



Effect of changes of the coating thickness on the in-line monitoring of the conversion of photopolymerized acrylate coatings by near-infrared reflection spectroscopy

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ABSTRACT

Near-infrared (NIR) reflection spectroscopy was used for in-line monitoring of the conversion and the thickness of thin UV-cured acrylate coatings applied to polymer foils. Quantitative analysis of the spectroscopic data was performed either with the aid of PLS-based chemometric models or by band integration according to the Beer–Lambert law. Unintended changes of the thickness of the coating, e.g. caused by variation of the web speed, were found to preclude the correct analysis of the conversion by chemometric methods. In order to correct the conversion data for such changes, NIR spectra were recorded before and after UV irradiation. The conversion was determined from the ratio of the band integrals of the overtone of the acrylic double bond at 1620 nm. It was shown that quantitative conversion data with high precision were achieved in this way. The method was used for in-line monitoring of the conversion in clear and pigmented coatings, which were applied to OPP foil by roll coating at line speeds up to 120 m min⁻¹.

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1. Introduction

UV photopolymerization of multifunctional acrylate monomers and oligomers is an efficient and versatile technology to produce polymer coatings with a wide range of potential properties [1]. This technology has found a large number of commercial applications, which range from decorative and protective coatings to coatings with specific functional properties. Further typical applications of UV-cured materials can be found in printing technology and adhesive processing as well as in numerous other areas [2].

During photopolymerization of thin oligomer layers, the conversion, which is achieved by UV irradiation, depends on numerous variables. The most important one is the applied irradiation dose, which is determined by irradiance and line speed. Other parameters, which may have an effect on the conversion, are the composition and the homogeneity of the lacquer formulation as well as the ambient conditions during irradiation such as temperature, inert atmosphere, humidity, and others. Only some of these influences can be easily controlled. However, most of the functional

properties of coatings, e.g. hardness, chemical stability, mechanical and weathering resistance etc., strongly depend on the conversion.

Process control has become an increasingly important technology in the chemical industry [3–5] which allows for a better control of reaction processes as well as of the physical and chemical properties of the products made. For a long time, process control systems have been applied for the monitoring of various polymerization reactions [6–9]. There, they can help to optimize the consumption of energy, raw materials, and reaction time. Moreover, they ensure a high level of quality of the products. Generally, NIR spectroscopy is widely used for such studies. This spectroscopic technique is characterized by high sensitivity, comprehensive analytical potential, and excellent accuracy of the results. In most cases, the analysis of the recorded data is supported by powerful chemometric methods. The equipment nowadays employed for in-line monitoring is rugged, compact, solid, and cost-effective. Most NIR process spectrometers are equipped with an optical fiber which allows for spatial separation of probe head and spectrometer. Thus, integration of such instruments into a production line is easily possible.

Up to now, only few authors reported on investigations of the monitoring of photochemically induced polymerization reactions by NIR spectroscopy [10–14]. Probably, this is related to the inherent problems of such studies. The typical thickness of

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UV-cured coatings is in the range of some micrometers only and therefore much lower than in the most other applications of NIR spectroscopy. In combination with the quite low extinction coefficients in the near-infrared, the detection of NIR spectra of such thin layers and the continuous in-line monitoring of various process parameters is a challenging task. In a previous paper, we reported on our first results on the monitoring of the conversion of acrylate coatings under process conditions [12]. However, analysis of the data was based on a simple band integration method. Moreover, accidental changes of the thickness were not considered. Such changes may result from variations in viscosity, temperature, etc., but they are also inevitably induced by changes of the line speed of the coating machine. These fluctuations of the thickness may have a detrimental effect on the correct determination of the conversion. In the current study, the influence of such thickness changes on the precision of in-line measurements of the conversion was studied quantitatively. Furthermore, it will be shown how this influence can be compensated.

2. Experimental

2.1. Materials

Coatings for laboratory and pilot scale studies of the conversion were made from a clear acrylate formulation which was based on an aliphatic urethane diacrylate (EB 270, 60 wt%), an amine modified polyether acrylate (EB 81, 30 wt%), and tripropylene glycol diacrylate (TPGDA, 10 wt%, all from Cytec Surface Specialities, Drogenbos, Belgium). For pigmented coatings, 10 wt% titanium dioxide (KRONOS 2300, KRONOS TITAN GmbH, Leverkusen, Germany) were dispersed in the formulation. Ethyl (2,4,6-trimethylbenzoyl) phenylphosphinate (TPO-L, BASF, Ludwigshafen, Germany) was used as photoinitiator. For pilot scale coating experiments, the initiator was added at a level of 0.25 wt% to clear varnishes and at 1.5 wt% to white-pigmented lacquer formulations.

