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In-line monitoring of the conversion in photopolymerized acrylate coatings on polymer foils using NIR spectroscopy

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Abstract

Near-infrared (NIR) reflection spectroscopy was used to monitor the conversion of double bonds in acrylate coatings after irradiation with UV light or electron beams. Quantitative analysis of the spectroscopic data was performed either with a chemometric method on the basis of the PLS algorithm or according to the Beer–Lambert law. FTIR spectroscopy was used for calibration. In-line monitoring of the conversion in pilot-scale was carried out on clear and pigmented coatings, which were applied to polymer foils or paper by roll coating. Useful data were obtained from layers with a thickness from 4 g/m^2 upwards and at line speeds of at least up to 120 m/min. It was shown that any change of the irradiation dose or other parameters such as inertization leads to an immediate response in the conversion record. Similar investigations were also performed on layers of UV-curable adhesives on the basis of acrylic hot-melts.

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1. Introduction

Process analytical tools are used in the chemical industry for a long time in order to control the actual state of the process and the quality of the products made [1,2]. Since some years, such systems are also increasingly employed for the monitoring of various polymerization reactions [3–5] where they can help to optimize the efficient use of energy and raw materials, but also to ensure that the properties of the produced polymers are within the given specification. Typical applications include batch, solution, and emulsion polymerization, thermal curing and extrusion processes. However, monitoring and control would be also interesting for radiation-induced polymerization reactions.

The most important parameter for process and quality control of UV and electron beam (EB) curing processes is the conversion of the (meth)acrylic double bonds since that determines all other functional properties of a coating such as scratch and abrasion resistance, hardness, weathering resistance, chemical stability, the content of extractables etc. Moreover, also for further processing of the coating a sufficient conversion is required, and wipe resistance must be attained before stacking or winding.

However, the conversion which is achieved during irradiation depends on a large number of factors such as the applied irradiation dose which is determined by both line speed and irradiance of the incident UV light (or the electron current in EB curing), the composition of the reactive formulation, temperature, inertization and other factors. Only some of the possible influences can be easily controlled. Hence, the compliance of the actual level of the conversion of a coating with the requirements determined by the specific application has to be controlled continuously in order to be able to respond to process variations. For an efficient process and quality control, the immediate and continual availability of current conversion data is an indispensable precondition.

Various analytical methods have been tested in respect of their applicability for in-line measurements of the conversion of a coating in a running coating line [6]. However, none of them was found to be sufficiently suited for this task. Fluorescence techniques [7,8] require the addition of expensive fluorescence probes which may interfere with

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the properties of the cured coating. Ion mobility spectroscopy [9] is limited to the detection of volatile compounds (e.g. fragments of photoinitiators) and lacks sensitivity and specificity. Moreover, both techniques are indirect methods, i.e. they do not detect the conversion of the acrylic double bonds but secondary properties.

Near-infrared (NIR) spectroscopy is widely used for process control in the chemical industry and in several other commercial applications [3,4,10–12] since it possesses sufficient time resolution and sensitivity for in-line measurements as well as comprehensive and versatile analytic potential. Moreover, efficient analysis of the recorded data stream can be supported by powerful chemometric methods. Dedicated NIR process analyzers based on multichannel detectors are compact, rugged and comparatively cost-effective. Generally, they are equipped with optical fibers which allows spatial separation of spectrometer and probe head and consequently easy integration of the instrument into an existing production line.

In the past, NIR spectroscopy was applied for the monitoring of various polymerization reactions such as the batch and solution polymerization of styren [13–15] or the thermal curing of epoxy resins [16–20]. Also acrylates and methacrylates have already been object of such investigations. Their analysis is based on the first overtone of the C–H stretching vibration of the (meth)acrylic double bonds which appears at 1620 nm [21]. In a number of previous works, the conversion of double bonds was followed during the bulk [22,23] and the solution polymerization [24–26] of methyl methacrylate (MMA), the copolymerization of MMA and styren in emulsion [27,28], and the thermal copolymerization of various methacrylates [29,30]. In these batch processes, the thickness of the layer in which the NIR probe light is absorbed lies in the range of millimeters or centimeters. Some authors also report the investigation of photopolymerization reactions of acrylates [31–33] and methacrylates [34–37] by NIR spectroscopy. However, those investigations were performed on thick samples as well (i.e. with a thickness of about 1–6 mm) since most of the samples were dental composites. In contrast, the typical thickness of photopolymerized acrylate coatings is some micrometers only. The investigation of such thin coatings is difficult because of the relative low extinction coefficients in the near-infrared. Nevertheless, in this paper it will be shown that NIR reflection spectroscopy is able to detect even small variations of the conversion in acrylate coatings studied directly in a running coating line inspite of the weak absorption and the very low thickness of the layers.

2. Experimental

2.1. NIR reflection spectroscopy

NIR spectra were recorded with a Kusta 4004 P near-infrared reflection spectrometer (from LLA). This process analyzer system was developed according to the specific requirements of inline measurements on thin photopolymerized acrylate coatings [38]. It consists of a spectrometer unit and a separate tailor-made probe head which is linked to the spectrometer by a fiber-optic cable.

