Solid-state NMR method for the quantification of cellulose and polyester in textile blends

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ABSTRACT

The valorization of cellulose rich textile waste is promoted by the development of a novel solid-state NMR method for the quantification of cellulose and polyester in textile blends. We applied ^{13}C CP-MAS NMR as a tool for the quantification and structural characterization of cellulose in cotton polyester blends. Gaussian functions were used to integrate the spectra obtained from a set of calibration standards in order to calculate a sigmoidal calibration curve. Acid hydrolysis was chosen as a reference method. The results demonstrated that solid-state NMR enables a reliable determination of cellulose and polyester in both preconsumer and postconsumer waste textiles and suggests a possible extension of the concept to blends of man-made cellulose fibers (MMCFs) and polyester.

1. Introduction

The advent of fast fashion combined with a rapidly growing population has triggered textile waste to increase drastically (Bhardwaj & Fairhurst, 2010; Tokatli, 2007). In Sweden, an average consumer produces about 8 kg of textile waste annually, in the United States almost four times as much (Ekström & Salomonson, 2014). After a lifetime of only a few washing cycles (Joy, Sherry, Venkatesh, Wang, & Chan, 2015), most garments are disposed on landfill or burnt instead of being recycled (Briga-Sá et al., 2013). Cellulose fibers represent one of the major components in textile waste. Global warming has however made their production increasingly challenging; in particular, cotton farming has led to an excessive exploitation of natural resources. At the same time, the growing amount of cellulose based textile waste cannot be accessed as an alternative feedstock of raw-material to produce new cellulose fibers. Its valorization is prevented by a multitude of different other components involved, which can neither be identified efficiently during sorting nor be separated fully in the recycling stage.

Cellulose polyester blends are one of the most prominent multi-component garments on the market aiming to tailor material properties regarding moisture uptake, wrinkle resistance, and wearing comfort. Once worn out, they are difficult to recycle within one process as both cellulose and polyester show an entirely different behavior when it comes to hydrophilicity and thermal stability. These distinct properties nevertheless enable them to be separated and reprocessed in different streams such as depolymerization/repolymerization (Gruntfest & Turner, 1974; Oakley et al., 1992) or respinning (Negulescu, Kwon, Collier, Collier, & Pendse, 1998; Brinks et al., 2013; Flynn & Stanev, 2016). As for any process, a proper analytical toolkit for material identification and quantification is crucial to these recycling strategies.

Lab scale experiments tend to apply gravimetric approaches to determine the content of cellulose and polyester in textile blends (Lv, Wang, Zhu, & Zhang, 2015; Rodgers & Beck, 2009; Silva, Wang, & Byrne, 2014). In doing so, both components first require separation involving the degradation of either component through acid hydrolysis (Ouchi, Toida, Kumaresan, Ando, & Kato, 2010) or alcoholysis (Oakley et al., 1992). Afterwards, both the degradation product and the residue are isolated and weighed to enable a subsequent calculation of the initial blend concentration.

On the contrary, near infrared (NIR) spectroscopy has extensively been studied for textile industry (Rodgers & Beck, 2009; Cleve, Bach, & Schollmeyer, 2000; Tincher & Luk, 1985; Blanco, Coello, Iturriaga, Maspoch, & Bertran, 1994). It is non-destructive and allows online measurements once a broad data set has been established (Blanco et al., 1994; Cleve et al., 2000). The resulting signals are strongly dependent on the nature of the sample surface comprising parameters such as particle size, moisture content, color, brightness, and finishing agents applied (Rodgers & Beck, 2009; Blanco et al., 1994; Cleve et al., 2000).

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Obtaining reliable results requires baseline corrections for all these individual factors posing challenges onto very heterogeneous samples such as textile waste. An underlying problem of all NIR methods in general is their strict restriction to surface measurements, which makes them unable to predict material compositions accurately in case of multilayer garments, or fabrics composed of different fibers on their face and reverse sides. In this context, a precise determination of material components based on diffuse reflectance spectroscopic techniques is, strictly speaking, not possible.

