.55 %.

Additionally to swelling of the single fibres, the tensile strength of handsheets was investigated. The results are shown in Fig. 3. Handsheets of RF are too fluffy for tensile strength measurement so no value was obtained for these samples. Adding cationic starch

to the fibres leads to handsheets having a breaking length of 521 m. This is nearly in the same range as the breaking length of AF1 which is 693 m. The highest result of 2,000 m is obtained for AF2.

Comparing the results of swelling and breaking length, the influence of charges and bonding area is evident. Compared to the reference, improved swelling was shown for the anionic fibres. Therefore, larger contact areas are possible between single fibres during the drying process. The improved tensile strength is achieved by induced surface charges and larger contact areas between single fibre–fibre bonds. A quantification of both effects is not possible. These results fit very well with the data found by Laine et al. (2002) and Blomstedt et al. (2007). Although they used kraft pulp fibers and a different method of CMC addition, an increase in swelling and tensile strength was found. For the cationic fibres the effect is different. While the swelling of CF1 is in the same range as the swelling of RF, breaking length is much higher. Since the swelling is similar, the specific bond strength must have been improved by the positive charges.

Titration

Titration was done to evaluate the charge distribution of the fibres. The results are shown in Table 2.

Regular viscose (RF) which was used as reference has a total charge of 0.17 meq/g. The charge increases with the amount of CMC which is evident in the results for AF1 and AF2. A small percentage of CMC added to the fibres leads to a huge increase in total charge.

Figure 4 shows the data from Table 2. In Fig. 4a the amount of additives versus the total charge, measured by titration is shown. The total charge of the fibres rises linearly with the amount of COOH-

Table 2 Detected charge of each fibre by Titration (total charge and surface charge) determined according to the methods described (see "Methods—Titration" section). CF2 as well as pure CMC were not titrated

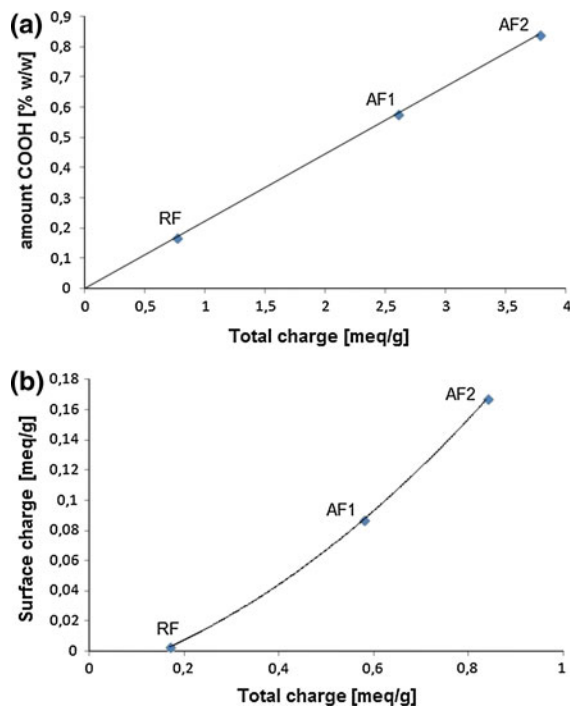| Fibre	Total charge [meq/g]	Surface charge [meq/g]
Reference fibre (RF)	0.170	0.003
Anionic fibre 1 (AF1)	0.578	0.087
Anionic fibre 2 (AF2)	0.839	0.167
Cationic fibre 1 (CF1)	0.186	n.a.

Fig. 4 Titration—evaluation of the results. Lines are just guides for the eyes

groups. Figure 4a illustrates the applicability of the measurement method. In Fig. 4b the surface charge versus the total charge is displayed. The charge of RF seems to be concentrated within the bulk due to a lack of surface charges. By adding CMC to the fibre suspension the surface charge is rising significantly. This can be seen for AF1 where the surface charge is raised by more than a factor of ten. The surface charge of AF2 is the same as the total charge of the reference. Assuming that the used polymere for surface charge determination does not penetrate into the fibre bulk, these results would mean that CMC is present in the outermost fibre layer.