The spectrometer is based on a concave holographic grating and a fast linear photodiode array as detector. The thermoelectrically cooled InGaAs detector with extended wavelength range consists of 256 elements and covers a spectral region from 1530 to 2000 nm. With its minimum integration time of 56 μs, the diode array provides the time resolution and the sensitivity which are necessary for in-line monitoring.

The tungsten halogen lamp used as light source of the spectrometer is integrated in the probe head. In order to prevent postpolymerization of the acrylate coatings by the short-wavelength part of its emission an UV filter is mounted in front of the probe head. Moreover, it is equipped with a diffusor plate in order to suppress interferences in thin transparent foils of optically highgrade polymers. Spectra of transparent film samples are measured in the transflectance mode [39], i.e. they are taken against a ceramic retroreflector behind the foil which is also attached to the probe head.

The probe head is to be installed above the moving web of a roll coating machine. For basic investigations in the lab, e.g. calibration studies, it can be mounted on a special frame.

2.2. FTIR spectroscopy

Samples for FTIR spectroscopy were made by drawing acrylate coatings on polyethylene (LDPE) foil using a drawing bar. Subsequently, they were irradiated under nitrogen in an UV lab-curing unit equipped with a conveyor and a mercury arc UV lamp (IST). In order to cover a wide range of conversions, the concentration of the photoinitiator, the power of the UV lamp and the speed of the conveyor were varied.

FTIR transmission spectra were recorded on a Digilab FTS 6000 spectrometer straight after UV irradiation. The acrylate conversion was determined from the band of the CH_2 scissor deformation mode at 1405 cm^{-1} [40].

2.3. Roll coating and curing

In-line monitoring studies were carried out on a pilot-scale roll coating machine. It is equipped with a Fusion F-600 mercury arc lamp, various excimer lamps (Heraeus), and a LEA electron beam (EB) accelerator operated at 150 kV (IOM) [41]. If not otherwise stated, the mercury arc lamp was used for irradiation. The conversion was followed in coatings from proprietary clear and pigmented acrylate formulations to be used as functional or protective layers on various polymer foils or paper. Lucirin TPO-L (BASF) was used as photoinitiator.

Application and UV irradiation of adhesive layers were performed with a dedicated slot die coating machine. After heating to 90 °C in order to get a melt viscosity being suitable for processing the adhesives were applied to a 220 μm thick polypropylene tape and subsequently irradiated at 308 nm with the monochromatic emission of a XeCl* excimer lamp (Heraeus) which was mounted lengthwise in order to increase the applied irradiation dose.

In both cases, the NIR probe head was placed above the web just behind the exit of the UV lamp or the EB accelerator, and spectra were recorded continuously at a rate of 100 spectra/min.

3. Results and discussion

3.1. Detection of double bonds in thin acrylate coatings

Usually, NIR spectroscopy is used to study batch processes or thick layers. In these cases, the inherent absorption of the sample is high enough to get spectra with a sufficient signal-to-noise ratio. However, it was shown recently [38] that one even can obtain spectra of good quality from coatings with a thickness of some micrometers only such as those in radiation curing processes when the spectra are taken in reflection with an instrument with sufficient sensitivity. As an example, Fig. 1 shows spectra of an acrylic clear coat with a thickness of 10 μm before and after UV photopolymerization.

The acrylate band at 1620 nm and its decay on irradiation can be clearly seen in the spectra. However, the reflection spectra are not only affected by the coating itself but also by the absorption of the polymer foil used as substrate what may cause problems, in particular when clear coatings are applied to thin transparent foils of optically high-grade polymers such as oriented polypropylene (OPP), polyethylene terephthalate (PET), etc. If the thickness of the foil is only little higher than the wavelength of the incident probe light (i.e. foils up to about 25 μm), interference fringes appear [42]. This pattern completely masks the actual spectrum and prevents any analysis. Since established spectroscopic techniques such as roughening of the sample cannot be used in process control a diffusor plate was fit in-between light source and sample to degrade the interferences. Moreover, the probe head was tilted against the sample since the amplitude of the fringes depends on the angle of incidence of the probe light. Both together, the diffusor plate and the tilt, completely suppress the interferences and enable in this way the determination of the acrylate conversion in clear coatings on thin polymer foils [38].

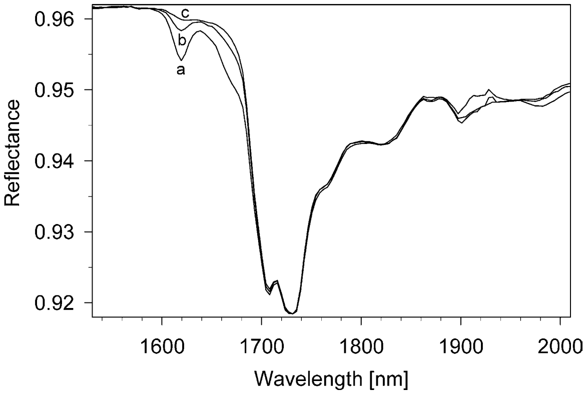

Fig. 1. NIR reflection spectra of a 10 μm acrylate coating on 20 μm OPP foil before (a) and after UV irradiation with 10 (b) or 500 mJ/cm^2 (c), respectively.