Although nuclear magnetic resonance spectroscopy (NMR) has always been a common tool in the structural analysis of cellulose, it has not been studied for the quantification of cellulose fibers in textile blends yet. Compared to NIR techniques, solid state NMR might show less efficiency and a lower sample throughput, but enables more precise measurements, which are not subjected to interferences such as different particle sizes, dyes, and surface structure. CP-MAS NMR spectra in particular have helped to gain fundamental insights into the crystallinity of cellulose and hemicelluloses. Crystalline and amorphous regions can be determined through peak deconvolution using Gaussian or Lorentzian fit functions (Atalla & VanderHart, 1999; Evans, Newman, Roick, Suckling, & Wallis, 1995; Liitiä, Maunu, & Hortling, 2000, 2003; Maunu, Liitiä, Kauliomäki, Hortling, & Sundquist, 2000; Newman, Davis, Harris, & Philip, 1996; Newman, Ha, & Melton, 1994; Park, Johnson, Ishizawa, Parilla, & Davis, 2009; Zuckerstätter et al., 2009). Comparable studies focus on the interaction of cellulose with other molecules such as water (Newman & Davidson, 2004) and urea (Holm Kristensen, Bampos, & Duer, 2004). Related approaches have also been used for polyethylene terephthalate (PET) to monitor changes in its crystallinity under various melt spinning conditions (Gabrielse, Angad Gaur, Feyen, & Veeman, 1994), and during other recycling processes (Nascimento, Dias, Menezes, & Silva, 2004).

This eventually makes solid-state NMR a promising alternative to current state-of-the art technologies as it combines non-destructiveness with improved accuracy and structural information, consequently also reducing extensive data sets requiring chemometric calibration models. The following sections present a novel solid-state NMR method to determine the concentration of cellulose in cotton polyester blended waste fabrics and provides an insight into the crystallinity of cellulose in blended waste garments. Different blend concentrations were measured by CP-MAS NMR to establish a calibration function. The approach was validated by analyzing commercially available textiles and postconsumer garments. Acid hydrolysis was used as a reference.

2. Materials and methods

2.1. Raw materials

White preconsumer cotton was supplied by Söktaş (Turkey), white preconsumer polyester (polyethylene terephthalate) by HT Sport Oy (Finland). Blended cotton polyester fabrics, 65% (2) and 50% cotton content respectively, were provided by Tekstina (Solvenia). Furthermore, 3 postconsumer samples purchased from a second hand store were analyzed. Viscose and Tencel fibers were supplied by Kelheim Fibres (Germany) and Lenzing (Austria). All materials were ground; and their dry matter content was determined.

2.2. Calibration standards

Ground cotton and polyester were mixed in a rotavapor for 3 h. The amounts were calculated according to the desired mass ratios. The calibration standards ranged from 2.5%, 10%, 25%, 50%, 75% and 90% cotton.

2.3. CP-MAS NMR

All ^{13}C NMR cellulose I spectra were recorded on a Bruker AVANCE III spectrometer with an UltraShield Plus 400 MHz magnet operating at 100.6 MHz and the use of a probe size of 4 mm. Settings: spinning speed 8 kHz, number of scans 8000, relaxation delay 5 s, CP contact time 2 ms, acquisition time 34 ms. A contact time of 2 ms was chosen to yield reasonable signal intensities of the resonances of both cellulose and PET. (cf. Figures S1-3). A variable amplitude crosspolarization ramped from 50% to a maximum amplitude of 85 kHz during contact time was used. During the acquisition period, the protons were decoupled using a SPINAL-64 1H decoupling. (Asaadi et al., 2016; Bai et al., 1998; Gabrielse et al., 1994)

The spectra of Viscose and Tencel (cellulose II) were measured using a Bruker Avance III 500 MHz spectrometer with a probe size of 4 mm. Settings: spinning speed 10 kHz, number of scans 8000–10000, relaxation delay 3 s, CP contact time 1 ms, acquisition time 27 ms. A variable amplitude crosspolarization ramped from 70% to a maximum amplitude of 80 kHz during contact time was used. During the acquisition period, the protons were decoupled using SPINAL-64 decoupling. All cellulose II samples were immersed in deionized water prior to their measurements. Moreover, the spectra of all pre- and postconsumer cotton polyester blends, pure cotton, Viscose, and Tencel were analyzed according to determine their degree of crystallinity (cf. supporting information) (Zuckerstätter et al., 2009).

