Chapter 21

Applications of NIR Techniques in Polymer Coatings and Synthetic Textiles

Tom Scherzer

Abstract This chapter provides a survey on the current state of the art of in-line analysis by various NIR techniques for process control of two very specialized categories of polymer materials: polymer coatings and textiles from synthetic fibers. In case of coatings, monitoring of the conversion of radiation-curable monomers such as acrylates, methacrylates, cycloaliphatic epoxies and vinyl ethers that is achieved during irradiation is primarily discussed, since the conversion strongly determines application and processing properties of such coatings. Moreover, in-line measurement of the coating thickness (from only a few up to several hundreds of micrometers), the spatial distribution of various parameters of interest across the coatings as well as the characterization of thin printed layers in the printing press are further subjects of the first part. The second part deals with the application of NIR methods for process monitoring and quality control in textile converting. Technical textiles are often subject of special treatment and finishing steps such as impregnation, coating, lamination etc. which have to be controlled in order to ensure adequate processing. NIR techniques have been shown to be an appropriate tool for this problem. In particular, hyperspectral imaging can help to retain the required homogeneity of textile webs or laminates after finishing, e.g., with respect to the application weight of functional finishes or adhesive layers. Furthermore, NIR spectroscopy is used for identification and sorting of textiles with the objective of recycling of the materials. Hence, an overview of the current status of the use of NIR spectroscopic techniques in textile technology is given.

Keywords NIR spectroscopy · Hyperspectral imaging · Monitoring of UV curing reactions · Characterization of coatings · Textiles · Process control

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21.1 Introduction

Polymers have become one of the most important classes of materials today, which is mainly due to the amazingly broad range of properties that may be achieved with this kind of materials. Accordingly, there is almost no range in our daily life, which goes without polymers. A multitude of different polymer materials has been developed so far and is commercially available. The widespread use and commercial importance of polymers makes also great demands on the analytics of such materials. With respect to the production of polymers, their converting, finishing, recovery or disposal, powerful and versatile analytical methods are required for characterization, identification, process and quality control etc. In particular, techniques used for sorting and control applications have to comply with special requirements such as robustness, reliability, durability, safety, significance of the data etc. [1–3]. Furthermore, in most cases they should be able to record data in a non-contact mode.

Near-infrared spectroscopy satisfies these specifications to a great extend. Moreover, due to its specific measurement principle NIR spectroscopy has high sensitivity to typical molecular structures in organic chemistry that are relevant for synthetic polymers. Consequently, NIR spectroscopy is particularly well suited for applications in polymer production and processing and related areas [4–9].

Apart from the underlying measurement principle, the great potential of NIR spectroscopy for its use in science and technology is mainly related to

(i) The high transmission of quartz and several glasses for radiation in this spectral range, which allows the use of conventional windows, lenses, prisms and last but not least optical fibers in experimental setups, which provides easy access to the region of interest,
(ii) The possibility to measure in reflection or transflection mode, which is advantageous in case of intransparent materials and
(iii) The rather low extinction coefficients of most organic matter in the near-infrared in comparison to other spectral ranges used in analytics such as mid-infrared or UV, which allows transmission measurements on samples with rather high thickness or optical path lengths in the range of several millimeters or even more without the need of dilution, cutting, pressing or other special sample preparation steps.

A quite recent application of NIR spectroscopy in polymer technology is the in-line analysis of polymer coatings. In particular, the conversion in coatings of radiation-curable monomers and oligomers such as acrylates, methacrylates, vinyl esters, thiol-ene systems, cycloaliphatic epoxies and vinyl ethers that is achieved after UV or electron beam (EB) irradiation is of great interest, since it strongly determines both the application and processing properties of such coatings. However, in-line analysis of rather thin coatings with thicknesses between a few up to several hundreds of micrometers is a considerable challenge for several reasons such as the required sensitivity and time resolution. Consequently, only very few attempts have been made in the past to monitor technical coating and curing processes by analytical methods. NIR spectroscopy does not appear to be an obvious method for in-line analysis of thin coatings due to the rather low extinction coefficients in this spectral range. Nevertheless, it has been shown during the last two decades that NIR spectroscopy has great potential for monitoring of the conversion, the thickness and other properties of polymer coatings if spectroscopic equipment with high sensitivity is combined with powerful chemometric approaches. Furthermore, the distribution of the parameters of interest across the coatings may be monitored as well by means of hyperspectral imaging.

An even greater challenge are printed layers since their thickness is even lower than those of most coatings. UV-curable printing inks applied for example by offset printing have typical thicknesses in the range between 0.5 and 3 g/m^2 (which very roughly corresponds to their thickness in micrometers). Moreover, printing speeds are at least one order of magnitude higher than in coating technology, which further increases the specific requirements. Despite these difficulties it has been demonstrated that the conversion in printed layers as well as their thickness may be predicted with surprisingly high precision from the NIR spectra. The first part of this chapter will provide a survey on the current state of the art of in-line monitoring of the properties of polymer coatings and printed layers by NIR spectroscopy.

Synthetic fibers and textiles play an important role in our daily life. They are widely used not only for clothes, but also for interior design of living rooms, offices, cars and other means of transportation as well as in numerous technical applications. Nevertheless, despite their widespread use, the diversified production and processing technologies and the high quality requirements, synthetic textiles have been rarely the subject of specific spectroscopic investigations dealing with their characterization or the monitoring of production and finishing processes. The majority of analytic studies is dealing with textiles made of natural fibers such as cotton, wool, flax, silk etc. However, technical textiles, which make particularly high demands on quality and compliance with the specification, are mostly based on fibers and textiles of synthetic polymers such as polyethylene terephthalate (PET), polyamide (PA), polypropylene (PP) or more special materials such as poly(p-phenylene terephthalamide) (para-aramid). Moreover, they are often subject of special treatment and finishing steps such as impregnation, coating, lamination etc. which have to be controlled in order to ensure adequate processing. Recently, NIR spectroscopy has been discovered as an appropriate tool for process monitoring and quality control in textile technology. Moreover, sorting of textiles with the objective of recycling the materials becomes a more and more established practice, and NIR spectroscopy is used for identification. The second part of this chapter will give an overview of the current status of the use of NIR spectroscopy in textile technology for the characterization of materials and in-line control of production and converting processes.

21.2 Polymer Coatings and Printed Layers

21.2.1 Specific Challenges of the Analysis of Coatings and Other Thin Layers by NIR Spectroscopy

21.2.1.1 Spectroscopic Characterization of Polymer Coatings

Polymer coatings are present everywhere in our daily life. They are applied to numerous materials for an extremely broad spectrum of functions ranging from decorative purposes only via protection against various external influences up to highly specialized coatings that provide the material with certain functional properties. Coatings can be made from a multitude of polymers, and also the methods of their application show a wide variety. Except for spray coating with solvent-containing varnishes or polymer dispersions one of the most widespread methods for the preparation of coatings is the application of resinous materials such as viscous monomer or oligomer formulations, which may be cross-linked by thermosetting (e.g., epoxy resins), UV photopolymerization (e.g., acrylates/methacrylates) or as reactive two-component system (e.g., PUR varnishes, polyester resins). Such coatings resulting from cross-linking reactions are characterized by high durability, excellent resistance to various impacts (mechanical, chemical, moisture, weathering, etc.), good adhesion and many other beneficial properties. However, it is obvious that the properties of such systems strongly depend on the degree of cross-linking that is achieved during curing. In particular, this applies for many protective and functional properties. If such coatings are applied in continuous processes such as roll coating, insufficient cross-linking may have fatal consequences because the high production speed will rapidly lead to large amounts of rejects. Consequently, monitoring the application process and the actual state of the applied coating would be highly useful for an efficient process control because it enables rapid intervention in case of serious deviations from the specification, e.g., the degree of cure.

Surprisingly, only very few attempts have been made so far to control technical coating and curing processes by analytical methods. Undoubtedly, this is related to the high experimental requirements. Appropriate measuring methods must have very high sensitivity since the conversion has to be determined in thin layers with a thickness in the range of some microns only. They must be able to record data at high sampling rates because of the usually high web speeds in coating technology. Moreover, high reproducibility and reliability of the data as well as robustness of the instrumentation to withstand the conditions in technical environments (dust, variations in temperature, vibrations, etc.) are required. The experimental method must not damage the material, hence measurement in a non-contact mode is desired.

The most promising analytical method for in-line monitoring of curing reactions in coating technology is NIR spectroscopy. It is non-destructive and possesses sufficient time resolution and sensitivity as well as comprehensive analytical potential for quantitative monitoring of chemical reactions. Measurements can be easily carried out in reflectance mode, which strongly expands the range of samples that are accessible to this technique. However, there is one significant potential obstacle of NIR-based techniques with respect to the characterization of coatings: the extinction coefficients in the near-infrared are much lower than in the mid-infrared range. Whereas this characteristic is useful in most other application areas of NIR spectroscopy in process control, where samples are typically rather compact objects with thicknesses of several millimeters or even more, it is rather unfavorable in case of the investigation of thin layers with a thickness in the range of some micrometers only. This constellation makes very high demands on the sensitivity of the spectroscopic equipment used for in-line monitoring as well as to the efficiency of the chemometric methods applied for quantitative analysis of the data.

Possibly, it is attributed to these experimental challenges that only very few studies dealing with the spectroscopic monitoring of coating processes can be found in the scientific literature. Most papers on the analytics of "*coatings*" by NIR spectroscopy are related to coatings on tablets or microspheres in pharmaceutics, which will not be discussed in this chapter. Studies on NIR-based monitoring of coating and curing processes with respect to the application of *technical* coatings are primarily focused on UV-cured coatings and printed layers. Therefore, this paragraph will mainly give an outline about the characterization of such coatings and layers.

21.2.1.2 Coatings Made by UV Photopolymerization

UV-curable coatings are advantageous with respect to saving of energy, environmental protection and waste reduction since UV curing consumes less energy than thermal drying or curing. Furthermore, solvent-free varnishes are widely used in UV curing technology, which may reduce environmental pollution. Due to the almost instantaneous cross-linking of the coating during the short irradiation with UV light (typically some tens of milliseconds), UV curing is a highly efficient coating technology. Moreover, the wide variety of acrylic and other monomers grants access to coatings with a broad spectrum of functional properties.

The most important parameter of UV-cured coatings is the conversion, which determines mechanical properties such as abrasion and scratch resistance or hardness, but also the content of extractables as well as their migration, chemical stability, weathering resistance, etc. Furthermore, sufficient conversion is also required for further processing of the coatings. For instance, wipe resistance must be achieved before stacking or winding. The conversion depends on a large number of chemical and technical parameters. Apart from the chemistry of the specific monomers (radical or cationic polymerization), the most important factor is the applied irradiation dose, which is given by the line speed and the irradiance of the incident UV light. Variations in the composition of the reactive formulation or the ambient conditions (e.g., temperature, humidity, inertization) may affect the conversion as well. Unfortunately, only some of these parameters can be easily controlled under the conditions of technical UV curing, whereas it is too complex for other influences. Consequently, monitoring of UV-induced photopolymerization reactions is an important issue.

In stationary applications of NIR spectroscopy, the conversion may be obtained from the ratio of a specific band of the corresponding functional group before and after irradiation. In case of acrylates, methacrylates, vinyl ethers, etc. the band of the first overtone of the C-H stretching vibration of the carbon double bond at 1620 nm can be used for quantification. This band is sufficiently separated from the corresponding absorptions of other C-H bonds (~1670–1750 nm), which usually allows integration without complex pretreatments such as band separation. In contrast, no specific band is available for the epoxide groups in cylcoaliphatic epoxy resins [10]. However, this approach comes to its limits in most in-line process control applications. For example, variations of the thickness during the process due to changes of the line speed [11] or the inherent polymerization shrinkage (e.g., of acrylic coatings [12]) distort the band ratio and prevent a correct determination of the conversion. Moreover, the precision of the integration method decreases at very high conversions. Therefore, almost all applications of NIR spectroscopy in process control are based on efficient chemometric methods.

The preparation of photopolymerized samples with a predefined conversion, which are required for calibration, is hardly possible. Therefore, the conversion resulting from the application of different UV doses and/or the use of different amounts of photoinitiator in the samples has to be characterized independently. Usually, the preferred reference method for the conversion is FTIR spectroscopy in the mid-infrared range. In case of (meth)acrylates, quantification is obtained by band integration of the peak of the $=CH_2$ twisting vibration of the acrylic bond at 810 cm^{-1}. However, infrared spectra obtained by FTIR-ATR spectroscopy reflect the chemical state close to the surface only due to the limited penetration depth of IR radiation into the layer, which is typically a few microns if a diamond is used as ATR crystal (~ 1-3 μm) [13]. However, many coatings in UV curing technology are much thicker (tens of μm). Moreover, UV-cured coatings often show a strong gradient of the conversion with increasing depth due to the limited penetration of UV light. Thus, ATR spectra do not provide precise information about the conversion across the profile of a coating.