Since NIR measurements are performed in reflectance the applicability of the method is not limited to transparent coatings and substrates. It can be also used for opaque substrate materials like paper, cardboard or filled polymer foils as well as for pigmented coatings. Pigment particles such as titanium dioxide do not affect the investigation of the acrylate band since they do not or only weakly absorb in this spectral region. Moreover, there are no restrictions with respect to the color of the pigment except of black ones whose reflectance is too low to get a signal with sufficient intensity.

3.2. Quantitative analysis of the spectroscopic data and calibration

The quantitative analysis of the spectroscopic data in most NIR applications is carried out with chemometric evaluation methods such as partial-least squares (PLS) regression [43] which are able to detect even minor concentration differences. The use of these multivariate analytical techniques first requires the setup of a specific calibration model which relates the spectral variation in the NIR data to the parameter of interest.

For the creation of a powerful model, a large set of well-defined calibration samples is needed. Most studies using chemometrics for the analysis of NIR spectra deal with investigations on the composition of complex mixtures. Samples with a known composition to be used for calibration can be easily prepared in this case simply by mixing the components in a well-defined ratio. Even the degree of polymerization in many polymerization reactions can be determined in this way by using defined mixtures of the polymer and the monomer [14,23,25]. However, in UV photopolymerization the specific preparation of coatings with an exactly predetermined conversion is difficult to achieve, and the accurate characterization of cross-linked polymers can be a complex and laborious task, which moreover, might be prone to stochastic and methodic errors. Definitely, a PLS-based calibration cannot be better than the set of calibration samples on which it is based. With respect to in-line monitoring of technical curing processes chemometric methods may have another drawback: the calibration procedure usually cannot be carried out directly on the curing line. On the other hand, transfer of the calibration from the lab to the technical line may be difficult or even impossible [39]. Nevertheless, a separate calibration is required for each coating system, i.e. for each acrylate formulation and each combination with a specific substrate.

Considering this, we used two different ways for the quantitative determination of the acrylate conversion in UV-cured coatings in the present study: a chemometric approach on the basis of the PLS algorithm and a simple band integration method according to the Beer–Lambert law using the acrylate band at 1620 nm.

For both methods FTIR spectroscopy in the mid-infrared was used as independent reference method. Usually, FTIR spectra of thin polymer coatings are easily taken in attenuated total reflection (ATR). However, the depth of penetration of the infrared radiation into the sample which is defined as the depth in which the electric field strength is only 1/*e* of its value at the interface, typically is in the range between 1 and 2.5 μm [44]. Consequently, the conversion is measured in a thin top layer of the coating only. In contrast, near-infrared radiation passes through a transparent sample which means that the conversion which is obtained from the NIR spectrum represents an average of the conversion within the coating. Strongly UV-absorbing acrylate systems, e.g. those with a high photoinitiator content, show a distinct conversion gradient. If the irradiation is carried out under air, an additional inverse conversion gradient may occur close to the surface due to inhibition of the radical reaction. For these reasons, measurements with FTIR-ATR spectroscopy in the mid-infrared and reflection spectroscopy in the near-infrared are not equivalent, which leads to considerable differences between the results from both methods. In order to avoid this, FTIR spectra were recorded in transmission. However, this strongly limits the range of samples which can be studied, i.e. with respect to the type of the substrate and the thickness of both coating and substrate.

In this paper, the investigation of the two methods for quantitative analysis was carried out with 10 μm thick acrylate coatings on a 30 μm LDPE foil. Samples with a wide range of conversions were prepared. In order to avoid significant postcuring, NIR reflection and FTIR transmission spectra were recorded immediately after UV irradiation. With both methods, spectra were taken at several points of the each sample, and the resulting spectra were averaged before further processing.

On the basis of more than 50 data sets (including several non-irradiated layers) a PLS calibration model was build up using the algorithm which is implemented in the software package of the Kusta NIR spectrometer. For an adequate description of the spectral variation of the NIR data four eigenvectors were found to be required. In Fig. 2, the acrylate conversion predicted with this calibration model from the NIR spectra of the calibration samples is plotted against the conversion measured with FTIR spectroscopy. The results show an excellent linearity and low scattering which proves the high potential of the created model for the reliable determination of the acrylate conversion.

The predictive capability of the PLS model was tested with some additional samples which did not belong to the calibration set. They were processed in the same way like the calibration samples, and the conversion obtained from their NIR spectra using PLS was compared to the conversion determined from the FTIR spectrum. The data points are also plotted in Fig. 2. The close correlation ones again demonstrates the power of the calibration model generated.

As a simple and less time-consuming alternative for the quantitative analysis of the NIR spectra, the conversion in the acrylate coatings can be also determined directly from the ratio of the integrals of the overtone band at 1620 nm before and after irradiation of the sample. In this case, calibration is done just by recording some spectra of non-irradiated coatings. On the basis of the same set of calibration samples, the precision of the integration method was tested by comparing the conversion data obtained in this way with those from FTIR spectroscopy. Results are summarized in Fig. 3. In the complete range of conversion studied a close linear correlation between the data from the two spectroscopic methods was found. However, NIR spectroscopy slightly underestimates the conversion in comparison to FTIR spectroscopy. This offset gradually increases with increasing conversion. Basically, there is no difference expected when comparing the results from the two spectroscopic methods. Probably, it might be due to baseline effects in either one or both methods.