In this picture no data about the CF1 fibres are shown because no surface charge could be measured for CF1 by titration.

It can be said that an increase of surface charge can be seen by adding CMC to the fibres. No clear statement about the charge distribution can be made by this data. To verify these results and for getting a better understanding of the charge distribution, ATR and XPS measurements were done. Moreover, Titration did not deliver information about the surface charge of cationic fibres which was another reason for using additional measurement methods.

ATR

Attenuated total reflection (ATR) measurements were done to verify if CMC is on the fibre surface. The refractive index of diamond is given with $n_1 = 2.42$ (Giancoli 2010), the refractive index of regenerated cellulose is $n_2 = 1.51$ (Buchholz et al. 1996; Karabiyik et al. 2009). The incidence angle in the ATR is $\gamma = 45°$. The COOH-peak was seen at a wavelength $\lambda = 1,580$ cm^{-1}. By adding these parameters into Eq. 1, a penetration depth of the evanescent wave into the viscose paper sheet of 1.3 μm is obtained.

Taking into account that the used fibres have an average diameter of 20 μm, the ATR measurements are surface sensitive to a certain extend. Therefore, it is possible to measure the CMC on and near the fibre surface. The amount of CMC attached to kraft pulp

fibres can be estimated by integrating the corresponding peaks of the IR spectra. Gilli et al. (2009) have shown that the amount of CMC correlates well to the calculated peak area. In contrast to GILLI, the aim was not to show that ATR can be used to determine the amount of CMC. The goal was to verify if CMC is predominantly on the fibre surface. Besides, CMC is not attached to the used viscose fibres, but blended to the viscose liquid before spinning. Therefore, CMC should be uniformly distributed. Anyway, the results of the Titration lead to the assumption that CMC diffuses onto the surface to some extent after spinning. Figure 6 shows the peak area versus the amount of COOH. The corresponding CMC peak is growing linearly with the amount of the additive.

Figure 5 shows the ATR spectra of pure viscose handsheets. In Fig. 5a the spectra of classic viscose as
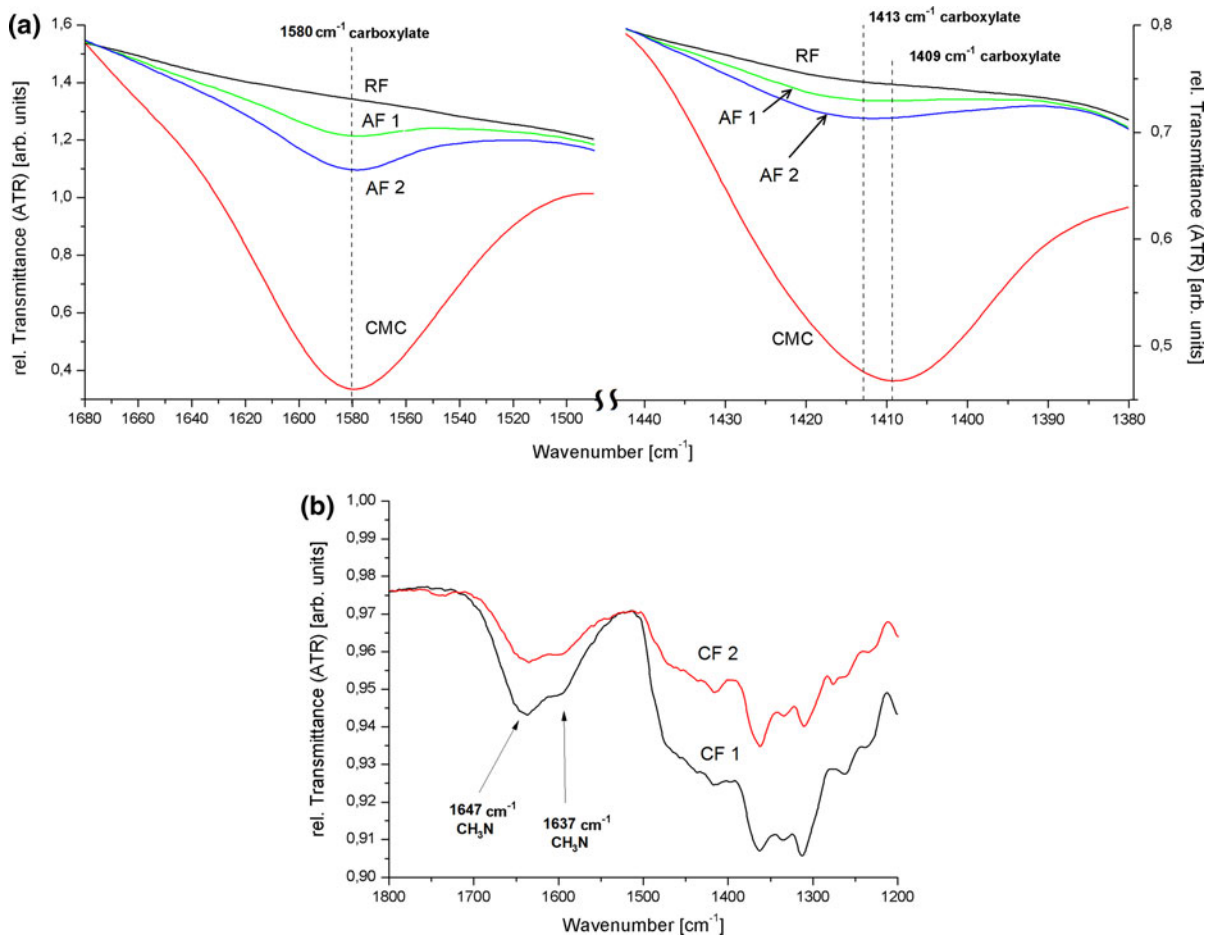