In contrast, it is well known that NIR radiation penetrates to much greater depths of organic coatings as a consequence of the lower molar absorptivity in this spectral region, in particular in transparent systems. Thus, NIR spectra give an average response of the whole depth profile of the coating. Therefore, conversion data obtained from the ratio of band integrals before and after irradiation represent an average value of the conversion within the coating. Consequently, they are better suited for the calibration of chemometric models [14].

21.2.1.3 Interference Suppression in the Spectra of Thin Polymer Films

In order to be able to monitor the properties of coatings on both transparent and intransparent substrates with the same equipment, NIR spectra are taken almost exclusively in reflection in process control. Due to the low reflectance of transparent substrates such as thin polymer films, the spectra of coatings on those materials are

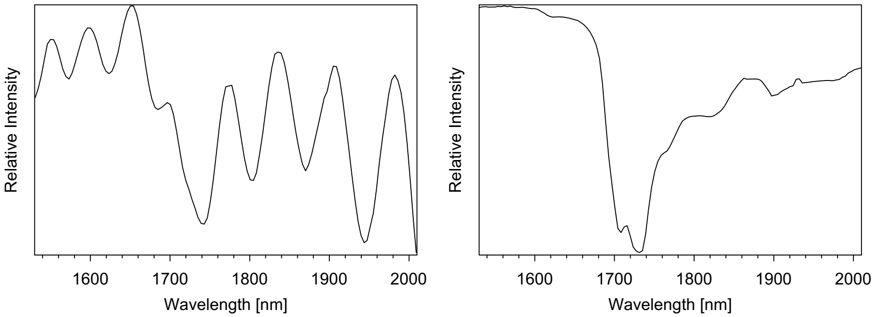

Fig. 21.1 NIR reflection spectra of a 10 g/m^2 acrylate coating on 20 μm PP film after UV irradiation. **a** without diffuser plate (left), and **b** with diffuser plate (right). Moreover, the probe head was tilted against the surface normal of the polymer film. Reprinted with permission by Wiley-VCH from Ref. [15]

recorded in transflection mode using a ceramic or metallic reflector that is placed underneath the coated film. However, in the spectra of thin transparent films of optically high-grade polymers such as polypropylene (PP), polyester (PET), polycarbonate (PC), etc. that have a thickness in the range of or only little higher than the wavelength of the probe light (i.e., up to ~30 μm) interference fringes may appear, which result from the superposition of the incident probe light with the light reflected at the front and back surfaces of the polymer film. Such interference patterns may completely mask the spectrum and accordingly prevent any analysis of the properties of the coating, which is applied to the film (see Fig. 21.1a). The removal of the interferences by mathematical means, i.e., Fourier transformation of the spectrum and cut-out of the sharp peak resulting from the sine wave, fails due to inevitable vibrations of the film web in the roll coating machine. Moreover, the calculation of the Fourier transform is too time-consuming for process control applications. Instead, the interference problem can be overcome by experimental means, i.e., (i) by use of a diffuser plate, which is mounted between probe head and sample, and (ii) by a tilt of the optical path of the incident light against the surface normal of the polymer film [15]. The combination of both approaches suppresses the interferences very effectively (see Fig. 21.1b) and thus enables quantitative analysis of coatings on thin transparent polymer films.

21.2.2 Monitoring of the Thickness of Coatings by NIR Spectroscopy

Although there are several measuring methods and specific sensors for in-line monitoring of the thickness of extensive laminar materials such as paper, polymer films and textile webs, there is no established method to monitor the thickness or the surface weight of UV-cured or other polymer coatings applied to such substrates. Currently, control of the thickness of the applied layers in technical coating processes is mostly carried out off-line by gravimetric determination of the coating weight. However, it is apparent that this approach is not able to respond to sudden changes of the thickness, and thus it is poorly suited for process control. However, it was shown that thickness or coating weight can be followed by NIR reflection spectroscopy under the conditions of technical coating processes [16, 17].

Clear acrylate coatings with thicknesses in the range from 5 to 100 μm were studied [16]. Although calibration samples were prepared with different thicknesses for PLS modeling with a set of various Baker applicators with well-defined gaps, the resulting thickness had to be measured after UV curing mainly due to the well-known shrinkage of acrylate formulations during the cross-linking reaction and spreading of the applied wet coating. Shrinkage and other effects affecting the thickness may lead to a decrease of the thickness up to 30%. Instead of direct thickness measurements (e.g., with a thickness gauge), gravimetry may be used alternatively to provide reference data. Depending on the range covered by the specific PLS model, prediction errors were found to be in the order between less than one and about 4 μm [16, 17]. Similar results were also found for white-pigmented coatings containing 10 wt% titanium dioxide [18]. For example, the thickness of such coatings with a thickness from 5 to 60 μm was predicted with a precision of about 1 μm.

Moreover, in-line monitoring of the thickness was carried out at a pilot-scale roll coating machine. Quantitative data were recorded at line speeds up to 50 m/min. Very close correlation between data predicted from NIR spectra and reference data determined off-line after the end of the coating trials was observed. Prediction errors were found to be very similar to those obtained in the external validation tests although the experimental conditions at the coating machine were less optimal than in the lab. In particular, in-line measurements were exposed to disturbing factors such as vibrations of the coating machine including the mount of the probe head and flutters of the moving film web. In order to simulate abrupt changes of the thickness during a real coating process, the nip between the applicator rolls was stepwise reduced and increased. An example for clear coats is shown in Fig. 21.2 [17]. Similar investigations were also carried out for pigmented coatings [18]. It was demonstrated that changes in layer thickness lower than 1 μm can be clearly detected by NIR spectroscopy.

The thickness of clear and pigmented UV-cured coatings was also monitored at different line speeds up to 100 m/min [16–18]. A marked increase of the thickness with increasing speed was observed up to about 50 m/min, which was followed by a decrease at even higher web speeds. Although this behavior seems to be somewhat surprising, it is well-known in coating technology [19, 20]. In fact, it is due to a very complex interaction of several physical and technological parameters of the coating process. In particular, acrylate formulations are typical non-Newtonian fluids, i.e., their viscosity depends on the shear rate. In-line NIR spectroscopy offered for the first time the unique possibility to monitor the thickness changes upon variation of the line speed directly during the coating process in a quantitative manner.

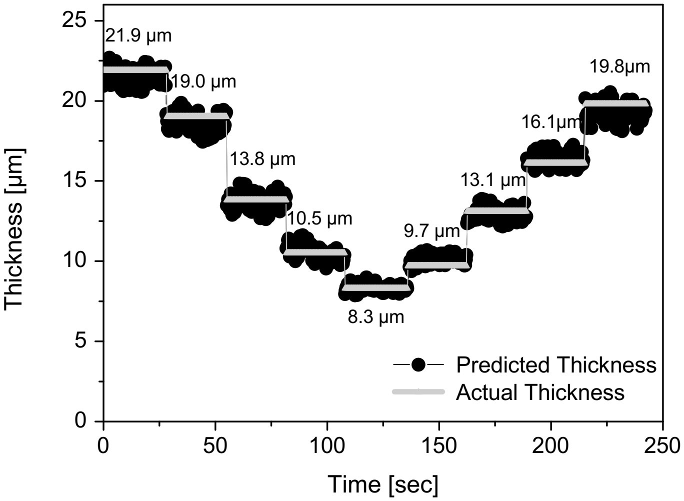

Fig. 21.2 In-line monitoring of the thickness of an acrylate coating on 20 µm PP foil upon stepwise decrease and increase of the nip between the applicator rolls of the coating machine at a line speed of 40 m/min. Actual values were obtained off-line by a thickness gauge. Reprinted with permission by Elsevier B. V. from Ref. [17]

The dependence of the applied thickness on the web speed has serious consequences for the in-line measurement of the conversion. Calibration models are typically based on calibration samples that have different conversions, but the same thickness of the coating. Variation of the thickness in the process as compared to the calibration samples may lead to significant mispredictions of the conversion during process control. Approaches to avoid such errors will be discussed paragraph 21.2.3.3.

Pigmentation of varnishes hampers the penetration of near-infrared radiation into polymer coatings. At high thicknesses, this may lead to a non-linear relationship between the thickness of the coating and its reflectance. Therefore, several investigations were carried to study the effect of increasing thickness on the total absorbance in the NIR spectrum quantitatively in order to determine the maximum thickness, up to which the thickness of pigmented coatings can be predicted from NIR spectra using PLS algorithms. Obviously, this limit depends on the kind and the percentage of pigmentation as well as on the chemistry of the specific varnish. In case of white-pigmented acrylate coatings (10 wt% TiO_2), linearity was found for thicknesses up to 300 µm at least [21]. This is possible since titanium dioxide does not significantly absorb in the near-infrared region. In contrast, investigations on a red pigmented PUR varnish applied by spray painting to steel sheets clearly showed that the integral of the absorbance in the region of the first C-H stretching overtones (1650 to 1850 nm) was linear to the thickness up to 180 µm only, which restricts the effective measurement range of NIR spectroscopy for thickness measurements (Fig. 21.3).

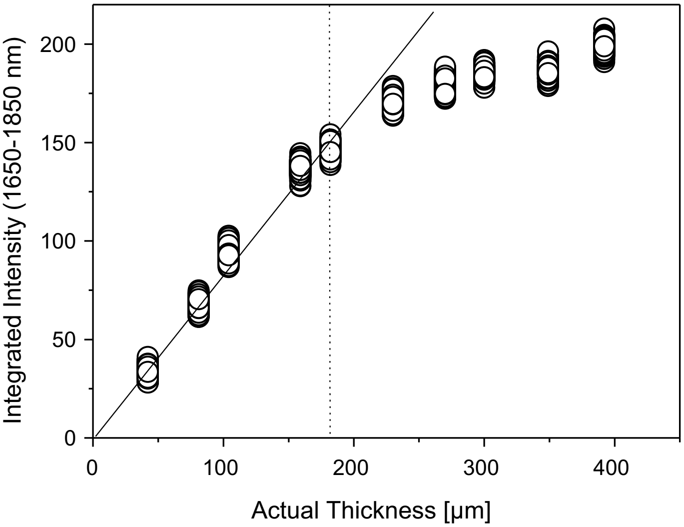

Fig. 21.3 Integrated intensity of the absorbance in the first overtone region of C-H stretching vibrations in dependence on the coating thickness of a red pigmented PUR varnish applied to steel sheets by spray painting

PUR coatings with thicknesses higher than 100 µm may be used for example for protective coatings against weathering in demanding outdoor applications.

In case of very thin coatings, the sensitivity becomes an issue that has to be considered with respect to the detection limit of the NIR method, since the low extinction coefficients in the NIR region pose a considerable challenge. For example, thin acrylate layers with a thickness of a few microns only can be photopolymerized without addition of a photoinitiator by irradiation with short-wavelength UV radiation. The initiating mechanism is based on direct excitation of the acrylate molecules by photons with high energy. An investigation by NIR in-line monitoring at a roll coating machine [22] demonstrated that a photoinitiator-free acrylate coating with an application weight of 4 g/m^2 can be cured by irradiation at 222 nm under inert conditions using a KrCl* excimer double lamp system (175 mW/cm^2). Adequate conversion was achieved at line speeds up to 30 m/min. Despite the low thickness of the coating, spectra were found to show sufficient signal-to-noise ratio to provide significant conversion data.

Ink jet printing is widely used not only in home office applications, but also for labeling in packaging technology, in electronics, nanotechnology and similar applications. Inks for such applications are aqueous systems, which poorly wet most polymer surfaces. Therefore, very thin hydrophilic ink absorption layers have to be applied to polymers to make them printable. The typical thickness of such coatings may be 1 g/m^2 or less. JIANG et al. [23] applied polyvinyl alcohol layers with nanoscale titania particles to PET films with thicknesses between 0.25 and 1.25 g/m^2. For controlling the application process and the quality of the applied layers, they developed a method based on FT-NIR spectroscopy. Several parameters such as coating weight, gloss and smoothness were predicted from appropriate PLS models. In case of the coating weight, reference data were obtained by gravimetry before and after dissolution of the layers. RMSEP was found to be 0.054 g/m^2 with a coefficient of determination (R^2) of 0.98. Convincing results were also obtained for the smoothness, whereas the method was of limited suitability only for the determination of the gloss. It was demonstrated that all three parameters could be also predicted in-line during the coatings process.

21.2.3 Conversion of UV-Cured Coatings

21.2.3.1 Acrylic Coatings

The conversion that is achieved during UV irradiation is the most important parameter of any UV-cured coating. As outlined above, it determines all functional and handling properties of the coatings, which are relevant for their application or further processing. Consequently, continuous monitoring of the conversion during a coating process would be highly desirable. However, until recently no efficient analytical method was available, which allowed direct in-line monitoring of this important parameter. At-line or off-line determination of the conversion is state of the art, which is often carried out by FTIR spectroscopy. But IR spectroscopy in the mid-infrared (MIR) region is not suited for in-line control, since non-contact reflection measurements over a rather large measuring distance are difficult or even impossible.