2.4. Acid hydrolysis

The cotton and polyester content was determined based on the EU regulation no. 1007/2011. All blended fabrics were treated in 10 M H_2SO_4 at 95 °C between 20–30 min with a liquor to sample ratio of 100:0.2 to ensure complete dissolution of the cellulose component. Afterwards, the mixture was poured into ice water to stop the reaction. The polyester residue was filtered off, washed with water and acetone, and dried in a vacuum oven for 6 h at 50 °C. The resulting weights were compared to the initial blend concentration. The dry matter content of the starting materials and the resulting products was included in the calculation (1007)/(2011) (2011).

3. Results and discussion

3.1. CP-MAS NMR

As indicated in the introduction, CP-MAS NMR provides various information on the molecular structure of a polymer. Parameters such as peak shape, intensity, and chemical shift help to examine molecular interactions, crystallinity, and chemical compositions. Furthermore, peak areas, if used as relative intensities, can be used to quantify the molecules present in a mixture, which makes it possible to determine the composition of multicomponent garments, such as cellulose polyester blends, through the integration and comparison of certain NMR signals. Fig. 1 shows two typical NMR spectra of pure cotton and polyethylene terephthalate (PET).

Cotton fibers mainly consist of cellulose; its spectrum accordingly represents native cellulose (cellulose I) containing both crystalline and amorphous regions. The signals at 66 ppm and 68 ppm denote the C6 atom, while the peaks at 74 ppm, 75 ppm, 78 ppm describe the C2, C3, and C5 carbons of cellulose. C4 and C1 show a chemical shift ranging from 87 to 91 and 107–109 ppm, respectively. Signals at lower shifts, especially those of C4 and C6, indicate amorphous regions in the polymer. Depending on the overall extent of crystallinity in cellulose, these peak shapes can vary significantly. A higher resolution and sharper peaks usually imply a higher crystallinity, which however can be influenced by physical and chemical treatments such as swelling and pulping (Park et al., 2009; Zuckerstätter et al., 2009) Fig. 2 depicts the NMR spectra of typical C4 regions of commercially available cellulose fibers such as Tencel, Viscose, and cotton. Whereas the two peak maxima at 89.3 and 88 ppm clearly identify Tencel and Viscose as regenerated MMCFs (cellulose II) with distinct fibril surface areas (86.5
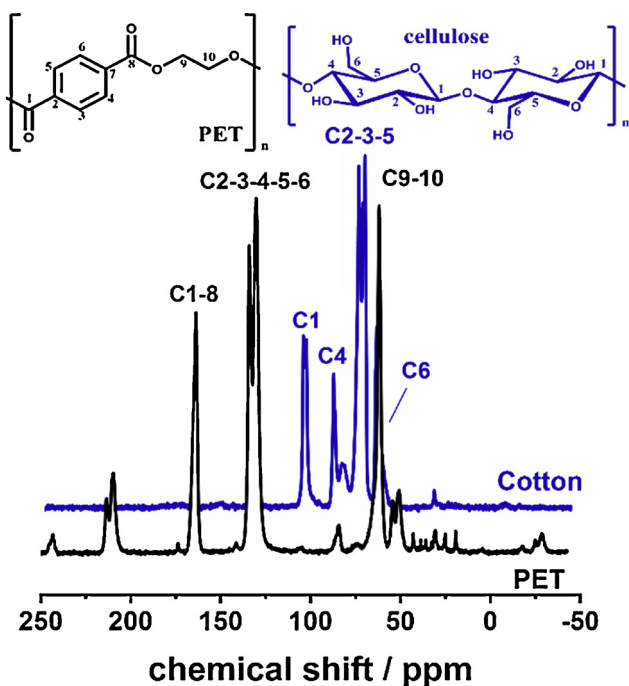
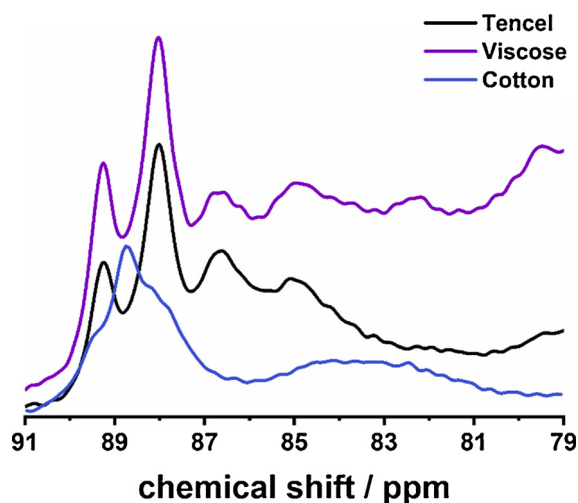**Fig. 1.** ^{13}C CP-MAS NMR spectra of PET and cotton.