Fig. 5 ATR spectra of the used samples. **a** shows the spectra of pure CMC, the CMC blended fibres and the reference. **b** shows the spectrum of the cationic fibres. RF—reference fibre, AF1— anionic fibre 1, AF2—anionic fibre 2, CF1—cationic fibre 1, CF2—cationic fibre 2, CMC—pure carboxymethylcellulose

reference, of the anionic fibre 1 (AF1), of the anionic fibre 2 (AF2), and of the pure CMC are shown. The background spectrum of the ATR crystal served as the reference spectrum (see "ATR" section). The spectra were normalized to the intensity of the RF spectrum and show the relative transmittance of the IR beam versus the wavenumber. RF represents the reference without CMC. AF1 and AF2 include 2.6 and 3.8 % of COOH as seen in Table 2. Peaks representing CMC are seen at 1,580 and 1,413 cm^{-1}. A slight shift of the 2nd peak to 1,409 cm^{-1} can be seen for pure CMC.

The spectrum of cationic fibre 1 (CF1) is seen in Fig. 5b. There are peaks, corresponding to the cationic starch at 1,647 and 1,637 cm^{-1} which were obtained only by using the RF spectrum as the reference spectrum. Hence, these spectra show the difference between RF and CF1, CF2. Without any cationic starch, a flat line would be seen in this region. These peaks result from the quaternary ammonium group of the starch and are growing with the amount of starch. In order to facilitate the interpretation of the data, the spectrum of CF1 was normalized with respect to the spectrum of CF2.

X-ray photoelectron specroscopy

In order to gain more information about the surface charge of the investigated fibres XPS was used. The analysis depth of XPS for paper is in the range of 0.5–10 nm (Conners and Banerjee 1995).
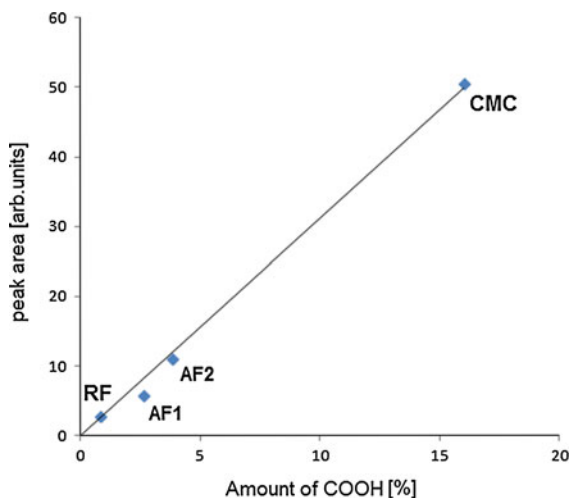
X-ray photoelectron spectroscopy (XPS) measurements of handsheets of all samples were done to gain information about the chemical composition. Knowing the amount of additives gives information about the quantity of the surface charge. A XPS-peak represents the amount of an element and the mean free path of the emitted electron. This has to be considered when evaluating the results. Information about the amount of additives was found by looking at the C 1s peak. Only this peak had a sufficiently high resolution for interpretation of the results.