In contrast, vibrational spectroscopy in the near-infrared range offers this possibility, which provides an opportunity for monitoring the conversion during the coating process. The overtone band of the C-H stretching vibration of the carbon double bond at 1620 nm is well separated from the corresponding bands of other C-H structures (methyl, methylene etc.). Hence, it might be used directly for the determination of the conversion in acrylates and methacrylates using band integration. However, this requires recording of some spectra of the uncured coating before irradiation, which is often difficult to realize in complex coating processes. Moreover, this approach involves considerable dangers resulting from unintended but inevitable changes of the thickness of the coating as discussed in paragraph 21.2.1.2. For this reason, chemometric modeling is the more time-consuming, but also the more reliable approach. Depending on the specific varnish (e.g., clear or pigmented), its thickness and other parameters, MIR (in transmission or using ATR) [15, 24] or NIR spectroscopy (band integration) [14, 21], Raman spectroscopy or other analytical methods [15] can be used as reference method for calibration. Even secondary parameters that depend directly on the conversion (e.g., the hardness of the coating) may be used as reference data for calibration models. A typical PLS-based calibration model for the conversion in an acrylic clear coat is shown in Fig. 21.4.

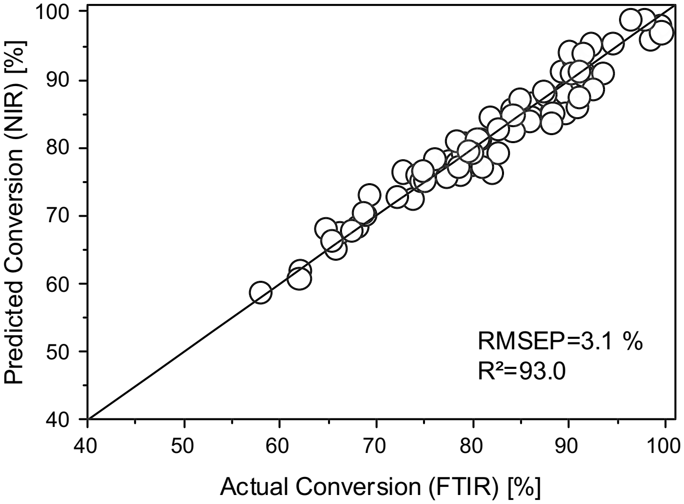

Fig. 21.4 PLS calibration model for the conversion in an acrylic clear coat. Reprinted with permission from Ref. [24]. Copyright 2010 American Chemical Society

Typically, the prediction error (RMSEP) of such models is in the order of 2–3% [14, 21, 24]. In most cases, the corresponding error of the external validation with independent test samples is only marginally larger.

When the probe head is mounted to a specific coating machine (e.g., a roll coating machine, conveyor, etc.) for in-line monitoring of the conversion after UV or electron beam (EB) irradiation, great care has to be bestowed on the correct alignment of the probe head with respect to its distance and the tilt angle relative to the film web and, if applicable, to the reflector behind the foil. It is obvious that an exact match of the measurement conditions is essential for the successful transfer of chemometric calibration models from the laboratory to process control in technical scale. It has been found, that even very minor differences between both arrangements substantially affect the precision of the predicted values.

In order to demonstrate the potential of NIR spectroscopy for monitoring changes of the conversion due to variations of the irradiation dose, both the power of the UV lamp (or the beam current of the EB accelerator) and the line speed can be varied repeatedly. An example is given in Fig. 21.5 [25]. It can be clearly seen that the conversion increases or decreases according to the applied UV dose. Evidently, changes of the line speed of the roll coating machine lead to an immediate change of the conversion. In contrast, changes of the power of the lamp appear after a delay only, what is due to the rather slow response of the mercury arc lamp, when its power is switched to a higher or lower level. Similar gradual increases or decreases of the conversion were also found for changes of the power of the EB accelerator [15, 25]. In contrast, faster response might be expected for UV LED light sources.

Analog results were obtained for acrylic coatings on both various transparent polymer films or non-transparent substrates such as paper, cardboard, opaque

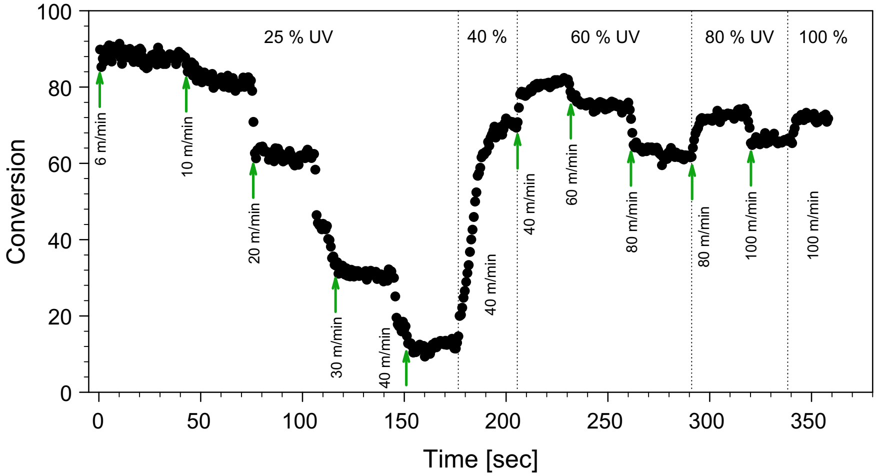

Fig. 21.5 In-line monitoring of the conversion in a 20 g m^{-2} acrylic clear coat on PET film (36 μm) after UV irradiation with variable power of the mercury arc lamp and at various line speeds of the roll coating machine. The power of the UV lamp is given in percent of its maximum output. Reprinted with permission by Elsevier Ltd. from Ref. [25]

polymer films etc. [15, 25, 26]. The only difference is that a diffuse reflector has to be placed behind the film web in case of transparent materials, whereas paper serves as a reflector on its own volition. The conversion in white-pigmented varnishes was monitored in the same way as well [25].

UV curing is widely used in the wood industry, e.g., for furniture and flooring. Therefore, the conversion in acrylate coatings on rigid substrates such as fiberboard or wood was monitored. In this case, both the UV lamp and the NIR probe head were mounted above a conveyor. Since the line speed of a conveyor is usually lower than that of a roll coating machine for the application of varnishes on web-like materials, time resolution of the monitoring method is less crucial. Hence, sampling rates of 2–10 spectra/s were used. It has been demonstrated that in-line monitoring by NIR reflection spectroscopy is well suited for this kind of applications as well [15].

A special type of UV-curable formulations are UV-curable adhesives. High-molecular weight acrylic copolymers containing photoreactive groups such as benzophenone in their side chains may be used as pressure sensitive adhesives (PSA). Cross-linking of these hot melt adhesives is required in order to improve their resistance to thermal distortion. However, their adhesive properties (i.e., peel strength and shear strength) were found to be heavily dependent on the conversion. Even minor changes of the degree of cure may affect the adhesive properties adversely. Therefore, a continuous control of the UV curing process is essential for ensuring optimum adhesive properties. For monitoring the conversion in acrylic hot melts, the probe head was mounted at a slot die coating machine [27]. The adhesive layers were applied to OPP film at 90 °C with coating weights between 200 and 500 g/m^2 and at rather low line speeds (2 to 5 m/min). After application, they were irradiated

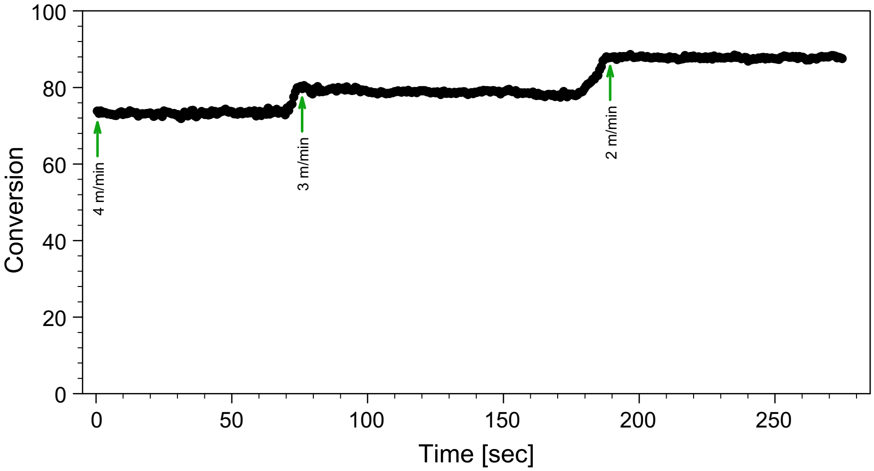

Fig. 21.6 In-line monitoring of the conversion in a 500 g m^{-2} coating of an acrylic hot melt adhesive on PP tape after 308 nm UV irradiation at various line speeds. Reprinted with permission by Elsevier Ltd. from Ref. [25]

with monochromatic UV light (308 nm) using a XeCl* excimer lamp. In spite of the very high thickness of the layers, good through cure was achieved due to the low extinction coefficient of benzophenone at the wavelength of irradiation.

In Fig. 21.6, a record of in-line monitoring of the conversion in an UV-cured acrylic hot melt after irradiation at different line speeds is shown. Similar data were also obtained upon variation of the UV intensity [25]. It is evident, that the scattering of the conversion data is distinctly lower than that of the acrylic coatings in Fig. 21.5. This is due to the much higher thickness of the adhesive layers (500 versus 20 g/m^2), which resulted in a higher signal-to-noise ratio of the recorded NIR spectra.

21.2.3.2 Epoxy Coatings

Cationic monomers and oligomers form another class of UV-curable systems. In particular, they involve cycloaliphatic epoxy resins and vinyl ethers, which may be used as photoreactive monomers and reactive diluents, respectively. Cationic photoinitiators such as diazonium, diaryliodonium or triarylsulphonium salts form Brönsted or Lewis acids as initiating species. Typically, the reaction rates of cationic photopolymerization reactions are lower than those of free-radical reactions. Consequently, the conversion in cationic formulations is mostly still rather low just after passage through the UV lamp. However, it is well-known that the cationic polymerization once initiated continues for a long time in the absence of light. This post-curing effect leads to a substantial further increase of the conversion. This time delay

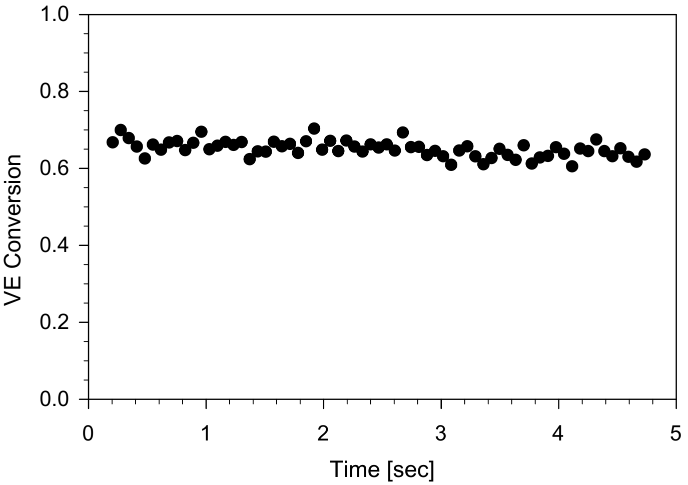

Fig. 21.7 In-line monitoring of the conversion in a coating made of 85 wt% of a cycloaliphatic epoxy resin and 15 wt% of a divinyl ether applied to OPP film at a line speed of 3 m/min. Reprinted with permission by Wiley-VCH from Ref. [10]

between irradiation and ultimate conversion implies significant consequences for in-line monitoring of such reactions. Usually, the NIR probe head is positioned immediately after the UV lamp. Consequently, the conversion that is found at this position is still pretty low. Figure 21.7 shows the conversion in a formulation consisting of a cationic epoxy resin (3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate; EEC) and a vinyl ether (tetraethyleneglycol divinyl ether; DVE-4) just after UV irradiation with a dose of about 2800 mJ/cm^2, which is only about 65% [10]. Although this is sufficient for winding-up the coated polymer film without blocking, it is far from the final conversion that determines the application properties of the coating. Consequently, NIR spectroscopy may provide a rough indication for the current state of the curing process, but no definite final conversion of the coating.

Evidently, the further development of the conversion during the dark reaction can be investigated only off-line. Some results are summarized in Fig. 21.8 [10]. It is apparent that most of the increase of the conversion was achieved within one hour after irradiation. Moreover, the results clearly reveal that both the initial and the ultimate conversion strongly depended on the applied irradiation dose. Whereas almost full conversion (98%) was achieved after two hours in coatings exposed to 2100 mJ/cm^2, the curing reaction leveled off at lower conversions after irradiation with lower doses.