Fig. 2. NMR spectra of the C4 regions of Tencel, Viscose and cotton.

Table 1

Parameters of crystallinity for the analyzed pre and postconsumer cotton polyester blends in comparison with pure cotton, Viscose, and Tencel. FW represents the fibril width, CrlNMR the degree of crystallinity obtained from the deconvolution of the NMR spectra, $\sum$ *cryst.* the sum of crystalline areas in cellulose II, and FS the fibril surface of cellulose II.

	cellulose content / %	FW / nm	CrlNMR / %	$\sum$ *cryst.* / %	$\sum$ *FS* / %
IGALO TPPT	50	3,3	42	–	–
IGALO KM	65	3,0	39	–	–
IGALO	50	3,5	45	–	–
RED SHIRT	17	3,1	40	–	–
BROWN SHIRT	60	3,9	50	–	–
WHITE SHIRT	35	3,2	41	–	–
Cotton	100	4,0	51	–	–
Viscose	100	5,1	46	28	18
Tencel	100	3,2	65	27	38

and 85 ppm), the signal at 87–89 ppm of cotton is composed of cellulose I$_\alpha$ and cellulose I$_\beta$, which are characteristic for natural fibers. The lower shift regions (79–86 ppm) represent amorphous structures in both cellulose I and cellulose II fibers. The most relevant parameters regarding the crystallinity of the cotton polyester blends analyzed in this study and a comparison to pure commercial cellulose fibers can be found in Table 1. A detailed description of the method of calculation and all respective deconvolution parameters are presented in the electronic supporting information.

In PET, amorphous regions affect the general resolution of the NMR spectrum. The lower the crystallinity the lower is the signal to noise ratio; peaks become broader and less symmetric as different forms of polymer orientation tend to increase (Gabrielse et al., 1994). The peak of the ethylene unit (C9, C10) can be found at 62 ppm, whereas the signal of the aromatic unit (C2, C3, C4, C5, C6) ranges from 130 to 134 ppm. The carboxyl carbons (C1, C8) show a shift of 164 ppm. The remaining multiplets in the spectrum are spinning sidebands caused by magnetic angle spinning. Parameters such as polymer crystallinity and spinning sidebands need be taken into account when establishing a quantification method for cotton polyester blends. They influence the choice of signals used for deconvolution, and the overall robustness of the method.