Figure 7 shows the high resolution C 1s peak of the reference fibre. The relative amounts of carbon-oxygen bonds were determined from these carbon 1s spectra using peak-fitting, (Fras et al. 2005; Freudenberg et al. 2005; Johansson et al. 1999). The C 1s peak of RF can be fitted by three peaks (C1, C2, C3). Table 3 shows the peak position and the atomic concentration percentages (ACP) of the fits. While the position of the peak is equivalent to the binding energy, the ACP corresponds to the peak area of each fit. Hence, the ACP correlates to the amount of a component.
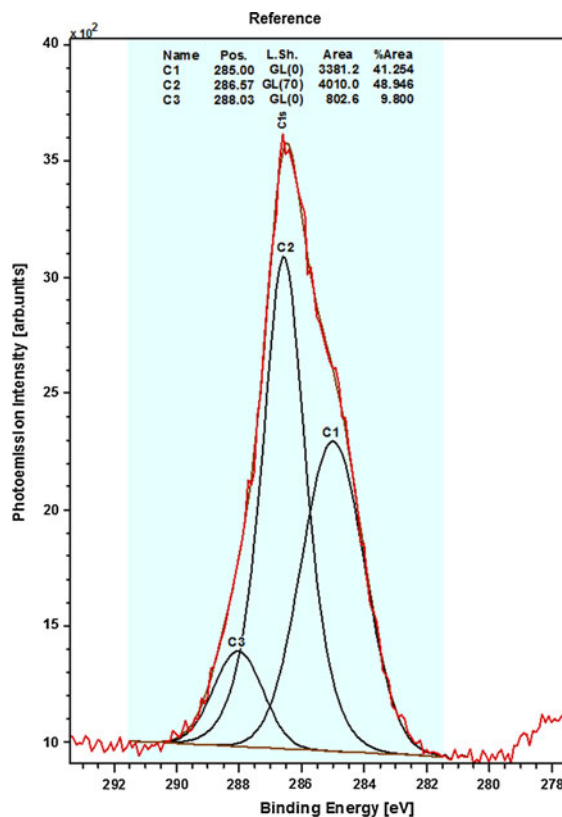

Fig. 6 Integrated peak area from ATR–IR measurements as a function of the CMC amount. The peak at 1,580 cm^{-1} was used for integration

Fig. 7 XPS spectra and fit of RF

Table 3 Result of XPS measurement—binding energys and atomic concentration percentages

Peak	Reference fibre		Anionic fibre 1		Anionic fibre 2		CMC	
	BE	At%	BE	At%	BE	At%	BE	At%
C1 [C–C]	285.00	41.25	285.00	28.64	285.00	32.75	285.00	4.51
C2 [C–O]	286.57	48.95	286.68	56.13	286.63	34.75	287.65	42.29
C3 [O–C–O / C=O]	288.03	9.80	288.15	15.24	287.25	32.50	289.04	25.41
C5 [C=O]	–	–	–	–	–	–	290.30	27.79