Nevertheless, band integration was found to be a quite rapid and in most cases practicable alternative to get quantitative conversion data from the NIR reflection spectra of acrylate coatings. In contrast to the chemometric method which is highly specific, it can be used in a much more universal manner. The slight deviation of the conversion obtained in this way from the reference data as shown in Fig. 3 could be easily corrected for because of the linear relation between the data from FTIR and NIR spectroscopy. However, the thickness of the coating has to be constant throughout calibration and measurement since there is no

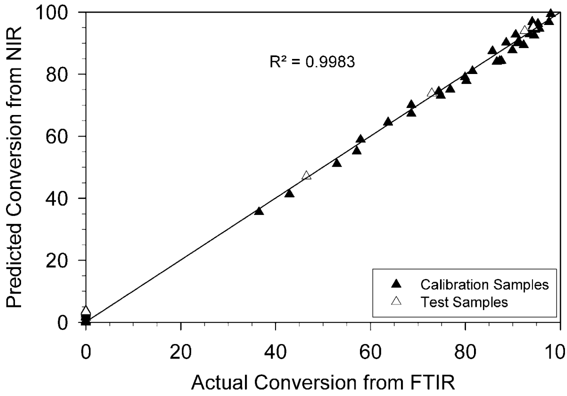

Fig. 2. PLS calibration of the NIR reflection spectra of 10 μm acrylate coatings on 30 μm LDPE foil to conversion data determined by FTIR transmission spectroscopy.

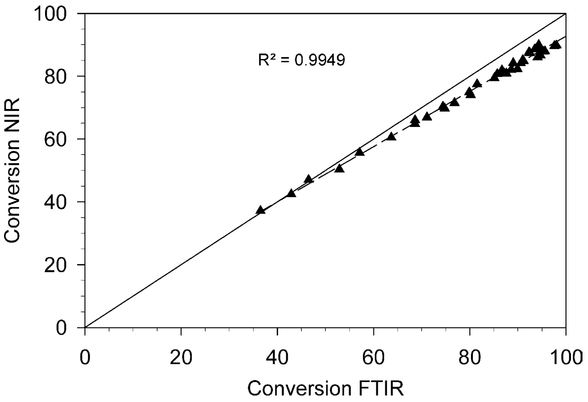

Fig. 3. Conversion in 10 μm acrylate coatings on 30 μm LDPE foil: comparison of data obtained from NIR reflection spectra by band integration with reference data from FTIR transmission spectroscopy.

suitable band in the NIR spectrum which could be used as internal standard.

3.3. In-line monitoring of the conversion in acrylate coatings

For in-line monitoring of the conversion in thin acrylate coatings on polymer foils the probe head was mounted on a pilot-scale roll coating machine. It was tilted against the web in order to suppress interferences arising for instance from thin OPP and PET foils [38].

Clear and pigmented acrylate coatings were applied to various substrates and cured with UV light or EB radiation. Simultaneously, NIR spectra were recorded. Instantaneous quantitative analysis of the resulting spectroscopic data was generally carried out by band integration of the peak at 1620 nm. Calibration to the specific sample system was carried out just before the monitoring trial and directly in the coating machine by taking spectra of the non-irradiated coating for at least 1 min.

Fig. 4 shows the in-line monitoring of the conversion in a clear coat on PET foil after UV irradiation. In order to simulate changes of the irradiation dose, both the power of the UV lamp and the line speed were varied repeatedly. The power of the lamp is given in percent of its maximum output (6 kW). Each change of the irradiation conditions is marked by an arrow. It can be clearly seen that the conversion increases or decreases according to the resulting irradiation dose. Any change of the line speed leads 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 fact that the response of the lamp itself is much slower than that of its electronic control when the power is switched to a higher level.

An analogous monitoring trial was also carried out with a clear coating on white paper which was used as a typical non-transparent substrate (Fig. 5). In this case, the paper itself serves as reflector for the near-infrared radiation, i.e. measurements are done in reflection instead of transflection using the external retroreflector. Nevertheless, the results obtained for paper coatings are quite similar to those on transparent polymer foils.

At the end of the two trials in Figs. 4 and 5 the monitoring of the conversion was performed at line speeds of 100 or 120 m/min. Even at these high line speeds, the scatter of the conversion data is low, i.e. it is in the order of about ± 2…4%. The results clearly show that in spite of the low extinction coefficients in the near-infrared and the low thickness of the layers in the range of some micrometers only NIR reflection spectroscopy is able to detect small variations of the conversion in such acrylate coatings even when they have to be analyzed in a running coating line. The time-resolution of the data (0.6 s/spectrum) is sufficient to be used for process control. However, if the coating line has to be operated at much higher speeds, the recording rate of the spectrometer can be further increased without a significant loss of the quality of the spectra.

Similar results like after UV irradiation were also obtained after EB curing. Fig. 6 shows the monitoring of the conversion in an acrylic clear coat on OPP foil after EB irradiation. The electron current and the web speed were varied alternately. Either the current was kept constant and the web speed was increased stepwise, or the current was varied at constant speed of the line. These variations of the irradiation dose can be directly observed as changes of the acrylate conversion. Changes of the web speed again lead to an immediate response of the conversion whereas after changes of the electron current it takes some time to set the EB accelerator to the new irradiation conditions which is reflected in a gradual increase of the conversion as can be clearly seen in the period between 200 and 330 s.