3.2. Fits and peak deconvolution

Reliable quantification results require hardly overlapping peaks of PET and cellulose in the NMR spectrum. The C1 and C4 signals of cellulose seem to fulfill this criterion initially; a closer inspection however reveals that an integration of C4 does not offer exact results. As mentioned before, the peak shape and shift of C4 vary according to the content of amorphous and crystalline regions. Fig. 1 also indicates that the intensity of C4 is influenced by spinning sidebands of polyester. The shape of C1, in contrast, is largely dependent on the type of cellulose, and hence also distinguishes for example cotton from man-made cellulose fibers (MMCF) (Atalla & VanderHart, 1999). Since C1 does not show any interference with other signals, its peak can nonetheless be integrated without a major effect on the fit quality. The ethylene signals of PET overlap with the C2-3-5 peaks of cellulose, whereas those of the aromatic unit and the carboxyl groups show intrinsically higher chemical shifts, which do not affect the signals of cellulose. Both C1-8(P) and Carom. (P) (cf. Table 2) were therefore used in the quantification method described below.

C1 (C) as well as C1-8(P) and Carom. (P) were integrated using Gaussian fit functions,

$$f(x) = a\,e^{-\frac{(x-b)^2}{2c^2}} \tag{1}$$

x describing the chemical shift within the predefined range of integration, a the function's intensity, b the absolute shift of the function in the spectrum, and c the function width. b was constrained to a range close to the respective peak maximum to achieve a better fit quality. The number of fit functions varied from 2 to 4 according to the peak shape and amount of multiplets (s. Table 2).

Most approaches in literature suggest a combination of both Gaussian and Lorentzian fits for the deconvolution of NMR spectra because the signals therein neither show entirely Gaussian nor Lorentzian behavior (Harris, Hodgkinson, Larsson, & Muruganantham,

Table 2

Integrated peaks, limits of integration, and number of Gaussian functions applied.

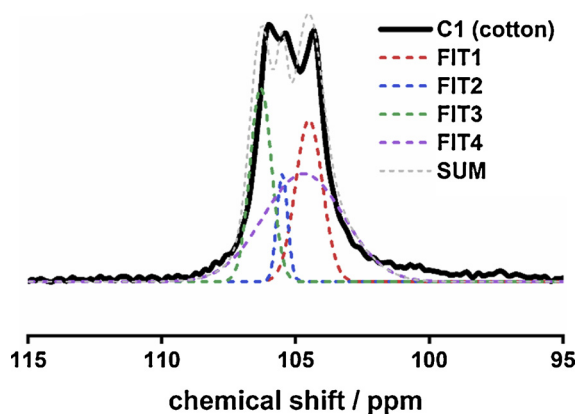| abbrev.	fiber	peak no.	constraints / ppm	no. f(x)
C1(C)	cellulose (cotton)	1	100–110	4
C1-8(P)	PET	1,8	160–175	2
Carom.(P)	PET	2, 3, 4, 5, 6, 7	120–140	3

Fig. 3. C1(C) integrated with four Gaussian functions.

2005; Zuckerstätter et al., 2009). In general, the application of single Gaussian functions leads to an insufficient coverage of the peak areas in regions at lower intensities. It is hence indispensable to employ at least one additional function of either Gaussian or Lorentzian type to improve the fit quality. Fig. 3 depicts the deconvolution of C1(C) using a set of four Gaussian functions.

As cotton represents a native form of cellulose, neither of the C1, C4, and C6 signals are singlet peaks. In the case of C1(C), the peak shape is a combination of cellulose I_α and I_β also overlapped by amorphous cellulose (Atalla & VanderHart, 1999). FIT1-3 thus aim to integrate the crystalline regions I_α and I_β, whereas FIT4 describes the amorphous sections in the polymer. At the same time, this also compensates for the Lorentzian behavior close to the baseline.

The respective peak areas were calculated from the sum of integrals over the Gaussian functions employed.

$$\sum \int_{-\infty}^{\infty} ae^{-\frac{(x-b)^2}{2c^2}} dx = \sum \sqrt{2}\, a\ |c|\ \sqrt{\pi} \qquad (2)$$

3.3. Calibration model

Distinct blend concentrations, i.e. 90%, 75%, 50%, 25%, 10%, 2.5% cotton were analyzed to generate a calibration curve. The cellulose concentrations were plotted vs. peak ratios (C1(C):C1-8(P) and C1(C):Carom.(P) respectively), which were calculated from the determined peak areas (s. Fig. 4). One reason to choose peak ratios instead of peak areas was to account for the variation in intensities resulting from the different natures of the polymers analyzed.