	Cationic fibre 1		Cationic fibre 2	
	BE	At%	BE	At%
C1 [C–C]	285.00	35.15	285.00	38.45
C2 [C–O]	286.60	16.03	286.50	13.63
C3 [O–C–O / C=O]	287.42	16.53	287.00	29.22
C4 [C–NR_3]	286.08	32.29	285.13	18.71
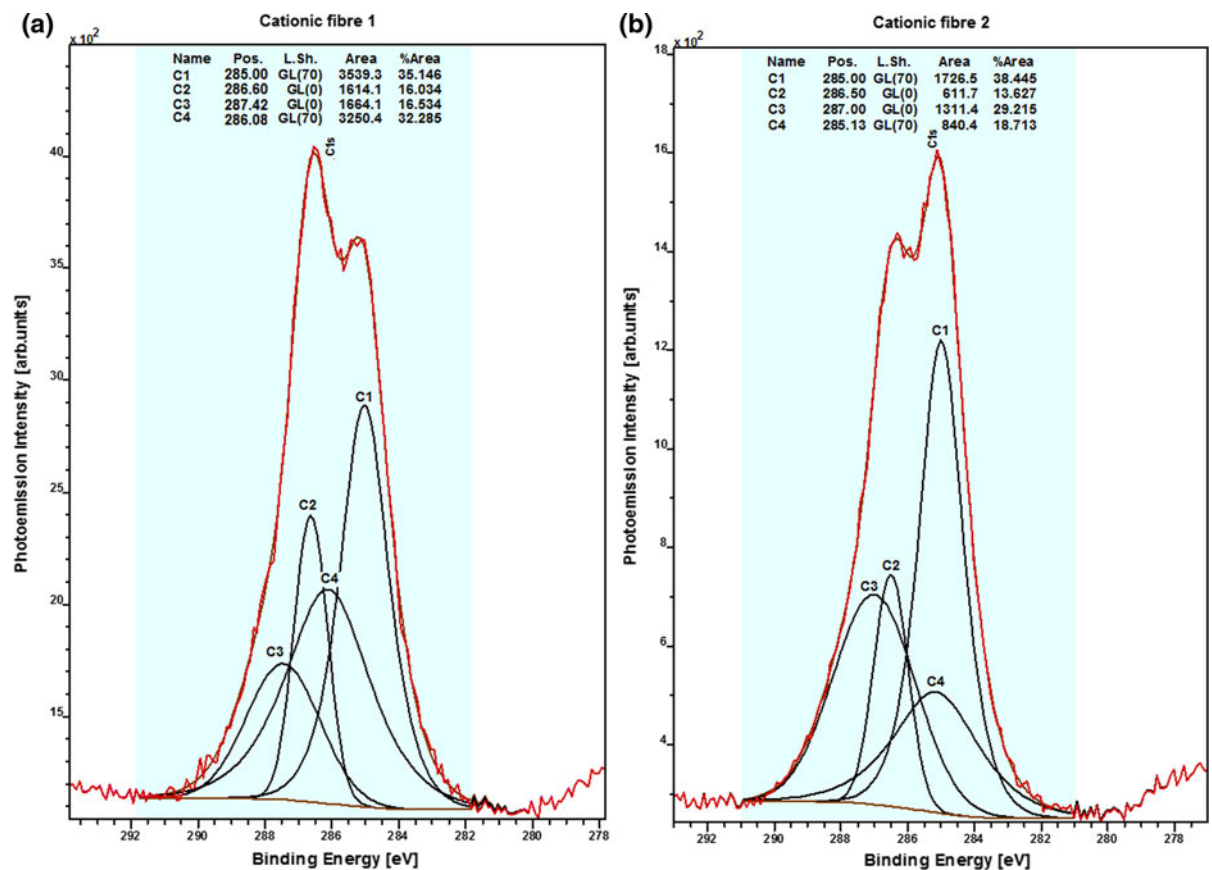
Fig. 8 XPS spectra and fit of CF1 and CF2

RF has peaks at 285, 286.57, and 288.03 eV attributed to C1 (C–C), C2 (C–O) and C3 (O–C–O and/or C=O). These results fit in very well with the literature (Conners and Banerjee 1995).

Figure 8 shows XPS spectra of CF1 (Fig. 8a) and CF2 (Fig. 8b). An additional peak (C4) is needed to fit the C 1s peaks of these fibres. This peak originates from the C–NR₃ species of the starch. It can be seen

that the spectrum changes depending on the amount of cationic starch. The ratio of C1, C2 and C3 changes only slightly compared to C4. C4 decreases from 32.3 to 18.7 At% which is a reduction by nearly half. Apart from that there is almost no difference between the peak positions of CF1 and CF2. This result reflects the quantity of cationic starch in a good way. CF2 has only half of the amount of starch compared to CF1 which fits with the result very well.