Besides clear coatings, pigmented systems make up a significant percentage of technical applications of UV-cured coatings, and among them white-pigmented coatings play the most important role. However, the curing of white-pigmented coatings is one of the most difficult problems in UV photopolymerization. On the one hand, sufficient amounts of pigment have to be added to the binder formulation in order to achieve sufficient hiding power of the coating. On the other hand, the pigment particles strongly impede the penetration of UV light into the deeper layers of the coating. Moreover, they compete with the photoinitiator for the incident UV light. The resulting conversion gradient may cause serious curing problems such as a lack of adhesion to the substrate. In order to avoid such problems, the curing process has to be carefully optimized. In-line monitoring may help to detect any deviation from these optimum conditions of the curing process.

Most white coatings are made on the basis of titanium dioxide. As already mentioned, titanium dioxide does not significantly absorb in the near-infrared what allows monitoring of the acrylate conversion in coatings with this pigment in the same way like for clear coats. In particular, since the NIR radiation deeply penetrates into the layer, the

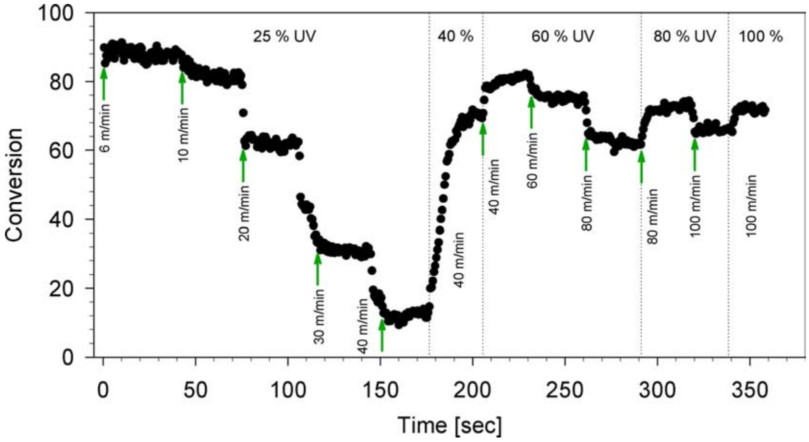

Fig. 4. In-line monitoring of the conversion in a 20 g/m^2 acrylate coating on 36 μm PET foil after UV irradiation with variable power and at various line speeds.

conversion gradient within the layer is averaged in the resulting spectrum. Fig. 7 shows some NIR spectra of a white coating containing 15 wt% titanium dioxide applied to polypropylene foil. It is obvious that the acrylate band at 1620 nm is visible as in a clear coating (see Fig. 1 for comparison). For the same system, the conversion in a pilot-scale curing trial was followed by NIR in-line monitoring. The result is plotted in Fig. 8. As expected, the record is not basically different from those of clear coatings. However, despite of roughly similar irradiation conditions and a higher photoinitiator content the conversion is tendentially lower than in the clear coatings in Figs. 4 and 5 what is due to the effect of the stronger conversion gradient within the pigmented coating. The lower conversion in its deeper layers is reflected in a somewhat lower average conversion in the in-line plot.

Recently, it was shown [45] that very thin acrylate coating can be photopolymerized without any photoinitiator when they are irradiated with short-wavelength UV light, e.g. from a KrCl* excimer lamp which has an emission at 222 nm [46]. Due to the high energy of the photons in this spectral range a direct excitation of the acrylate molecules can occur. A possible mechanism for the initiation of the polymerization reaction was discussed on the basis of investigations by laser flash photolysis and additional quantum chemical calculations [47]. According to that, the excitation of an acrylic double bond primarily leads to the formation of a triplet state, which later may add to an acrylate molecule in the ground state. The resulting biradical is the first step to the following polymerization reaction. Except of these basic studies it was also demonstrated that the direct initiation of the UV photopolymerization in photoinitiator-free acrylate systems does not only work in the lab but can also be performed in pilot-scale on a roll coating machine [48]. However, in that study the state of cure was determined only qualitatively.

In the present work, NIR reflection spectroscopy was used for quantitative in-line monitoring of the conversion in such photoinitiator-free coatings. This task makes high demands on the sensitivity of the measuring method, which is due to the very low thickness of the coating. The short-wavelength UV light is strongly absorbed by the acrylate coating. Consequently, its depth of penetration into the coating is very low, i.e. in the range of a few micrometers or even some hundreds of nanometers only depending on the molar extinction coefficient of the acrylate used [45].