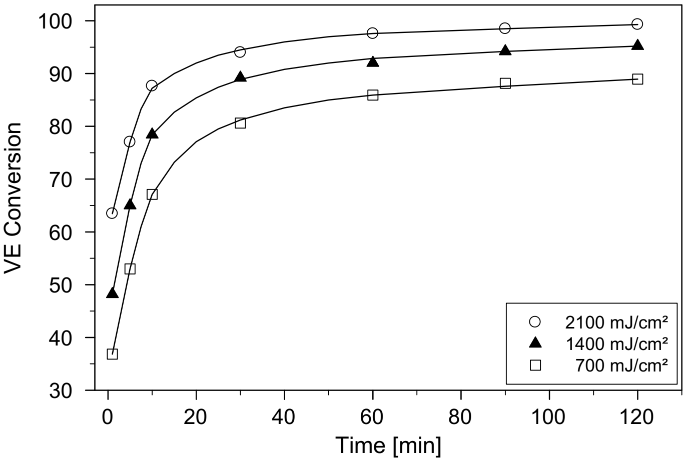

Fig. 21.8 Kinetics of the postcuring reaction of a mixture of a cationic epoxy resin (85 wt% EEC) and a divinyl ether (15 wt% DVE-4) after irradiation with various UV doses (line speed 10 m/min). Reprinted with permission by Wiley-VCH from Ref. [10]

21.2.3.3 Simultaneous Measurement of Thickness and Conversion

It was already mentioned above that variations of the coating thickness, which may be caused by accidental fluctuations or by intentional changes of the web speed, may considerably impair the quantitative monitoring of the conversion in UV-cured coatings regardless of the use of either band integration or chemometric methods. In case of the band integration method, the reference spectra defining the "zero conversion line" are no longer valid after any thickness change, whereas PLS1 models for the conversion are built up for coatings with a broad range of the conversion, but with one well-defined thickness only. However, the negative impact of variations of the thickness on the quantitative determination of the conversion during in-line monitoring can be overcome for both approaches.

If simple band integration methods are used for quantification, thickness changes may be included by a more complex analytical instrumentation. Instead of the use of a single NIR probe head, which takes spectra of the cured coatings after irradiation, two probe heads can be installed before and after the UV lamp. They may be linked to one spectrometer if a multiplexer is used to switch between both optical entrance ports. The conversion is obtained by band integration of the acrylate band at 1620 nm and calculation of the ratio of the band integrals before and after UV irradiation. In order to consider the time delay between the two probe heads, a specific offset that depends on the line speed has to be included in the evaluation scheme. Obviously, this approach corresponds to the conventional determination of the conversion in the analytical laboratory by recording spectra before and after irradiation. The efficiency of this analytic approach to compensate the effect of thickness changes on the determination of the conversion has been demonstrated by in-line monitoring experiments at a roll coating machine [11].

Alternatively, the variation of the thickness of the coating can be included as an additional parameter into the chemometric calibration models, which is certainly the most sophisticated approach. This can be achieved by use of the PLS2 algorithm, which is able to predict two or even more parameters from the same input data. Of course, this implies much higher efforts for calibration, since the calibration samples have to cover the full range of both conversion and thickness that can occur during process control. On the other hand, the higher complexity of the calibration process is offset by the fact that simultaneous prediction of both conversion and coating thickness can be achieved while using one NIR probe head only.

The suitability of this approach was demonstrated during application of clear and pigmented acrylate varnishes to PP film at a roll coating machine and their cross-linking by UV irradiation [24]. Reference samples for the setup of the PLS2 model covering a broad spectrum of combinations of conversion and thickness were characterized by FTIR spectroscopy and a thickness gauge. During roll coating, the line speed was increased in incremental steps from 20 to 100 m/min, which inevitably led to changes of the thickness as well as the conversion due to the corresponding decrease of the irradiation dose. Both parameters were predicted from the recorded NIR spectra using the PLS2 model. Results of one specific coating experiment are shown in Fig. 21.9. For quantitative evaluation of the predicted data, reference values were determined off-line for each step of the line speed after the end of the coating trial. These values are included in Fig. 21.9 as well. The data clearly prove that the conversion was predicted with a precision of 2–3% even under the conditions of changing thickness, whereas the error in the in-line measurement of the thickness was found to be about 0.5 to 1 µm. These error margins correspond to those found in independent predictions of both parameters by PLS1 models (see paragraphs 21.2.2. and 21.2.3.1.).

21.2.4 Hyperspectral Imaging of UV-Cured Coatings

In the studies reported so far, the parameters of interest (thickness, coating weight, conversion etc.) have been monitored by conventional NIR spectroscopy. Since the spot of most NIR spectrometers has a diameter of a few millimeters only, this means that these parameters can be determined in a small stripe only during monitoring a running process. However, for coatings as two-dimensional objects the spatial distribution of the parameter under investigation might be of interest for a comprehensive process control. For example, UV lamps have rod-like shape, which may lead to a decay of the intensity at their ends due to aging, pollution etc. In UV LED systems, single elements may drop out. Both effects lead to a reduced conversion in the corresponding region, which might be possibly insufficient for the intended application. Also in case of the application weight, local deviations may occur, e.g., due to running out of the varnish formulation in the roll gap or the reservoir of the coating machine,

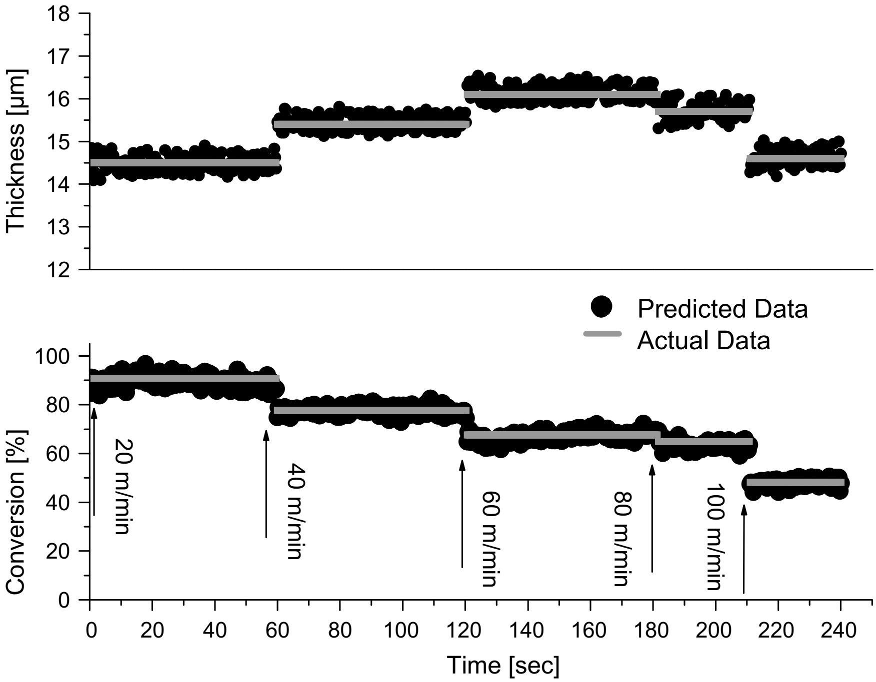

Fig. 21.9 Simultaneous monitoring of thickness and conversion of a clear acrylate coating at various line speeds of a roll coating machine. Quantitative data were predicted with a PLS2 calibration model. Gray lines represent reference values that were determined off-line by FTIR transmission spectroscopy or a thickness gauge, respectively, after the end of the coating experiment. Reprinted with permission from Ref. [24]. Copyright 2010 American Chemical Society

inclination of the web, local variation of the viscosity (e.g., due to temperature gradients) etc. In order to include the spatial distribution of the parameter of interest in process control, two-dimensional monitoring of the process is required. This is the domain of hyperspectral monitoring.

Traditionally, hyperspectral cameras have been mainly used for three-dimensional or at least rather thick objects, which resulted in applications in waste sorting, food monitoring (meat, fish, vegetables, fruits etc.) and the characterization of other objects in agriculture (e.g., logs and boards), art conservation etc. However, today's high-class hyperspectral cameras have sufficient sensitivity to monitor even thin samples such as coatings, laminates, finished textiles (see paragraph 21.3.3.), printed conductive polymer layers, pages in medieval illuminated manuscripts [28] and similar two-dimensional objects. Therefore, hyperspectral imaging was also used for monitoring thickness, conversion and other parameters of coatings. With an adequate calibration, each of these parameters can be predicted quantitatively. However, the main intention of the use of hyperspectral cameras in coating and lamination technology is monitoring the spatial distribution of these parameters across the samples as well as the detection of possible inhomogeneities.

PUR foam is widely used for cushioning and sound insulation. For faster and easier mounting in end-use applications such as automotive engineering, it may be provided with an adhesive layer forming a semifinished product. Due to the mostly coarse surface structure of such foam plastics, the adhesive cannot be applied as melted mass. Rather, melt-spun fibrous webs of thermoplastic adhesives such aliphatic polyamide or polyester are laminated to the surface of the foam mat. Higher thicknesses may be achieved by application of several adhesive webs. In this way, applications weights of the adhesive between 20 and 125 g/m^2 were achieved. The development of calibration models for the prediction of the coating weight is significantly impeded by the fact that calibration samples with well-defined homogeneous thickness can be hardly prepared due to the numerous open bubbles at the foam surface as well as due to the fibrous structure of the adhesive webs. Moreover, some of the PUR substrates are rather dark (e.g., dark gray), which leads to rather low reflectance. In order to consider a possible non-uniform distribution of the coating weight across the samples, the surface of each sample was divided into 20 rectangular regions by defining a grid of 5 columns $\times$ 4 rows. Spectra from each rectangle (several thousands in each) were averaged. The averaged spectra were allocated alternatingly, that is, according to a chessboard pattern, to the calibration and the validation set. This procedure resulted in RMSEP values of only 1.5–3.5 g/m^2 despite the heterogeneity of the adhesive web and the PUR foam substrates [29, 30].

Using these calibration models, the application weight of adhesive layers was quantitatively monitored with a hyperspectral camera mounted above a conveyor. At low coating weights, the adhesive layers shows significant local thickness variation (i.e., for samples with up to two adhesive webs), whereas it becomes more homogeneous at higher coating weights [29]. This effect mainly results from surface structure of the PUR foam. During the melting process of the web, the adhesive might partly flow into the open bubbles at the surface of the foam leading to an uneven distribution. For an overall evaluation of the quantitative prediction results, the individual values predicted from the spectra across the complete surface of each sample were averaged and compared to gravimetric values. Deviations were found to be less than 2–3 g/m^2 (the fact that some values are lower than RMSEP is related to the averaging process).

Spectral imaging was also used for the detection of inhomogeneities and coating errors, which may occur during the lamination process. During melting, the adhesives form continuous glossy transparent layers on the foam substrates, which usually prevents the detection of coating errors by visual inspection. In contrast, spectral imaging is able to highlight them. As an example, Fig. 21.10 shows the image of a coated foam sample, where the corner of one adhesive web was fold over during the lamination process [30].

Thickness and conversion of UV-cured acrylate coatings were studied by hyperspectral imaging as well. In particular, white-pigmented coatings were investigated. Calibration to the thickness was carried out for coatings with thicknesses up to 200 μm, although linearity between thickness and NIR signal was even found for much thicker coatings [21]. Calibrations to the conversion resulted in RMSEP values between 2 and 3% [14, 21]. However, specific calibration models were required for

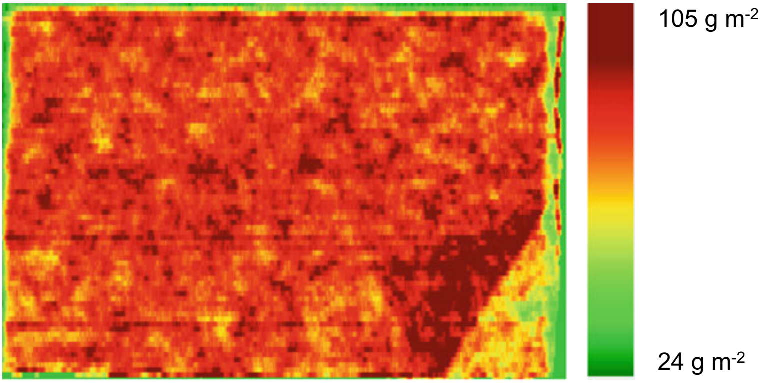

Fig. 21.10 Hyperspectral image of an adhesive layer of an aliphatic polyamide laminated on dark gray PUR foam. The lower right corner of one of the adhesive webs was fold over. Reprinted with permission by Elsevier B.V. from Ref. [30]

each varnish and each substrate. In order to reduce the considerable efforts required for the preparation of samples with different conversions, procedures for the transfer of calibration models to other substrates (e.g., glass, steel, glass fiber reinforced plastic plates) were developed. It was shown that only a marginal increase of the prediction error is caused by such transfers.

After the development of calibration models, both thickness and acrylate conversion were monitored with a hyperspectral camera installed above a conveyor belt. Similar to investigations by conventional NIR spectroscopy, quantitative data were determined for both parameters. It is well-known that curing of thick white coatings is one of the most difficult tasks in UV curing technology, since the excellent scattering power of white particles such as titanium dioxide strongly impede the penetration of UV light into the coating. This leads to strong conversion gradients within the coating. In fact, a conversion of less than 70% was found for coatings with a thickness of ~ 75 µm, which represents an average across the profile of the coating with almost complete conversion at the surface and rather low conversion in the depth. Aging of such samples led to some “self-structuring” of their originally homogeneous surface within a few days due to shrinkage and subsequent relaxation of the internal stress, which finally resulted in some kind of orange peel effect. The local thickness and conversion differences developed during this self-structuring process were clearly reflected in hyperspectral images taken from the relaxed samples [21].