Although the calibration curve seems to show logarithmic behavior, initial attempts to use such fit functions resulted in a poor fit quality.

We observed that particularly very high and very low concentrations of cotton could not be determined accurately, therefore separate calibration models for both lower (i.e. linear) and higher (i.e. logarithmic) concentrations would have been required. This issue results from the fact that the obtained curves cannot approach (0/0) because they are theoretically undefined at cotton concentrations of 0% and 100%, (i.e either $\frac{100}{0}$ or $\frac{0}{100}$) due to the use of peak ratios instead of absolute values such as peak areas. The behavior of the plotted values is accordingly not logarithmic but sigmoidal.

$$y = \frac{a^*x}{1 + |x|\ b} \qquad (3)$$

x denotes the calculated peak ratios at certain cotton concentrations y, while a and b describe the calibration constants, slope and intercept.

The confidence intervals represent the impact of single data points on the calibration curve when excluded from the overall data set. This assumption facilitates the calculation of a separate standard deviation for all calibration points, which subsequently allows to define the confidence intervals based on new sigmoidal fits. As shown in Fig. 4, their range depends on the content of cotton in the respective blend implying that low concentrations result in considerably smaller absolute values. Dependent on the desired application, an inversion of the x-values (peak ratios) could thus be favorable to yield accurate results for smaller cotton concentrations.

3.4. Acid hydrolysis of cotton

Acid hydrolysis is a commonly employed to depolymerize cellulose. Acid concentration, treatment time, and temperature play an essential role in this approach. Whereas low concentrations of sulfuric acid for example are not able to hydrolyze cellulose completely, high molarities as well as high temperatures foster a fast and efficient hydrolysis. Considerably short hydrolysis times result in a selective separation of different cotton/polyester blends implying that the cellulose component can still be recovered as undissolved powder. Longer treatment times were reported to result in water-soluble degradation products (Ouchi et al., 2010). In order to determine the cotton and polyester content in blended materials, a degradation of cellulose to water-soluble degradation products only is favorable. The residual polyester remains unaffected by the acid hydrolysis and can thus be separated easily yielding reliable information on the true blend concentration. Although polyester tends to adsorb less moisture than cotton, the dry matter content needs to be taken into consideration when determining the blend concentration. Treatment times and acid concentrations were therefore adjusted in a way to ensure a complete dissolution of the cotton component.
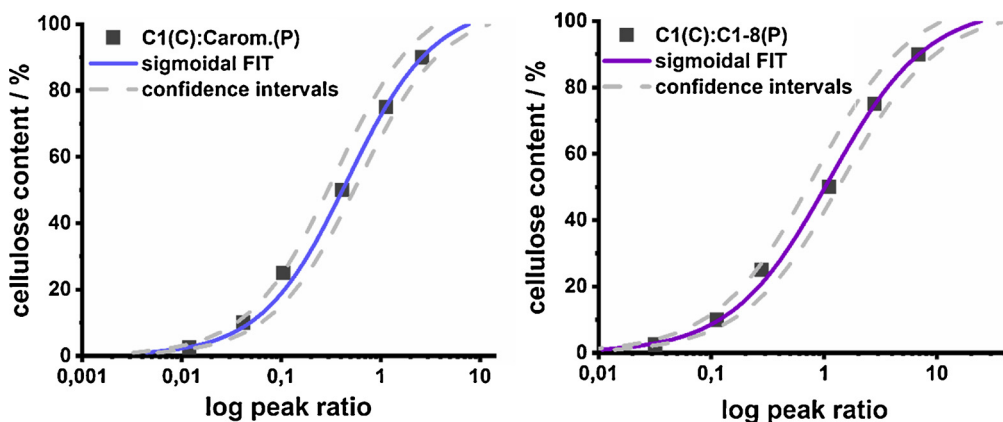