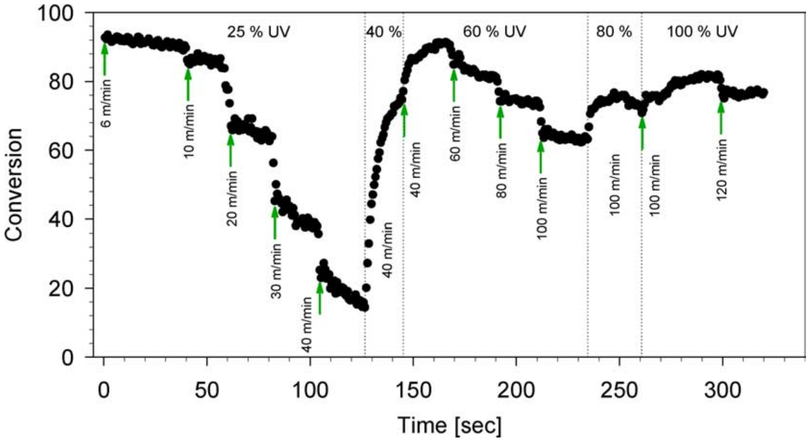

Fig. 5. In-line monitoring of the conversion in a 10 g/m^2 acrylate coating on a 60 g/m^2 paper after UV irradiation with variable power and at various line speeds.

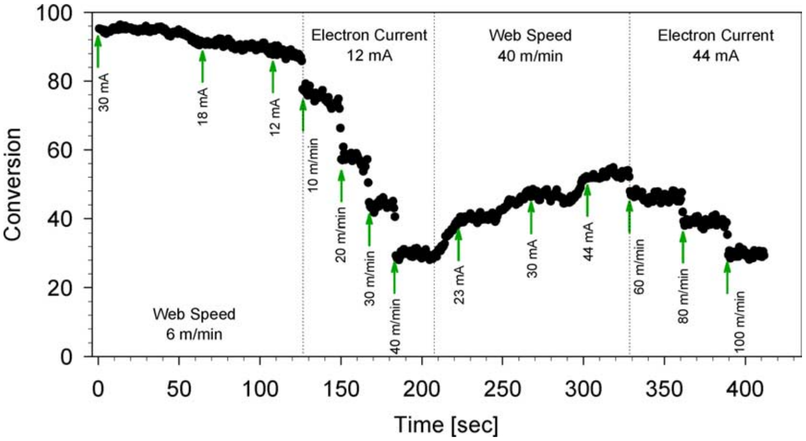

Fig. 6. In-line monitoring of the conversion in a 10 g/m^2 acrylate coating on 20 μm OPP foil after EB curing with variable electron current and at various web speeds.

Accordingly, only very thin acrylate layers with a thickness in this range can be photopolymerized that way which in turn causes rather low signal intensities in the investigations by NIR spectroscopy.

In order to optimize the penetration depth of the UV light a photoinitiator-free acrylate formulation to be irradiated at 222 nm has to be carefully composed with respect to the molar extinction coefficients g of the individual acrylates. Multifunctional aliphatic urethane acrylate oligomers were found to be a good choice [45]. In the present study, they were diluted with tripropylene glycol diacrylate (TPGDA) and hexanediol diacrylate (HDDA) to bring the viscosity to a level suited for processing. The composition of the formulation and the molar extinction coefficients of its constituents are given in Table 1.

Fig. 9 shows the conversion in a layer of this formulation applied to OPP foil with a coating weight of only 4 g/m^2 after irradiation with a KrCl* excimer double lamp system at an intensity of 175 mW/cm^2. Irradiation was carried out under nitrogen since the photoinitiator-free photopolymerization is extremely sensitive to oxygen due to the much lower radical concentration in comparison to photoinitiated reactions performed with photoinitiator. At the lowest web speed, the conversion in the layer is remarkably high. However, it rapidly decreases with increasing speed of the line until it is only 25% at 40 m/min. Moreover, it can be clearly seen that the scattering of the conversion data is much more pronounced than in the records of thicker coatings such as those shown previously where the thickness was in the range of 10–20 g/m^2. Nevertheless, NIR reflection spectroscopy is still able to supply quantitative data with a time resolution of about 2 spectra/s even from coatings with such a low thickness.

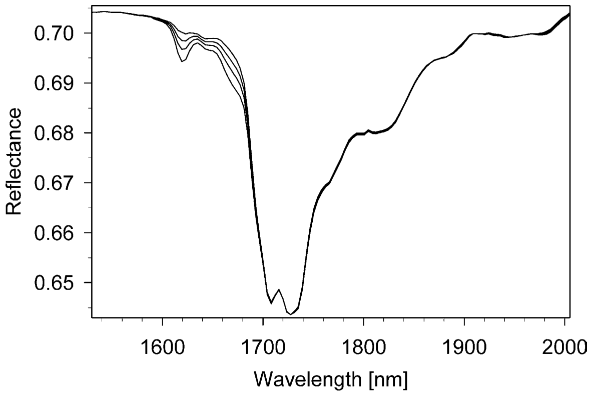

Fig. 7. NIR reflection spectra of a 12 g/m^2 white-pigmented acrylate coating on 20 μm OPP foil before and after UV irradiation.

3.4. *In-line monitoring of the conversion in UV-curable adhesives*

UV-curable acrylic hot-melts to be used as pressure sensitive adhesives (PSA) are a rather new development in UV curing technology [49]. They are made up of high-molecular weight acrylic copolymers and already contain photoreactive groups attached to side chains. The ratio of cohesion and adhesion can be varied in wide limits not only by the composition of the hot-melt formulation but also by the conversion, which is achieved during UV irradiation.