Conversion differences within a coated sample can be also intentionally induced by generation of thickness differences. Although the degree of cure at the surface is certainly the same across the sample, the averaged conversions differ upon variation of the thickness due to the conversion gradient. Examples of a uniformly cured coating and a sample with conversion differences resulting from thickness changes are shown in Fig. 21.11 [14].

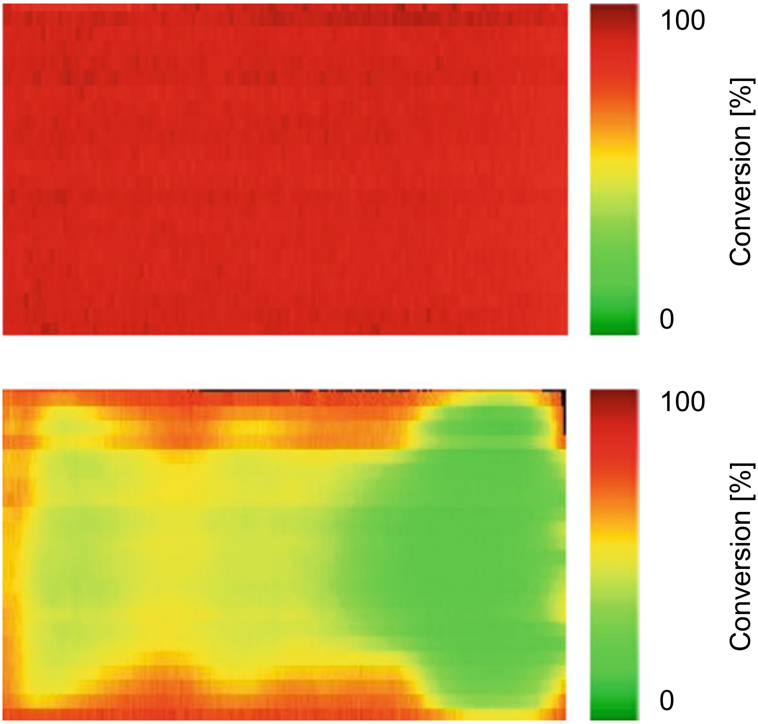

Fig. 21.11 Hyperspectral image of white-pigmented acrylate coatings: with homogeneous conversion (87%; top) or with inhomogeneous distribution of the conversion due to differences in coating thickness (bottom). Reprinted with permission by Elsevier B.V. from Ref. [14]

21.2.5 Spectroscopic Techniques in Printing Technology

21.2.5.1 Thickness of Layers in Offset Printing

Beside its application in coating and lamination technology, in dentistry, microelectronics and 3D modeling, for adhesives and composites, etc., UV curing is also widely used in printing technology and graphic arts. UV-curable inks and varnishes complement conventional oil- and water-based systems. Generally, they dry almost instantly, which results in higher printing speeds and hence in higher productivity of the printing process. Viscous UV inks and varnishes show less penetration into porous materials such as paper than other ink systems. Moreover, they result in printed layers with a high-grade optical appearance (e.g., high gloss), which makes them interesting for demanding printing applications, e.g., for packagings in cosmetics or for advertising materials.

The thickness of ink layers determines their color intensity as well as the color shade. Therefore, the exact observance of the specified thickness of the various colored layers is essential for the quality of the printed product. On the other hand, since offset printing is a complex process, numerous factors may influence the thickness of the layers. Consequently, it is indispensable to control the thickness continuously during the printing process.

The thickness of colored printed layers can be monitored in-line by use of reflectance densitometry, which relates the intensity of the reflected light to the color density. However, this method is limited to standard colors (cyan, magenta, yellow and black) only. It does not allow measurements of the thickness of layers with other color shades. Moreover, it is not suited for transparent top coats, which are widely used for the protection of printed layers, for upgrading their optical appearance, for achieving special design effects or for finishing the printed layers with special functional properties. It is obvious that the compliance of the required thickness (or coating weight) is crucial for those properties. Up to now, the surface weight of clear coats can be determined only off-line by gravimetry, which is a labor-intensive and time-consuming procedure. The typical thickness of printed layers is in the order around 1 g/m^2; it might be somewhat higher in case of clear coats. Due to the rather low extinction coefficients, NIR spectroscopy is certainly not an obvious approach to characterize such layers. Nevertheless, it was shown that similar methods like those described above for coatings with thicknesses in the range of about 5–100 μm (paragraph 21.2.2.) can be also used for process control in printing technology.

For monitoring of the coating weight, the probe head of the NIR spectrometer was mounted either above the impression cylinder of the coating unit of a sheet-fed offset printing press or in its delivery system behind the UV lamps. The first position allows easy access and enough space for mounting, but enables analysis of the wet layers only. In contrast, in the delivery unit the probe head has to be installed between the moving elements of the sheet transport system, which strongly limits the available space and requires special probe heads with reduced size and increased focal length. However, this position allows monitoring the thickness of cured layers.

Reference data of the coating weight for calibration models were determined by gravimetry. Test samples with different thickness of the layers were prepared with a printability tester. Gravimetry was also used for crosschecking the data predicted in-line. Blank sheets with known weights were numbered before laying them into the feeding system of the press. After printing, the weights of the printed layers were determined. The numbering of the sheets did not only enable an exact measurement of the coating weights, but allowed also an unambiguous assignment of coating weight and spectra to specific sheets.

During in-line monitoring, samples with different surface weights of ink or varnish were obtained by systematic variation of the operating parameters of the printing press. Investigations were carried out at printing speeds between 6000 and 12,000 sheets/h corresponding to about 90–180 m/min. NIR spectra were recorded at a rate of 30 spectra/s. At 12,000 sheets/h, this corresponds to about 3 spectra per sheet. Synchronization between NIR measurement and printing was achieved by use of a sensor that detected the front edge of each sheet. The coating weight of printed layers was checked by gravimetry after the end of the trial. As an example, Fig. 21.12 shows a result of in-line monitoring of the coating weight of printed layers of a clear varnish [31]. The labels *Opening* and *Speed* refer to specific parameters of the offset

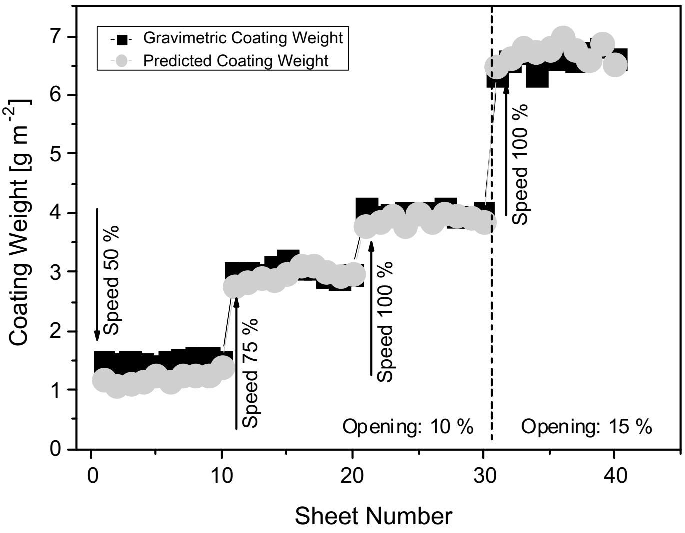

Fig. 21.12 In-line monitoring of the coating weight of a UV-curable printing varnish on paper in a sheet-fed offset printing press (printing speed 8000 sheets/h). For comparison, coating weights determined off-line by gravimetry are shown. Explanation of other labels is given in the text. Reprinted with permission by SAGE Publications Ltd. from Ref. [31]

printing press that control the amount of ink or varnish on the printing plate. An increase of these values corresponds to higher coating weights. The results demonstrate that the applied coating weight can be determined with very high precision. The prediction error was found to be about 150 mg/m^2.

Further studies on both printing inks and clear varnishes were directed toward the investigation of the influence of different printing speeds [32], the recipe of the varnish formulation [32], the color of the ink, the use of different paper and cardboard materials as substrate [33] as well as different gloss levels of the printed layers [34] on the accuracy of the prediction results. Complex calibration procedures including multistage and universal calibration models were developed, which were adapted to the requirements of each specific problem. Despite the rather low thickness of printed layers, the precision of the predictions from NIR reflection spectra recorded in-line is rather high: RMSEP values for the determination of the coating weight were found to be in the order between 120 and 200 mg/m^2.

21.2.5.2 Conversion of UV-Cured Printed Layers

Similar to UV-cured coatings, numerous factors in the printing process may influence the conversion of printed layers. This includes the characteristics of the ink or varnish (e.g., its composition and viscosity), the ambient conditions (e.g. temperature, humidity), and technical factors such as UV irradiance, printing speed and the specific setting parameters of the printing press. Any change of one of these parameters may lead to a change of the conversion of the printed layers. Generally, printing is a high-speed process, which rapidly produces large amounts of printed sheets. Therefore, sufficient conversion must be achieved before stacking in order to avoid blocking of the sheets. Moreover, adequate wipe resistance is required. It would be therefore desirable to monitor the conversion continuously during the printing process in order to ensure high quality and uniformity in this way.

However, monitoring the conversion in a printing machine is extremely difficult. So far, no in-line method for control of the conversion exists, and also its off-line determination is usually impossible in a printing plant, since no adequate analytical equipment for these measurements such as conventional IR spectroscopy is available at a printing press. Typically, indirect methods such as the determination of the coefficient of sliding friction with simple test equipment are used. NIR spectroscopy would open completely new possibilities for direct quantitative (or at least semi-quantitative) monitoring of the conversion during the printing process.

For developing a calibration model, calibration samples with well-defined thickness have to be prepared. As outlined above for coatings (paragraph 21.2.3.3.), variations of the thickness seriously disturb measurement of the conversion and may completely prevent quantitative analysis. Therefore, great care was bestowed on the preparation of printed layers with constant thickness. For each color, a number of printed paper stripes were prepared using a printability tester. The application weight depended on the color of the ink and varied between 0.8 g/m^2 (cyan) and 1.2 g/m^2 (yellow). Moreover, samples with a clear lacquer were prepared with about 3 g/m^2. Printed layers were irradiated with different UV doses in order to obtain samples with a broad conversion range. After recording the NIR spectra, discrete calibration models were developed for each color and the printing varnish. FTIR/ATR spectroscopy was used as reference method. As an example, the PLS calibration of a yellow UV printing ink is shown in Fig. 21.13 [35].

It is apparent that the scattering (and consequently RMSEP) is higher than in case of coatings with thicknesses, that are at least one order of magnitude higher (paragraph 21.2.3.1.). Nevertheless, it can be clearly seen that there is a linear correlation between reference conversion and predicted signal, which clearly proves that the conversion can be predicted from NIR reflection spectra by adequate chemometric tools. Generally, RMSEP for all inks is in the order of 3–4.5%. Due to the somewhat higher thickness of the layers of the printing varnish, RMSEP of the corresponding model was found to be only 2.3%. External validation tests confirmed the precision of the predictions [35, 36].

Using the various PLS models, the conversion of UV-cured ink and varnish layers was monitored directly in a sheet-fed offset press. It is obvious that only the position in the delivery unit behind the UV lamps can be used for mounting the probe head (see paragraph 21.2.5.1.). Except of the spatial limitations mentioned above, the probe head is exposed to vibrations, dust (e.g. talcum powder used for oil-based printing inks handled at the same press), heat, airflows, etc. at this position. Moreover, the printed sheet, which is fixed by clamps at its front edge only, glides on an air cushion through the delivery system, which may lead to sheet flutter. Variations of the

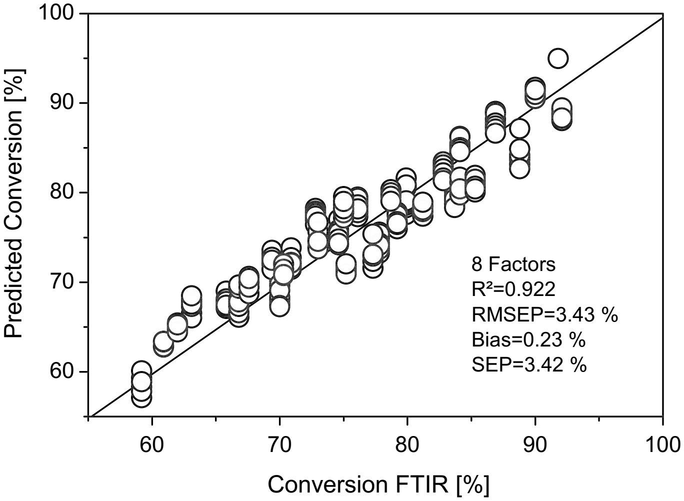

Fig. 21.13 PLS calibration model for the conversion in layers of a yellow UV-curable printing ink printed on 135 g/m^2 paper. Reprinted with permission by Elsevier B.V. from Ref. [35]

distance between probe head and paper are expected to strongly disturb quantitative NIR measurements. After several tests, the probe head was finally installed between the air nozzles in the middle of the bottom plate in order to minimize the influence of flutter on the measurement process [36].