The results of AF1 and AF2 are shown in Table 3. Similar to RF the spectra of the anionic fibres can be fitted by three peaks. Nevertheless, due to a change in chemistry the shape of the peaks changes. While the peak position is nearly the same for all investigated fibres, the atomic concentration changes for AF1 and AF2.

Finally, pure CMC was investigated. Figure 9 exhibits the spectra of the CMC (Fig. 9a) sample and of AF2 (Fig. 9b). A substantial difference can be seen comparing these two spectra. The amount of C–O, O–C–O, and C=O bonds is predominant. Hence C1 becomes the smallest peak. Due to the hight amount C=O bonds in pure CMC (as compared to AF2) the new C5 peak is detected. The binding energy of this new peak (290.30 eV) is in the range found in the literature for C=O (Beamson and Briggs 1992) or rather C(=O)OH (Conners and Banerjee 1995).

The changes of the C3 peak is of major interest for the anionic fibres, because the amount of CMC is reflected by this peak. Hence, the C3 peak of all samples is pictured in Fig. 10. C3, representing the amount of O–C–O and C=O bonds grows with the extend of CMC. The smallest C3-peak can be found for RF, followed by AF1. The CMC sample has the largest C3 peak area as C5 has to be added to C3, because both peaks (C3, C5) represent the COOH group. These results fit very well with the titration data. It can be assumed that C3 represents the amount of acid-groups. As can be seen in Fig. 10, the cationic fibres show a large C3 peak area as well, resulting
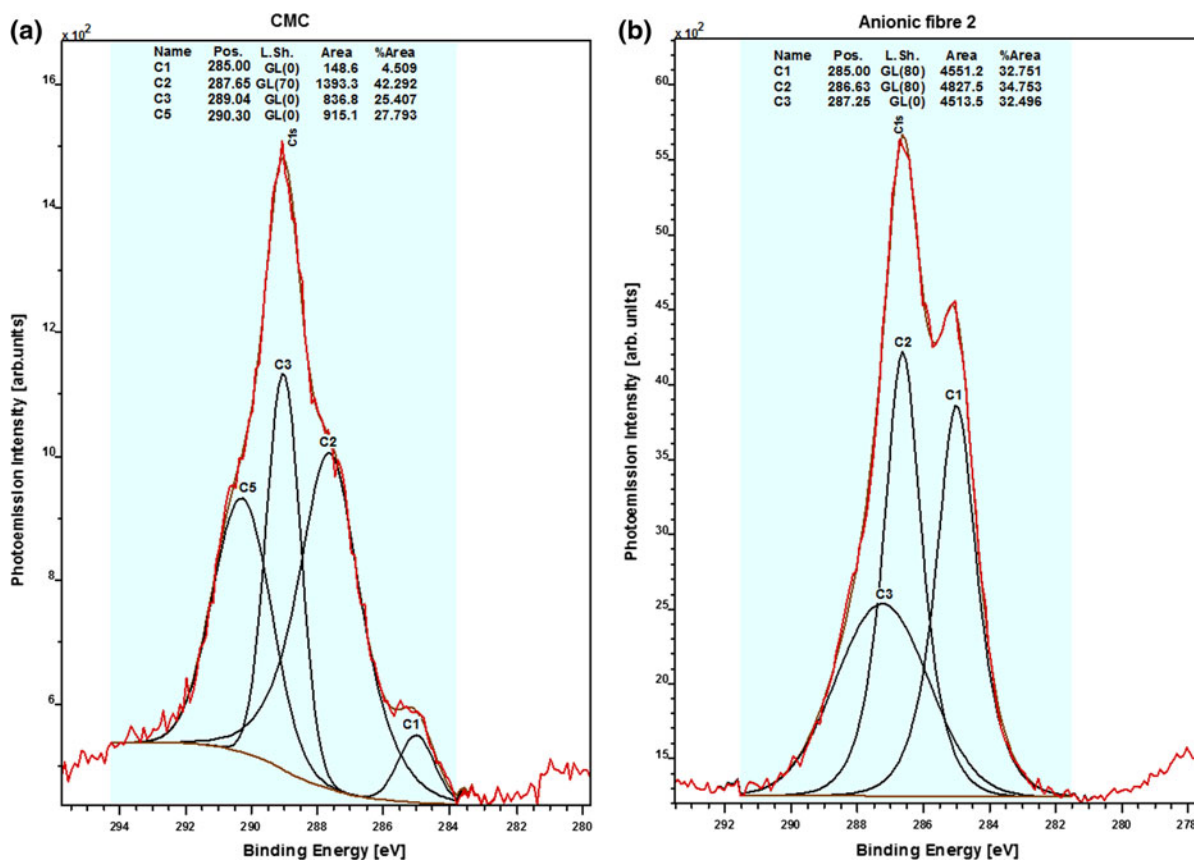