2.2. Preparation of the coatings and UV irradiation for calibration

Samples for investigating the conversion on a laboratory scale were prepared by coating the formulation on 20 μm thick polypropylene foil (OPP, Treofan GND 20) using an automatic film application machine (SIMEX, Haan, Germany) and a 10 μm Baker applicator (TQC GmbH, Haan, Germany). In order to obtain samples with a wide range of conversion, the photoinitiator content was varied from 0.25 wt% to 1 wt%, and the coatings were cured at various irradiation doses (i.e. by variation of UV intensity and line speed). Irradiation was carried out under nitrogen in a UV curing unit equipped with a 120 W cm^{-1} medium pressure mercury lamp (IST Metz, Nürtingen, Germany). The irradiation dose per pass was 700 mJ cm^{-2} at a conveyor speed of 10 m min^{-1} and an irradiance of 620 mW cm^{-2} .

2.3. Roll coating and curing

In-line monitoring studies were carried out on a pilot scale roll coating machine. It was equipped with a 160 W cm^{-1} medium pressure mercury lamp (PrintConcept UV Systeme, Köngen, Germany, maximum power 8 kW, adjustable between 30 and 100%). At full power, the irradiation dose at 10 m min^{-1} was determined to be 850 mJ cm^{-2} . In order to achieve coatings with different conversions and thicknesses, the roll gap, the UV intensity, and the web speed were varied. OPP foil with a thickness of 20 μm was used as substrate.

2.4. NIR reflection spectroscopy

Spectra were recorded with a Kusta 4004 P process spectrometer (LLA, Berlin, Germany). This instrument is based on a concave holographic grating and an InGaAs photodiode array detector with 256 elements which was set to cover a spectral region from 1470 nm to 1950 nm. The reflection probe head is linked to the spectrometer unit by a fiber-optic cable. It contains a tungsten halogen lamp as light source. A UV filter is used to cut the short-wavelength emission of the lamp. Spectra were taken in transreflection mode against a ceramic retroreflector behind the sample. A diffuser plate in front of the probe head suppresses interferences which occur in thin transparent foils such as 20 μm OPP foil. A more detailed description of the spectrometer system is given in Ref. [15]. Some of the in-line monitoring trials were carried out with two process spectrometers which allows for the correction of the conversion for the influence of the variation of the thickness of the coating.

NIR spectra used for calibration were recorded immediately after irradiation in order to avoid any possible influence of post-curing. For each measurement, 10 spectra (each of them averaged from 1000 accumulations) were taken.

For in-line studies with only one measuring position, the NIR probe head was installed behind the UV lamp above the moving web and very close to a guide roll in order to minimize the influence of vibrations of the polymer foil. NIR spectra were recorded continuously at a rate of 140 spectra min^{-1} . In case of the use of two probe heads, the second NIR probe head was mounted directly after the roller application unit in order to record the spectra of the uncured layer.

2.5. Reference methods

The conversion of the double bonds after UV irradiation was determined with FTIR transmission spectroscopy. Spectra were recorded prior to and immediately after UV irradiation using a Digilab FTS 6000 spectrometer. Spectra were taken at several positions of the sample and averaged. The acrylate conversion was determined from the band of the CH_2 scissor deformation at 1405 cm^{-1} [16].

The coating thickness after irradiation was measured with a digital thickness gauge with a resolution of 0.2 μm (Heidenhain MT 1201, Dr. Johannes Heidenhain GmbH, Traunreut, Germany).

3. Results and discussion

3.1. Development of calibration models

Quantitative analysis of the spectroscopic data in most NIR applications is carried out with chemometric methods such as partial-least squares (PLS) regression [17], which is able to detect even minor differences between various samples. However, the application of such multivariate analytical methods first requires the development of an appropriate calibration model. The creation of such a model needs a large amount of well-defined calibration samples.

For the calibration to the conversion in clear acrylic coatings, 160 samples with different conversion were prepared and characterized by FTIR spectroscopy. The resulting data set was split into a calibration and a validation set containing the data of 100 and 60 samples, respectively. Various PLS models were built up from these two data sets using the test set validation method. Calculations were carried out with the KustaSpec software package supplied with the NIR spectrometer. After regression, the root mean square error of prediction (RMSEP) and the coefficient of determination R^2

were calculated. This procedure was repeated several times using different kinds of pre-processing of the spectra (e.g. normalization, derivatives, limitation of the spectral range). The model with the lowest RMSEP and the highest R^2 was selected for in-line analysis. The resulting calibration curve is shown in Fig. 1. The underlying PLS model was based on 7 fundamental factors. The RMSEP was determined to be 2.968.

The performance of the developed model was tested with an additional set of independent test samples. These samples were neither included in the calibration nor in the validation set. Their conversion was predicted with the created chemometric model and compared with FTIR reference data. Results are given in Fig. 2. The close correlation of the predicted conversion with the actual conversion clearly demonstrates the high predicting power of the created calibration model.