Parameters of NIR sampling were the same as those during in-line monitoring of the thickness. Similar to in-line monitoring tests on coatings, the conversion was intentionally affected by variations of the applied UV dose, that is, by variation of either the intensity of the UV lamps or the printing speed. Figure 21.14 shows the effect of variation of the irradiance on the conversion of a cyan offset printing ink [36]. Apparently, even at irradiation with half intensity only a moderate decrease of the conversion is observed, which is due to the very high reactivity of printing inks. Although the data show somewhat stronger scattering due to the much lower thickness of the layers as compared to typical coatings, the conversion could be determined with rather high precision, which was confirmed by subsequent off-line measurements by FTIR/ATR spectroscopy. Investigations on inks with various colors as well as on clear printing varnishes in in-line monitoring tests at the printing press resulted in typical prediction errors for the conversion of 4–5%, which is only little higher than the error margins for coatings with thicknesses of 10 μm or more (2–3%). Only in case of black inks, it was found to be 5.5% due to the low reflectance of such layers.

The content of extractables in UV-cured coatings, that is, the amount of components that are not covalently bound to the cross-linked network, is directly related to the conversion that is achieved during irradiation. Extractables may lead to migration if printed materials are in contact e.g. to liquids. For this reason, the amount of extractables is an important parameter in packaging technology, in particular

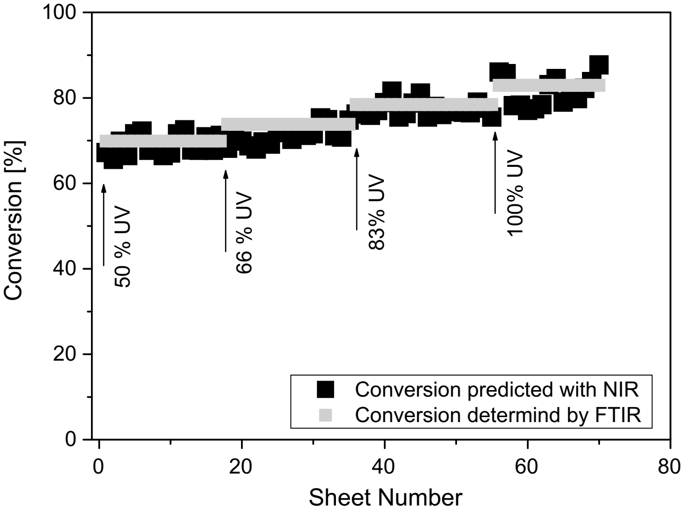

Fig. 21.14 In-line monitoring of the conversion in a cyan printing ink after irradiation with various UV doses (black). Conversions determined off-line by FTIR spectroscopy are given for comparison (gray). Reprinted with permission by Elsevier B. V. from Ref. [36]

in food packaging. The relation between conversion and the migration of acrylic compounds was studied quantitatively in dependence on the UV irradiation dose [36]. In fact, a linear relationship between the conversion and the acrylate migration was found. Using this linear relationship, the amount of acrylic extractables was directly predicted from NIR data during printing at the offset press (see. Fig. 21.15). For each irradiation dose, some random samples of printed sheets were analyzed by FTIR/ATR spectroscopy and HPLC measurements for comparison. For both the conversion and the migration, close correlation with the data predicted in-line was found. For the acrylate migration, the prediction error was estimated to be 0.03 g/m^2.

Certainly, this indirect method for the estimation of the content of extractable acrylate can neither achieve the accuracy of direct measurements by HPLC nor can replace such chromatographic analyses of the samples, which might be required e.g. for certification. However, it can provide a rough estimation of the actual state of the printed materials with respect to the migration behavior in running printing processes in real time, which allows rapid intervention, if deviations from the requested specifications occur.

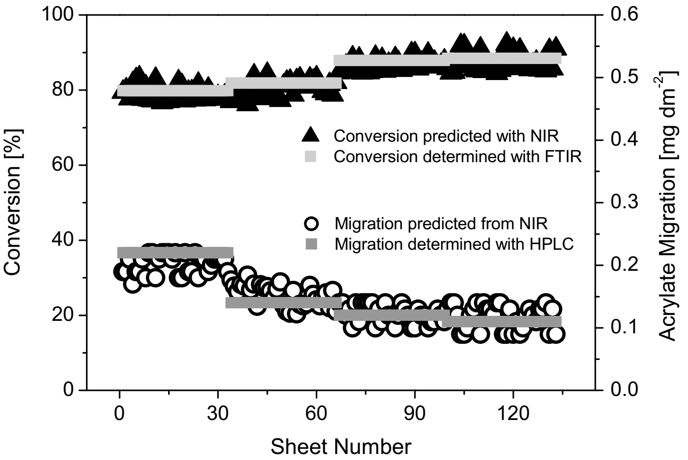

Fig. 21.15 In-line monitoring of the conversion in printed layers of a cyan printing ink and estimation of the specific acrylate migration from the NIR data. Reference values determined off-line are given for both the conversion and the migration. Reprinted with permission by Elsevier B. V. from Ref. [36]

21.3 Synthetic Fibers and Textiles

Despite their important role in daily life, the broad spectrum of different materials and forms of appearance as well as the multiplicity of production and processing technologies, textiles have been the subject of comparatively few studies in the scientific literature only that deal with their characterization or process monitoring by NIR spectroscopic methods. Moreover, the majority of the studies published so far is dealing with natural fibers such as cotton, wool, flax, silk etc. and the fabrics made there from. In the context of the present chapter on NIR investigations on special polymeric materials, we will limit this review to studies, which are only or at least mainly focused on synthetic fibers and textiles.

21.3.1 Classification of Textile Fabrics

Similar to polymers, the most important and most widely used application of NIR spectroscopy in textile technology is the sorting of used textiles. Identification of different materials (made from natural and synthetic fibers as well as blended fabrics) is indispensable for subsequent recycling processes, but typically requires extensive complicated and time-consuming analysis due to the endless broad range of different colors, patterns, specific appearances, pretreatments, construction differences, manufacturing technologies etc. In particular, the sorting of carpets became popular because of the rather large quantity of such materials resulting e.g. from the redesign of hotels, office buildings etc. [9, 37, 38]. Therefore, several special NIR-based analyzers for carpet analysis including both stationary and hand-held fiber-optic instruments are commercially available on the market.

However, identification of fibers and quantitative analysis of the composition of textiles is also beneficial in process control during production processes or for inspection purposes, e.g. in import and export of textile materials. A numbers of studies is dealing with material analysis for such applications [39–42]. A more recent application of textile classification is authentication of materials. In particular, in case of high-value materials the type and the percentage of fibers used in textiles and their blends becomes more and more important in order to prevent fraudulent supply of low-grade materials. This does not only apply to certain natural fibers (e.g. wool versus cashmere), but also to expensive synthetic materials such as aramid fibers used for example for bulletproof vests [41].

Based on the experiences with the sorting of polymer waste, NIR spectroscopy has been proven to be an extremely powerful tool for the fast and reliable identification of fibers and textiles, when it is combined with powerful chemometric algorithms such as principal component analysis (PCA) for the reduction of the dimensions of the data set and linear discrimination analysis (LDA) for classification. The majority of studies have been carried out by conventional NIR spectroscopy, but recently hyperspectral imaging has been used for data acquisition as well [41]. Most studies deal with the identification of combined sets of natural and synthetic fibers. Polymers, which are usually included in such studies, comprise typical fiber materials such as polyethylene terephthalate (PET), polyamide (PA), polypropylene (PP), polyethylene (PE), acrylic fibers such as polyacrylonitrile (PAN) [6, 9] and regenerated fibers such as viscose or tencel, but also more exotic materials such as polylactic acid (PLA) [42] and poly(p-phenylene terephthalamide) (para-aramid) [41]. Due to their different molecular structures, the differentiation between these fibers is rather easy. However, fibers with different, but very similar molecular structures of the same polymer such as PA 6 and PA 6.6 can be classified as well despite the marginal differences in their spectra [38]. More sophisticated methods such as neural networks are required to consider further properties of the fiber materials like color/dyeing or pretreatments such as heat setting.

21.3.2 Quality Control in Fiber and Textile Production

Blending is a common practice in textile manufacturing in order to combine technical and economic advantages of two or more fibers in a textile fabric. Therefore, blends make up a significant part of the textile market. In most cases, natural fibers (e.g. cotton, wool) are combined with synthetic fibers (usually polyester), but blends of synthetic fibers (e.g. PET/PA) are common as well. Typically, quality and price of textile fabrics are closely correlated with the composition of the blend. Monitoring of the actual composition is a critical issue for the control of conformity with the initial specifications, but also for process control, since certain properties that are relevant e.g. in technical applications (e.g. fire resistance, wear resistance) strongly depend on the ratio of the components [43]. Conventional analytic standard methods are time-consuming, labor-intensive and might require harmful chemicals (e.g. H_2SO_4 solution). NIR spectroscopy has been proven to be a powerful tool for the quantitative analysis of textile blends [38, 43–46]. The prediction of the content of the individual materials in such blends is often difficult due to the complex influence of a multiplicity of chemical, physical and textile parameters. Therefore, very large sample sets (e.g. about 200–300 cotton/PET samples [44–46]) are required for calibration of the models, which span not only the complete range of blend compositions (0–100% of each component), but also cover the variability of all other parameters. The immense data volume requires advanced mathematical pretreatment of the spectra as well genetic algorithms [44, 45] for variable selection in order to reduce the complexity of the multivariate models. Quantitative analysis itself is often based on the PLS regression. Moreover, support vector machine models have been tested [46]. In most cases, RMSEP for the determination of the cotton/polyester ratio was found to be 1–2% (with respect to cotton content) [43–46]. An example of a PLS model is given in Fig. 21.16 [44]. Apart from the widely studied cotton/polyester blends, wool/polyester blends were analyzed by NIR spectroscopy as well [43].

Acrylic fibers typically consist of copolymers of polyacrylonitrile (~ 85% w/w) and another vinyl monomer such as vinyl acetate, methyl methacrylate or methyl acrylate. Copolymerization is carried out in aqueous dispersion. The resulting polymer is not soluble in water. So, sodium thiocyanate has to be added to the suspension do dissolve the copolymer before fiber spinning resulting in a solution

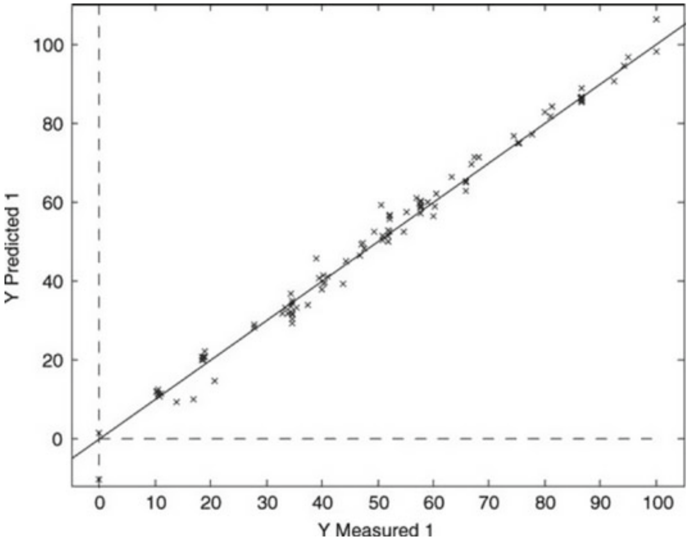

Fig. 21.16 Predicted versus measured reference values for the percentage of cotton in cotton/polyester blends using a full-spectrum PLS model. Reprinted with permission by SAGE publications Ltd. from Ref. [44]

called "dope." Extrusion of this solution through a spinneret into cold water leads to precipitation of the copolymer and the formation of fibers, which may be drawn to the desired thickness. For optimum process conditions, the actual ratio of thiocyanate and copolymer in the dope needs to be controlled continuously. NIR reflection spectroscopy was used for in-line monitoring of this ratio [47]. Difficulties in PLS modeling resulted from the fact that a variation of the NaSCN concentration led to a shift of the O-H bands of water, since the electrolyte prevents the formation of hydrogen bonds. Individual PLS1 models for NaSCN and the copolymer were developed resulting in RMSEP values of 1.6% (NaSCN) and 2.6% (copolymer), respectively. Similar results were also obtained with a PLS 2 model for simultaneous prediction of both concentration values.

Physical parameters of textiles may be determined as well. PA flocks with different degrees of fineness are used for the production of upholstery fabrics, which are indistinguishable by the human eye. Nevertheless, flocks with different degrees of fineness lead to different appearances of the final product. NIR spectroscopy was found to be an efficient tool for their discrimination [39].