Table 1
Composition of the acrylate formulation for photoinitiator-free UV photopolymerization and molecular weights, functionalities and molar extinction coefficients ε of its constituents

Acrylate	Weight portion (wt%)	Molecular weight ($g\ mol^{-1}$)	Functionality	ε (222 nm) ($mol\ l^{-1}\ cm^{-1}$)
Aliphatic urethane acrylate UA-1	16.7	800	6	2100
Aliphatic urethane acrylate UA-2	30.7	2000	3	1800
HDDA	5.4	226	2	480
TPGDA	47.2	300	2	740

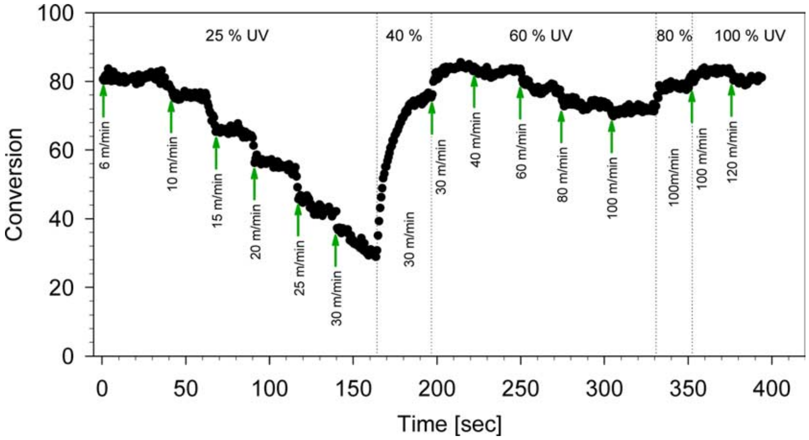

Fig. 8. In-line monitoring of the conversion in a 12 g/m^2 white-pigmented acrylate coating on 20 μm OPP foil after UV irradiation with variable power and at various line speeds.

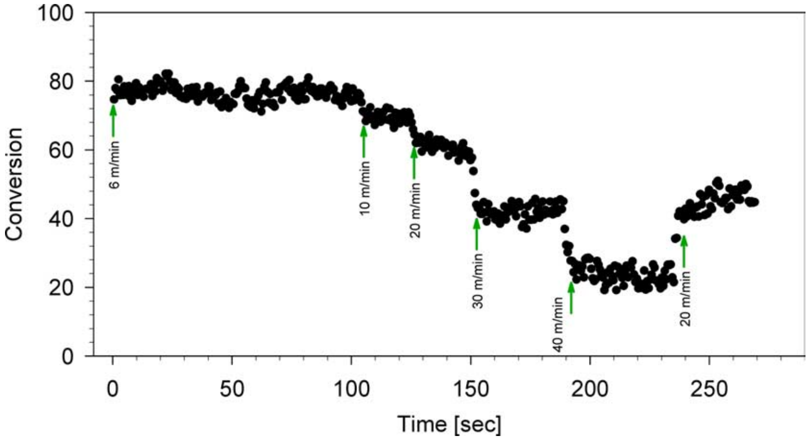

Fig. 9. In-line monitoring of the conversion in a 4 g/m^2 coating of a photoinitiator-free acrylate formulation on 20 μm OPP foil after UV irradiation at 222 nm at various line speeds.

Accordingly, the adhesive properties of hot-melt layers, i.e. their peel strength and shear strength, were found to respond extremely sensitive even to minor changes of the conversion which in turn strongly depends on the applied UV dose [50]. In particular this applies to the peel strength. In order to avoid that too high or too low conversion affect the adhesive properties adversely, an exact and continuous control of the UV curing process is required. Similar to conventional coatings such as those described above, NIR reflection spectroscopy offers the unique possibility to monitor the actual conversion also in acrylate-based adhesives. Fig. 10 shows spectra of a hot-melt applied to PP foil which was irradiated with different UV doses at 308 nm. The overtone of the acrylic double bonds likewise appears at 1620 nm as in liquid acrylate monomers and oligomers.

Figs. 11 and 12 show two examples of the in-line monitoring of the conversion in acrylic adhesives after UV curing at various web speeds and with various UV intensities, respectively. Due to the very high thickness of the layers, spectra with an excellent signal-to-noise ratio (SNR) were recorded which results in minor scattering of the conversion data. It can be clearly seen that changes of the irradiation dose due to both a variation of the line speed or the irradiance lead to changes of the conversion whereby the latter seems to have the stronger effect.

Moreover, the influence of the inertization of the irradiation zone with nitrogen was studied. Purging was

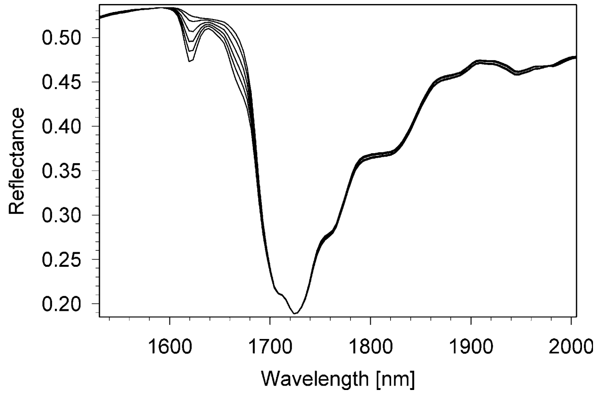

Fig. 10. NIR reflection spectra of a 300 g/m^2 layer of an acrylic hot-melt adhesive on 220 μm PP foil before and after irradiation with different UV doses.