Besides clear coatings, pigmented systems, in particular those with white pigmentation, play an important role in technical applications of UV curing. Therefore, the same chemometric procedures as described for clear coats were also used to develop chemometric models for the conversion of white-pigmented coatings. The results were quite similar to those obtained for clear coats. For instance, calibration models are typically based on 5 factors. Their predicting power was examined with independent samples as well. Again, a close correlation with the reference data was found.

3.2. In-line monitoring of pilot scale coating processes

3.2.1. Clear coats

The created calibration model was used to follow the conversion in acrylic clear coats during the coating process on a roll coating machine. In order to vary the irradiation dose, the line speed was stepwise increased, whereas the power of the UV lamp remained constant (30%). The resulting changes in conversion were followed by NIR spectroscopy. At each line speed, spectra were recorded for 1 min. From each spectrum, the conversion was predicted by use of the PLS calibration. Fig. 3 shows mean values for each line speed. For comparison, reference values are given, which were determined off-line by FTIR spectroscopy. Moreover, the thickness of the layers is shown, which was measured off-line as well.

At low web speeds ($\leq 20 \text{ m min}^{-1}$), a close correlation between the predicted and the actual conversion was observed. With increasing line speed, however, both curves increasingly diverge.

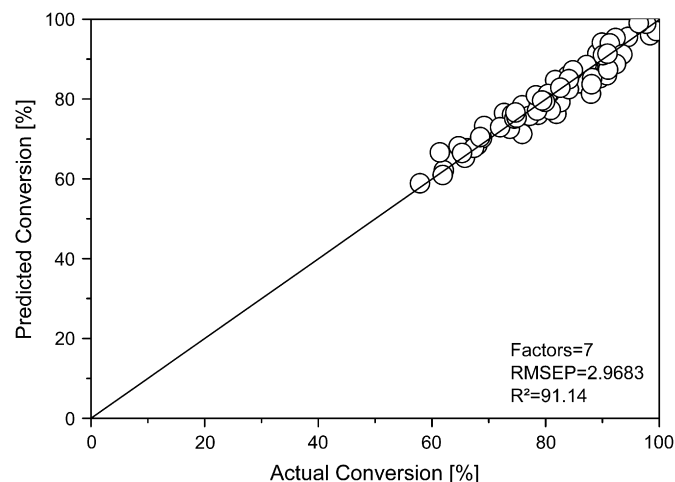


Fig. 1. PLS calibration curve to the conversion of $10 \mu\text{m}$ clear acrylate coatings on OPP foil.

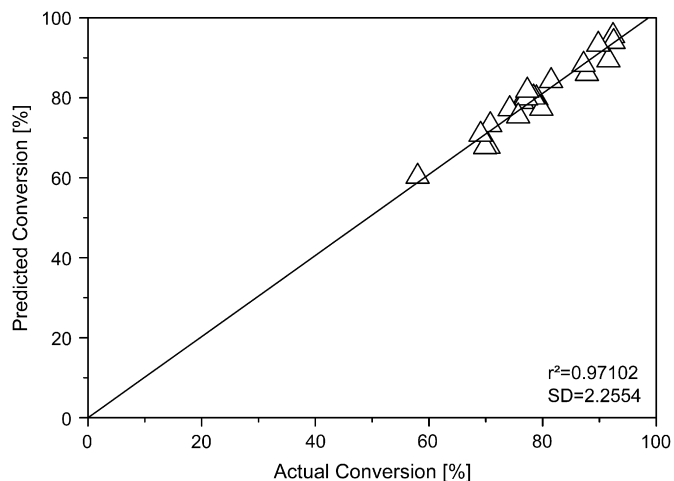


Fig. 2. Prediction of the conversion of independent samples using the PLS calibration shown in Fig. 1.

Simultaneously, the thickness of the layer applied to the foil was found to increase from 8.7 to $13.8 \mu\text{m}$. Such an increase of the coating thickness with increasing line speed even at a constant gap between the application rollers is well-known in roll coating technology. However, the increase of the thickness has a destructive effect on the prediction performance of the PLS calibration. This is due to the fact that the calibration to the conversion was carried out with samples with a constant nominal thickness of $10 \mu\text{m}$. The resulting thickness of the layers after UV curing is even lower due to the inherent shrinkage during polymerization. Consequently, correct predictions of the conversion during in-line monitoring were only obtained at low line speeds where the applied thickness corresponds to the thickness during the calibration procedure. With increasing thickness, the predicted conversion more and more deviates from the real conversion.