Another parameter that influences the properties of textiles is the heat setting temperature applied during the production process. Heat has a significant effect on the molecular structure and the morphology of yarns. Heat setting is typically applied in order to improve textile properties with respect to shrinkage, warping, relaxation of internal stress, dye or finish fixation etc. When applied under tension, it may increase the tensile strength of fibers or fabrics and improve the behavior of the material during further manufacturing steps. For some applications (e.g. carpet manufacturing), very low variation and a high spatial homogeneity of the heat set temperature are required for the intended properties of the final products. NIR spectroscopy has been shown to be able to reveal the thermal history of the polymers in synthetic fibers [38]. In case of carpets based on PA, heat treatment is carried out at about 190–220 °C or occasionally at even higher temperatures depending on the specific method. PLS models could predict the heat set temperature of PA yarns from their NIR spectra with a precision (SEP) of about 1–2 °C for greige yarns and 2..3 °C for dyed yarns. Below 185 °C some deviation from linearity was observed, which was attributed to the Brill transition. The Brill transition in PA 6.6 occurs at about 160–180 °C and is due to the gradual transformation of the crystalline state from one triclinic structure existent at room temperature into a different triclinic structure stable at higher temperatures.

21.3.3 Finishing of Yarns and Textiles and Subsequent Drying

It is common practice in textile industry to provide fibers and yarns with special agents such as sizes (e.g. fatty acid ethoxylates, waxes, polyethylene) or lubricants (finishing oils) before processing them to textile fabrics in order (1) to make them more resistant to mechanical stress during those processes (e.g. weaving, knitting) by reinforcement and improved filament cohesion and (2) to reduce electrostatic charging as well as frictional wear and abrasion during passing them over machine parts such as needles, rolls, guides etc. The specific treatment depends on the fiber material and the intended use of the product.

Typically, very low amounts of finishing oils are deposited on the fibers (< 1 wt%). In order to achieve maximum quality of the products and optimum manufacturing conditions, the amount of finishing agents has to be controlled continuously. Conventional quantitative determination of the finishing oils is based on their removal by chlorinated solvents and analysis of the solutions by FTIR spectroscopy, which is a time-consuming and laborious procedure. BLANCO et al. have shown [48] by investigations on acrylic fibers made up of a acetonitrile–vinyl acetate copolymer that quantitative data on the amount of finishing agent can be obtained directly from the fiber during the spinning process by NIR reflection spectroscopy. The weight content of the finishing oil varied between 0.22 and 0.62 wt%. These low application weights require an excellent sensitivity of the spectroscopic method. Moreover, the properties of the acrylic fibers varied with respect to fineness, color, gloss and other possible sources of variability. The first component of the PLS model accounted for 99.99% of the spectral variance, which was related to spectral scattering due to variations in fineness of the fibers used for calibration. Generally, black samples and those dyed with dark colors were found to result in rather high absolute errors (up to 0.06 wt%). For all other samples, relative prediction errors (RMSEP) between about 6 and 7% were obtained, which roughly corresponds to the precision of data from the reference method. Similar investigations on the quantitative determination of finishing oil on the surface of PA 6.6 yarns have been reported as well [38]. Using a four-wavelength multiple linear regression (MLR) model, the amount of oil could be predicted with a SEP of 0.04 wt% for deposits of about 1 wt%.

After manufacturing of the textile fabric, the processing agents have to be removed carefully before further processing steps such as finishing with functional agents, coating, lamination, printing, etc., since the finishing oils and sizes are often hydrophobic and hence strongly affect wettability and adhesion. In particular, it has to be made sure that the oil or size is completely removed everywhere across the surface in order to avoid local wetting or adhesion problems. However, due to the invisibility of the very thin and colorless layers, the detection of local remains of the processing agents is hardly possible. Recently, NIR spectral imaging has been shown to be a powerful tool for this analytical task [49]. A size consisting of hydrocarbons and fatty acid ethoxylates was applied to polyester fabric with application weights between 0.4 and 5.5 g/m^2 in order to provide samples for calibration of a PLS model. Using this model the amount of size was determined with a precision of about 0.2 wt% by averaging the predicted individual values across the surface of the fabric. Monitoring of the distribution of the size across the textile web is of no technical relevance since it is applied to the yarn before weaving. After washing-out of the size and drying of the textile, the cleanness of the desized fabric was inspected by spectral imaging with respect to both quantification of the residual amount of size and its spatial distribution. The amount of remaining size was found to be at or below the prediction error of the external validation, which was sufficient for further processing such as ink jet printing. Moreover, traces of size applied by arbitrary spraying of a dilute solution to clean fabrics could be detected and quantified by this method as well.

Aside from the treatment with such processing agents, which have to be removed before subsequent processing, textile fabrics may be also finished with finishing agents in order to provide them permanently with certain functional properties such as flame retardancy, optical brightening, stiffening, hydrophilicity or hydrophobicity, water repellence, biocide or stain resistance, anti-static behavior and other features. Typically, such agents are applied by impregnation in aqueous solutions in a foulard, which is often followed by heat setting to improve fixation to the textile fibers. Depending on the special substrate, agent, and intended application finishes are applied with application weights in the range from less than 1 g/m^2 and to several tens of g/m^2. The finishes have to be applied according to the specified value of the application weight and with exceedingly homogenous spatial distribution across the textile fabric, which is required for both further processing of the finished textiles as well as for optimum application properties. However, similar to sizes and finishing oils most of the finishing agents form colorless layers on the surface of the textile, which usually prevents in-line detection by optical methods in the visible range. Rather, quantification is mostly carried out off-line by extraction, gravimetry etc. Recently, SCHERZER et al. [49] have demonstrated the immense potential of hyperspectral imaging for both quantitative analysis of the applied amount and monitoring of the spatial homogeneity of finishing layers on textiles fabrics. For example, it was shown that the application weight of flame retardant layers (in the order of several tens of g/m^2) applied to polyester fabric can be detected with a prediction error (RMSEP) of 2.2 g/m^2. The corresponding PLS calibration is given in Fig. 21.17. Figure 21.18 shows spectral images of two finished polyester fabrics. In one of them, a spot pattern resulting from several drops of finishing solution that were dripping down to the already dried material, can be seen. The average application weight obtained by integration over the individual values across the complete surface of the spectral image of each finished sample proved a very close correlation with the corresponding reference values obtained by gravimetry (i.e., differences < 2 g/m^2). Moreover, local inhomogeneities of the density thickness were clearly detected. In particular, the dotted pattern forming a rectangular frame close to the cut edges originates from pinning the fabric on a tentering frame for drying after impregnation and squeezing.

Similar investigations were carried out with other textile materials such as PA fabric and with other finishing systems such as stiffening agents, optical brighteners, adhesion promoters and hydrophilic layers. Depending on the specific material combination, prediction errors were found to be in the order of 1–2 g/m^2. However, there is one exception of finishing layers that cannot be monitored by NIR imaging. Water-repellent finishes are often based on fluorocarbon compounds, which cannot be detected by NIR spectroscopy.

The next step in finishing of textiles by impregnation in aqueous solutions is the drying process. Typically, this is a multistage process consisting of dewatering

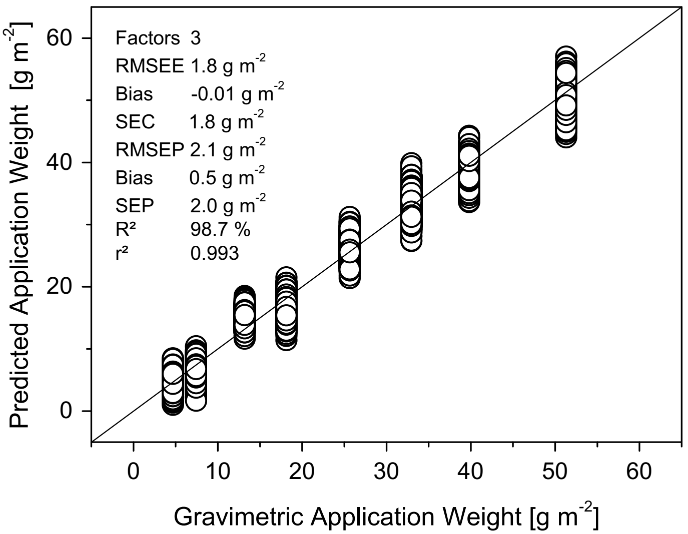

Fig. 21.17 PLS calibration model for the application weight of a flame retardant on pale beige polyester fabric (200 g/m^2). Reprinted with permission by Elsevier B. V. from Ref. [49]

by squeezing, suction by low pressure and thermal drying. Obviously, drying is an energy-intensive process, which should be carried out up to the technically required level only. NIR spectroscopy or imaging are predestined for monitoring the state of the drying process due to the strong absorbance bands of water in this spectral region (e.g. the strong combination band around 1940 nm and the first overtone at about 1450 nm). Accordingly, the determination of the water content is probably the most widely used application of NIR spectroscopic methods, in particular in agriculture, food processing, pharmaceutics etc. With respect to textile processing, NIR methods are particularly suited for monitoring the content of remaining moisture at the end of the process. SCHERZER et al. [50] determined the residual damp of finished textiles by NIR hyperspectral imaging using PLS calibration models. Textile substrates and finishing systems were largely the same as those, which were studied above with respect to application weight. Figure 21.19 shows NIR spectra of a PA fabric finished with a flame retardant at different moisture levels. Figure 21.20 shows the corresponding PLS calibration model. Reference data were determined by gravimetry using a moisture analyzer. The prediction errors (RMSEP) of the PLS models of all material combinations were found to be around 0.5%, since this was the lower detection limit of the analyzer. Probably, an improved detection limit could be achieved with the NIR-based technique if a reference method with higher sensitivity would be used. Hyperspectral imaging does not only provide quantitative data on the dampness, but reveals also its spatial distribution, which can help to evaluate the homogeneity of the drying process. For example, the visualization of differences between the outer areas on both sides of broad textile webs could assist with improving the control of the drying oven.

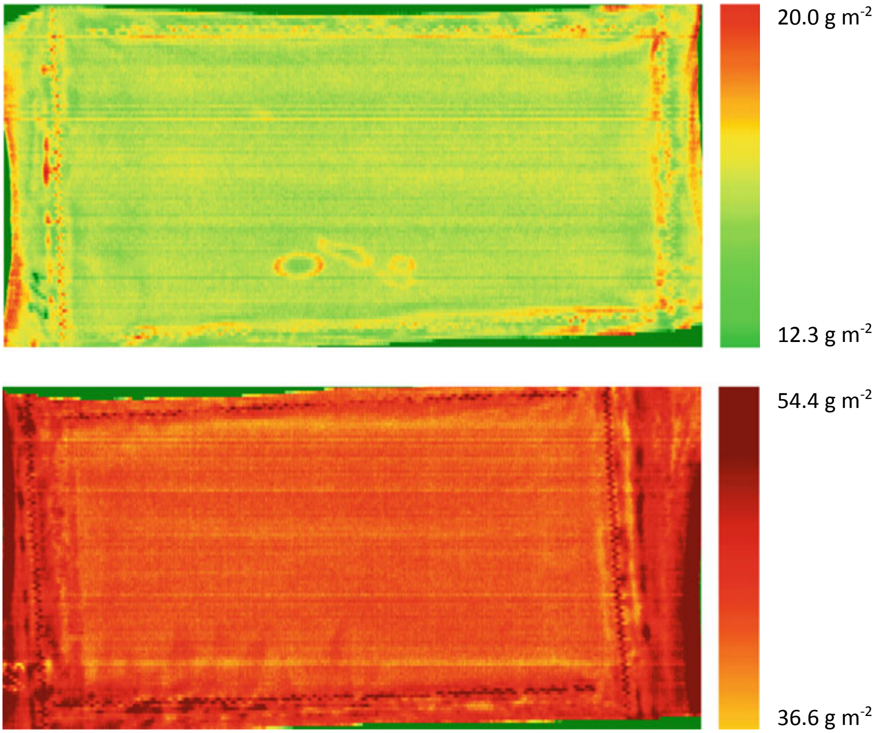

Fig. 21.18 Hyperspectral images of the distribution of a flame retardant on polyester fabric. In the upper one, a spot pattern resulting from dried drops of finishing solution can be identified. The gravimetric application weights of the samples were 13.2 (top) and 43.1 g/m^2 (bottom). Reprinted with permission by Elsevier B. V. from Ref. [49]

The moisture content of synthetic fibers and yarns has been studied by NIR spectroscopy as well. Moisture is a critical parameter with respect to both properties (e.g. morphology, many physical parameters such as glass transition temperature, tenacity etc.) and processing (e.g. dyeing or lamination) of the textile materials. On the other hand, the water content of hydrophilic polymers such as PA depends on the relative humidity of the air or the occurrence of moisture in technical processing steps. The maximum water content of PA is in the order of 2.5–3.5 wt% depending on the specific type of PA. The moisture content of spun PA fibers was determined by NIR spectroscopy with precisions (SEP) between 0.3 and 0.5% [38]. Similar investigations were reported for PAN and viscose [39].