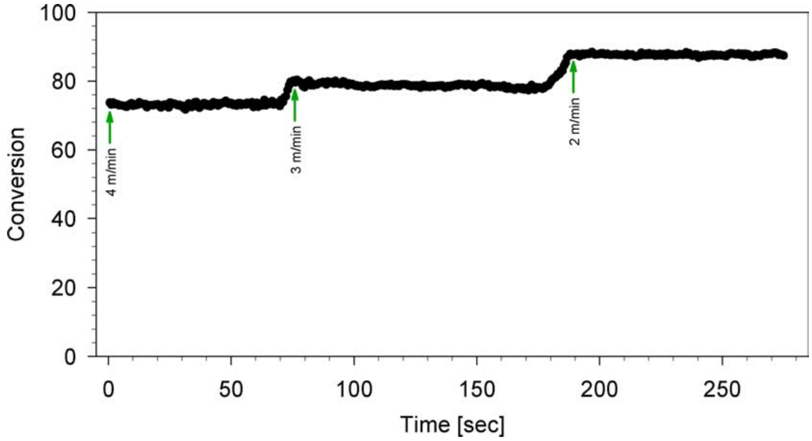

Fig. 11. In-line monitoring of the conversion in a 500 g/m^2 coating of an acrylic hot-melt adhesive on PP tape after UV irradiation at 308 nm at various line speeds.

found to have a minor but nevertheless detectable effect on the conversion of the acrylic double bonds what clearly demonstrates the sensitivity of the NIR method. The unusually low influence of inertization might be due to the extremely high thickness of the adhesive layers in comparison with conventional acrylate coatings which limits the penetration of atmospheric oxygen into the deeper-lying layers and impedes this way the replenishment of the exhausted oxygen.

The response of the conversion to any changes of the reaction conditions, in particular after changes of the power of the UV lamp, seems to be quite slow. However, in contrast to the behaviour of the mercury arc lamp mentioned above the excimer lamp responds much faster to control commands, i.e. the delay of the conversion is not due to the inherent properties of the lamp. In fact, it is a consequence of the low line speeds and the lengthwise installation of the excimer lamp being about 40 cm in length which both together lead to a rather long passage time through the lamp. This long irradiation time is necessary for achieving sufficient cross-linking of the adhesive layers.

4. Conclusions

In this study, it was demonstrated that NIR reflection spectroscopy can be effectively used for inline monitoring of the conversion of double bonds in thin acrylate coatings after UV and EB irradiation. This method provides the time resolution and the sensitivity which are necessary for such measurements.

Quantitative analysis of the data was carried out either with a chemometric method using the PLS algorithm or by integration of the acrylate band at 1620 nm. For both methods, it was shown that there is a close correlation between the results from NIR spectroscopy and data from FTIR spectroscopy used as independent reference method. However, the calibration step is less laborious for band integration, which makes this method better suited for practical applications. In a number of pilot-scale investigations the conversion of double bonds was determined in-line. The method can be used for both clear and pigmented coatings on the basis of acrylates and methacrylates, and it was demonstrated that reasonable conversion data can be

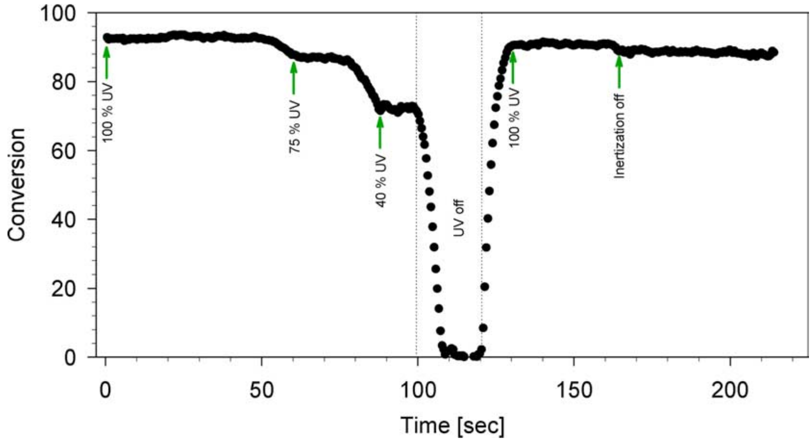

Fig. 12. In-line monitoring of the conversion in a 300 g/m^2 coating of an acrylic hot-melt adhesive on PP tape after UV irradiation at 308 nm with variable power at a line speed of 2 m/min.

recorded even from thin layers with a thickness of 4 g/m^2 only and at line speeds of at least 120 m/min. Furthermore, NIR reflection spectroscopy has been proven to be useful for monitoring of the conversion in layers from hot-melt adhesives which is crucial for an efficient control of their adhesive properties.

Thus, for the first time there is an analytical method available which can be reliably applied for process and quality control in technical curing processes. In the present study, it was used for coatings on polymer foils and paper only. However, the method is not limited to this kind of substrates. In a succeeding paper it will be shown, that it is also suited for coatings on panels and plates such as wood, fibreboard etc.

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