Fig. 4. Calibration curves and confidence intervals obtained from plotting the cellulose content (%) as a function of peak ratios. Left: C1(C): Carom.(P). Right: C1(C):C1-8(P).
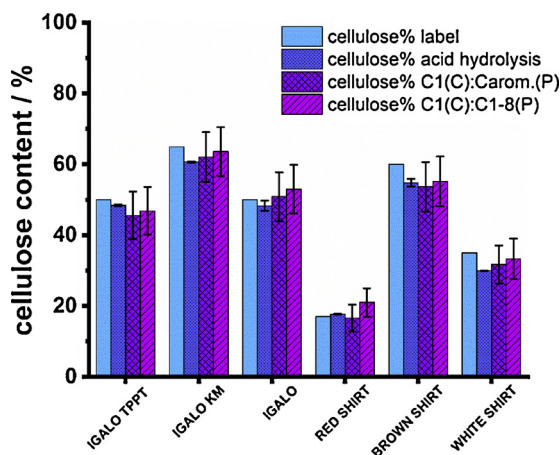
Fig. 5. 3 preconsumer (IGALO) and 3 postconsumer (SHIRT) cotton polyester samples were analyzed. The cellulose content of each sample is depicted as described on the textile label, and as determined by acid hydrolysis and by solid-state NMR.

3.5. NMR quantification results

CP-MAS NMR spectra of 3 preconsumer (IGALO) and 3 post-consumer samples (SHIRT) were recorded and integrated as described above. The peak ratios of C1(C):C1-8(P) and C1(C):Carom.(P) were inserted into Eq. (3) to obtain the respective cotton content. Fig. 5 summarizes the results obtained from both acid hydrolysis and solid state NMR.

First of all, it appears essential to highlight that the compositions of textile blends provided by their manufacturers usually represent rough guidelines rather than exact concentrations. Different laws and regulations leave room for interpretation. Depending on the manufacturing process, fibers for example amounting less than 2–5% do not need to be stated on a fabric produced in the European Union even though a deviation of only 3% is allowed when it comes to quality control (EU 1007/2011).

This discrepancy is also evident in the results depicted above. 4 out of 6 samples were shown to have a lower cellulose content than described by the manufacturer. The deviations ranged from about 0,5% to more than 5%. In each of these cases, the results of both solid-state NMR and acid hydrolysis were comparable. In 2 samples, the two different approaches led to different conclusions showing deviations between 0,7–3,0%. A coherence between preconsumer and postconsumer sample could not be observed. Moreover, neither dyes nor finishing agents seemed to have an effect on the calculated results, as they did not appear in the NMR spectra.

On average, the calibration function C1(C):C1-C8(P) yielded higher cellulose concentrations than C1(C):Carom.(P), which on average tended to be closer to the compositions obtained by acid hydrolysis. Inevitably, multiple factors such as the heterogeneity of the sample analyzed and the number of calibration points applied influence the accuracy of the quantification method as well as the resulting confidence intervals. In this respect, the solid-state NMR approach, exhibits higher standard deviations than the gravimetric methods. An extension of the set of calibration standards would hence decrease the margins of fluctuation.

4. Conclusion

CP-MAS NMR allows to determine the composition of cellulose polyester blends through the deconvolution and integration of pre-defined peak areas. Sigmoidal fit functions were found to adequately describe the correlation between the concentration of cotton and the ratios of distinct cotton and polyester signals appearing in the NMR

spectra. The calculated concentrations were also shown to be comparable to the results obtained by acid hydrolysis, which has been the standardized approach to determine the content of cotton in textile blends so far. Accordingly, solid-state NMR represents a viable alternative to conventional quantification methods as it is non-destructive and insensitive to different surface structures, colors and finishing agents applied. After further development, this quantification method would potentially also qualify for possible atline or online applications on an industrial scale, thereby facilitating a future valorization of cellulose based textile waste.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.carbpol.2018.11.052.

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