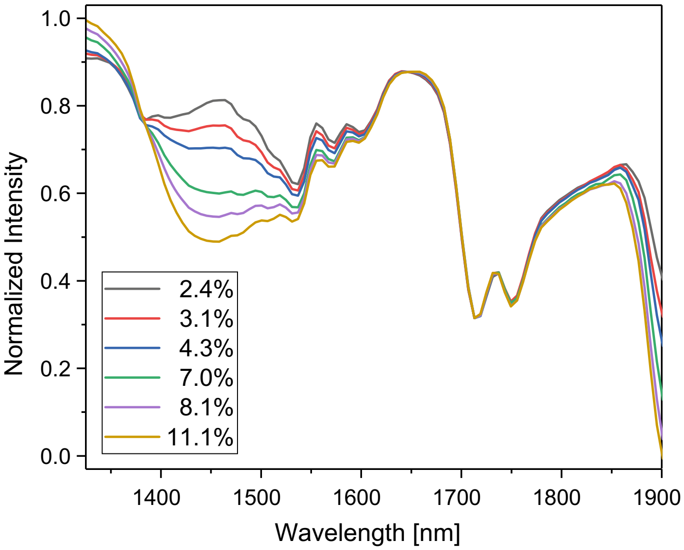

Fig. 21.19 NIR spectra of PA fabric finished with a flame retardant containing various amounts of residual moisture. Spectra were normalized to the double peak of the C-H overtone peak at 1720/1750 nm

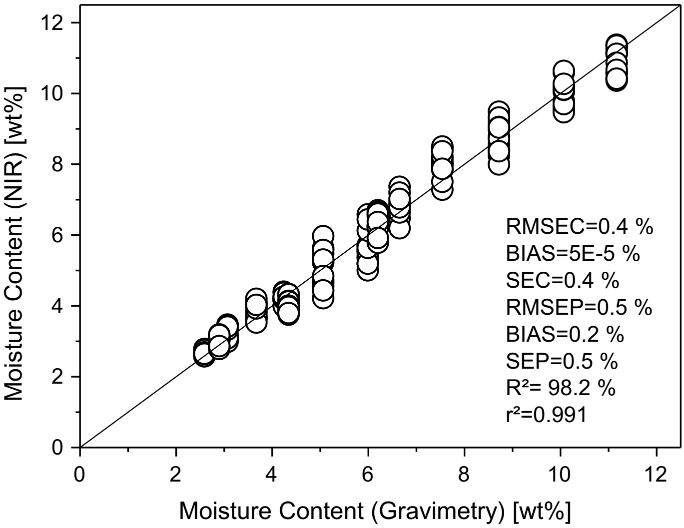

Fig. 21.20 PLS calibration to the moisture content of PA fabrics finished with a flame retardant

21.3.4 Lamination of Textiles

In several technical applications, textiles are used as laminates in order to combine the properties of different materials. For example, combinations of a fabric as top layer for the optical appearance and a hidden nonwoven material for sound insulation are widely used for interior design in automotive engineering (e.g. for door and roof linings or rear panel shelfs) and similar applications. Both textile layers are bonded to each other by laminating hot-melt adhesives. Such adhesives can be applied as powder, hot melted mass or melt-spun fibrous webs. During application of the adhesive and the subsequent lamination of the two webs, several deficiencies may occur depending on the specific adhesive system such as over/underdosage or uncoated areas for powders and melts as well as tears, holes or buckle formation in case of adhesives webs. Generally, lamination defects lead to deficient bond strength or even delamination, impairment of the visual appearance etc. Therefore, continuous monitoring of the homogeneity of the inside adhesive layer would be essential for an efficient control of the lamination process. However, visual inspection of the hidden layers or use of a corresponding camera is prevented by their invisibility and inaccessibility from outside.

Near-infrared radiation is well-known to penetrate to a certain degree into polymer materials, at least for some tens of micrometers depending on the specific material, its color and morphology. Materials for interior design in automotive engineering often contain a top layer made up of polyester piqué fabrics with weights between about 100 and 200 g/m^2. Colors may cover a broad range, but the majority of materials is beige, gray or black. Due to their weave structure, such fabrics appear to be slightly translucent. On the other hand, the fibrous structure of the materials may lead to diffuse scattering of incident radiation. Therefore, investigations were accomplished in order to clear up if adhesive layers hidden in textile laminates can be visualized and quantitatively analyzed by hyperspectral imaging. Generally, spectral analysis was carried out from the top side, since the nonwoven is usually thicker than the fabric and shows much stronger scattering of the probe light. In fact, it was demonstrated that the reflection spectra of such three-layer laminates show significant contributions of the adhesive layers based on aliphatic polyester [30] (see Fig. 21.21). In particular, a specific absorption was observed around 1410 nm, which is attributed to a C-H combination band in aliphatic hydrocarbons ($2\nu CH_2$ and δCH_2) [51], as well as in the range above 1700 nm. Similar results were obtained for laminates containing PA-based adhesives webs. Even reflection spectra of corresponding black textile laminates can be recorded in high quality and with explicit effect of the coating thickness of the adhesive layers [52], although the optical conditions are far from being ideal for this kind of measurements.

Reflection spectra were found to correlate with the application weight of the hot melt adhesive. A principal component analysis (PCA) of the NIR spectra of the laminates showed that the scores plot of the first two components (PC1 versus PC2) only allowed a discrimination between samples with and without adhesive layer, whereas

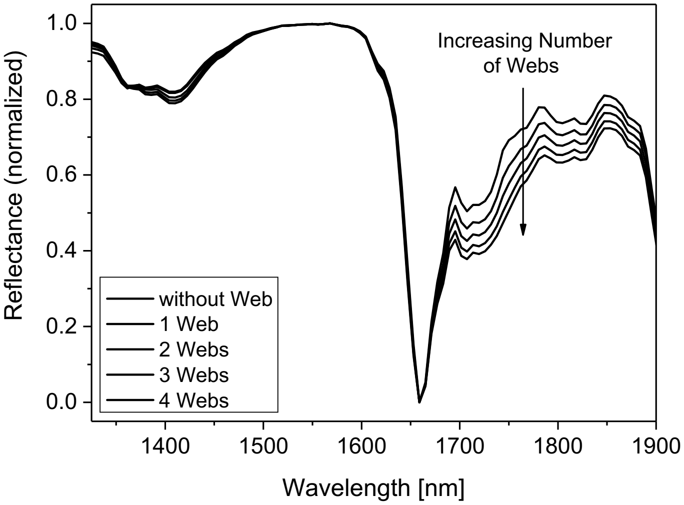

Fig. 21.21 NIR spectra of bright three-layer laminates with different numbers of adhesive webs. Reprinted with permission by Elsevier B. V. from Ref. [30]

the plot of the second and third component (PC2 versus PC 3) also enables a differentiation between adhesive layers with different thicknesses [30]. Consequently, PLS calibration models were developed. Reference data were obtained from gravimetry during sample preparation. For each sample (roughly 20 × 30 cm), several tens of thousands spectra were recorded with a hyperspectral camera. In order to consider a possible non-uniform distribution of the adhesive coating weight across the samples, their surfaces were divided into rectangular regions by defining a grid of n columns x m rows. Spectra from each region were allocated alternatingly, that is according to a chessboard pattern, to the calibration and the validation set. In case of bright laminates (beige or light gray top layer), this resulted in RMSEP values around 3.5 g/m^2 [30] for adhesive layers between about 25 and 125 g/m^2 (see for example Fig. 21.22), whereas the prediction error was higher (around 6 g/m^2) for laminates made up of black textiles only [52]. Accordingly, the color of the latter laminates somewhat impairs the precision of the predictions, but by no means it prevents the quantitative analysis of the thickness of the buried hot melt layers. External validations confirmed that the application weight of the inside adhesive layers can be actually predicted within this error limits. Moreover, averaging the predicted individual values from all NIR spectra across each sample enabled a direct comparison with gravimetric reference data. Due to this averaging process, the deviations are lower than the corresponding RMSEP (up to ~ 2 g/m^2 for bright laminates and up to ~ 5 g/m^2 for black laminates). As an example, the spectral image of a three-layer laminate consisting of black textiles is shown in Fig. 21.23 [52].

Aside from the prediction of quantitative data of the application weight of the adhesive layers, the main objective of investigations by spectral imaging is monitoring of the homogeneity of the layers and the detection of coating errors. In fact,

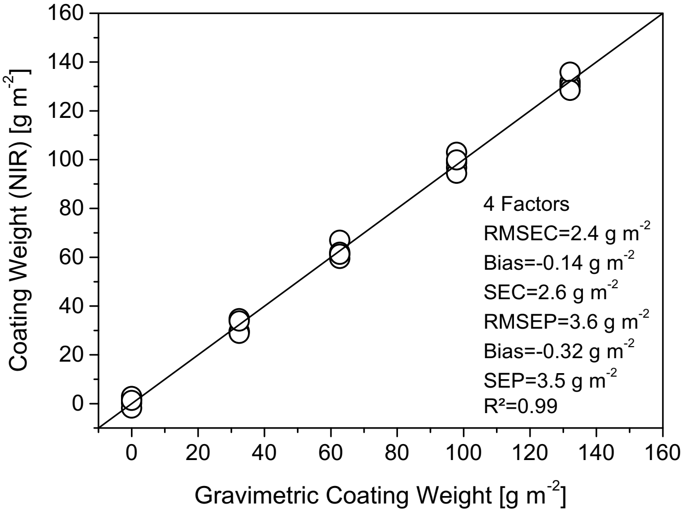

Fig. 21.22 PLS calibration model for the coating weight of the adhesive layer in bright polyester-based three-layer laminates. Reprinted with permission by Elsevier B. V. from Ref. [30]

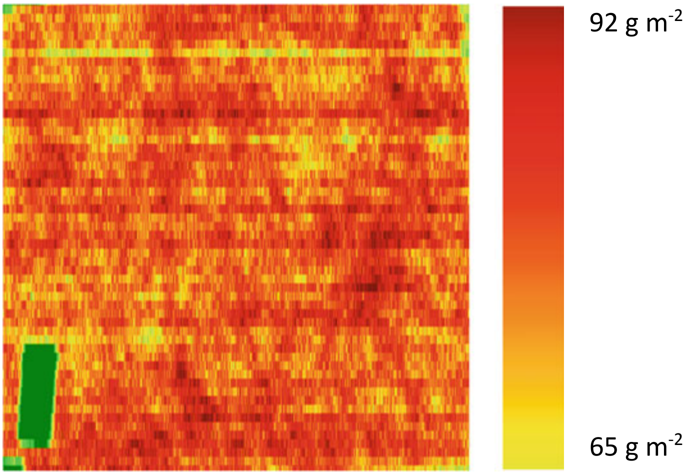

Fig. 21.23 Hyperspectral image of the distribution of the adhesive inside a black polyester-based three-layer laminate. The gravimetric application weight of the adhesive was 80.9 g m^{-2}. Reprinted with permission by Elsevier Ltd. from Ref. [52]

it was shown that the calibration and validation samples of the textile laminates had a very high homogeneity. On the other hand, laminates with specific error patterns (uncoated areas, overdosage, tears, folds, thick adhesive droplets etc.) were prepared. All defects were clearly detected in the spectral images [30, 52]. In most cases, even quantitative information about the defects were obtained. Figure 21.24 shows a repre-

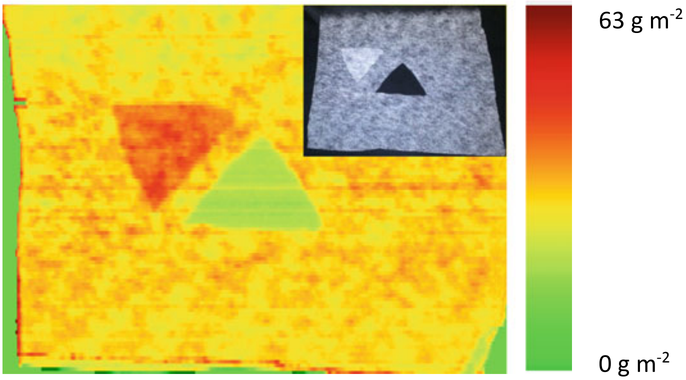

Fig. 21.24 Hyperspectral image of a bright polyester-based three-layer laminate containing an adhesive web with an intentionally prepared defect (see inset). Reprinted with permission by Elsevier B. V. from Ref. [30]

sentative example of a textile laminate with an intentionally prepared defect in the adhesive web [30]. The triangular area that was cut out of the web was placed close to the hole during lamination.

Finally, it was shown that acceptable predictions of the application weight of the adhesive can be even obtained if the thickness (or the weight per area) of the polyester top fabric varies, e.g. if laminates with different specifications have to be produced alternately [52]. The variation was included in the PLS model as well, which resulted in some increase of RMSEP (by ~ 50%), but still allowed predictions with reasonable precision.

The investigations proved the excellent potential of hyperspectral imaging for monitoring the homogeneity of hidden hot melt adhesive layers inside textile laminates, even if these laminates consist of black components only. This opens up new possibilities for continuous large-area quality and process control in technical lamination processes.

21.4 Conclusion

This chapter demonstrated that NIR spectroscopy cannot only be used for “classical” applications in polymer science and technology such as monitoring of polymerization and curing reactions. Rather, it may be also applied to a broad range of thin layers such as polymer coatings, printed layers, laminating adhesives, functional layers in textile finishing etc., although the thickness of such layers is far below that of typical subjects of investigations by NIR spectroscopy, which broadens the application range of NIR-based methods for the analysis of polymeric materials considerably. This expansion was enabled and pushed by the tremendous performance, in particular the considerably enhanced sensitivity, of modern NIR instrumentation in combination with powerful chemometric approaches.

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