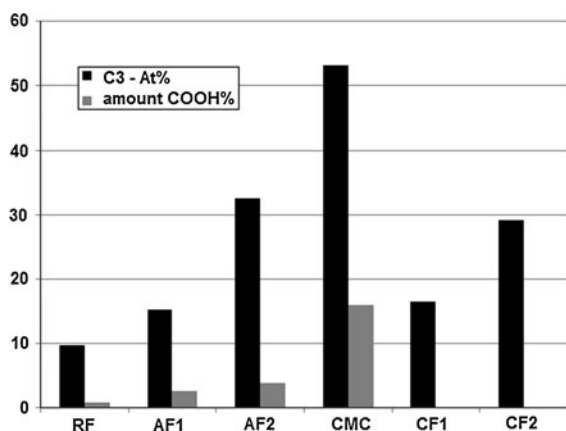**Fig. 9** XPS spectra and fit of CMC and AF2

Fig. 10 Comparison of C3 peak area and the amount of COOH groups—the peak grows with the amount of COOH groups. C5 of pure CMC was added to C3 because both peaks represent the total COOH amount

from additional O–C–O groups of the starch. Hence, the C3 peak area is not only due to anionic charges. Nevertheless, it is an indicator for anionic surface charges. This circumstance has to be considered when evaluating the data of the cationic fibres. Although CF1 and CF2 have a larger C3 than the RF, in total these fibres are cationic. The cationic species lead to the additional C4 peak which is only found for these fibres.

A comparison between the data provided by Kelheim Fibres GmbH and the COOH groups detected by XPS is also shown in Fig. 10. From RF to AF1 the increase in peak area is just a slight one although the amount of COOH rises from 0.77 to 2.60 %. If the COOH amount is boosted up to 3.78 %, the measured C3 peak increases significantly. The pure CMC sample (COOH amount of 16 %) leads to a measured concentration measured by XPS of 53.2 % (see Fig. 10). Apparently the C3 peak does not increase linearly with COOH concentration. The interpretation of these results has to be done very carefully. The investigated spot diameter on the sample surface is in the range of 4–5 mm. Because of the different fibre properties, the hand sheets have shown different flocculation. Therefore, a not assignable difference in the amount of investigated fibres measured by XPS may occure. Accordingly, the ACP has to be standardized to the number of fibre in the investigated spot which is not feasible. Therefore the amount of additives detected by XPS can not be established quantitatively.

Summary

In this paper fibre swelling, breaking length, and surface charges were investigated, to gain insight into the effect of charges on tensile strength.

By titration, an increase of surface charges due to anionic additives (CMC) is seen. Additional ATR and XPS measurements were done to verify the titration results.

The penetration depth of ATR measurements for the fibres used is around 1.3 μm. It was shown that the corresponding IR peaks are linearly growing with the amount of CMC and cationic starch. According to the ATR results, additives are present in the outermost fibre layer. This result was also confirmed by XPS.

While the current results clearly show that charged specieces are on and close to the fibre surfaces, no information about the charge distribution across the fibre diameter could be obtained with the analysis methods used. Anionic fibres show the highest breaking length which correlates to the increased swelling and increased surface charge. Cationic fibres also show increased breaking length compared to the reference fibres. However, in this case no increased swelling was found. Therefore, in this case the increased breaking length is mainly due to the increased surface charge.

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