In order to get accurate results for the conversion in thin acrylic coatings, a correction of the influence of changes of the coating thickness was necessary. Basically, there are two possibilities to consider such changes in the quantitative evaluation. The first one includes the variation of the thickness of the layer into the chemometric calibration model, which is certainly the most

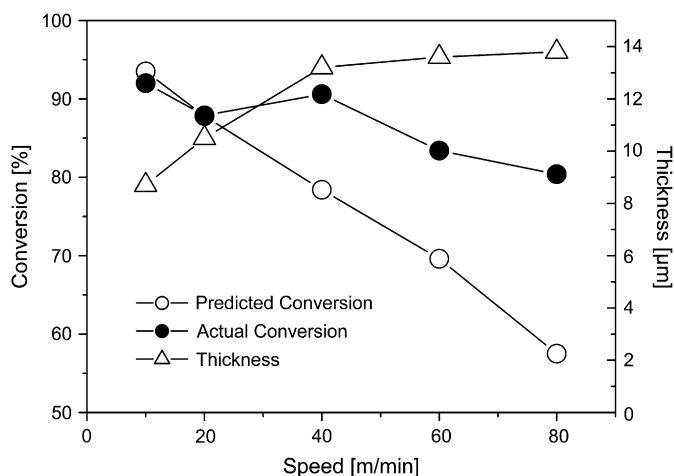


Fig. 3. Effect of the line speed on the prediction of the conversion of acrylate coatings applied to OPP foil. For comparison, the actual conversion (from FTIR spectroscopy) and the coating thickness are shown.

sophisticated solution. This can be done by use of the PLS2 algorithm which is able to predict two or more parameters from the same input data [17]. However, this implies that the enormous efforts for calibration even more increase since the calibration samples have to cover the full range of both conversion and thickness which can occur during analysis. Such investigations are subject of our current work and will be reported in a forthcoming paper.

In the present study, a simple alternative method was developed, which allows for a quantitative analysis of the NIR spectra without any time-consuming calibration procedure. It is based on the first overtone of the C–H stretching vibration of the vinyl bond, which appears at 1620 nm in the NIR spectrum of acrylates. Since this band is well separated from most of the other C–H bands, it can be easily evaluated by band integration. In this way, the conversion in UV-cured acrylate coatings can be directly estimated according to the Beer–Lambert law from the ratio of the band integrals before and after irradiation.

The precision of the integration method was tested by comparing the conversion data obtained in this way from the NIR spectra with conversion data of the same samples determined with FTIR spectroscopy. Results are shown in Fig. 4.

A linear correlation between the conversion data from NIR and FTIR spectroscopy was found. Moreover, no offset was observed, which implies that the two data sets are completely equivalent. Therefore, band integration of NIR spectra may be regarded as an easy, rapid, and in most cases practicable method to get quantitative conversion data which is an alternative to chemometric approaches.

On the basis of the band integration method, the influence of unintended changes of the thickness of the layer, e.g. caused by changes of the web speed, can be easily compensated for by recording NIR spectra of the coating before and after UV curing and determination of the conversion from the ratio of the band integrals. For this reason, two probe heads were mounted on the pilot scale roll coating machine, i.e. one before and one after the UV lamp, respectively. The first NIR probe head was installed directly after the application unit for recording the spectra before irradiation. The second one was mounted just behind the exit of the UV lamp in order to take the spectra of the cured layer. With both probe heads, spectra were recorded continuously and simultaneously at a rate of 2.3 spectra sec^{-1} . During merging of the two data streams in order to calculate the

conversion from the band integrals, a time offset had to be considered in order to include the delay time between the two probe heads.

By use of this technique, the conversion in clear acrylic coatings on OPP foil was followed. In order to test the capability of the method to compensate for changes of the thickness, the thicknesses of the layer were purposely varied by variation of the nip between the application rolls. In contrast, the web speed and the irradiation dose were not changed during this trial. For comparison, an additional test was carried out. In that case, spectra were recorded with only one probe head, i.e. with that behind the UV lamp. Spectra of the uncured layer were taken just before switching-on the UV lamp by collecting data at constant nip (i.e. the narrowest nip) for at least 1 min. The band integrals determined from these spectra were averaged, and the mean value was used as reference value for band integration during in-line monitoring. The results of both tests are compared in Fig. 5.

It can be clearly seen that the conversion, which was determined with the setup consisting of two probe heads, does not depend on the thickness of the applied coating. This is due to the low thickness of the coatings studied here and the high reactivity of the phosphine oxide photoinitiator. This observation was also found to be in accordance with random off-line measurements of the conversion by FTIR spectroscopy. This result clearly proves the power of the method based on two probe heads for measuring the acrylate conversion accurately in spite of any variations of the thickness of the layer, i.e. the effect of changes of the thickness is completely compensated.

If only one probe head is used, a decrease of the conversion with increasing thickness of the coating is observed. Consequently, the difference between this conversion and the conversion resulting from the trial monitored with two probe heads increases with increasing coating thickness. However, the decrease of the conversion is only due to the change of the thickness and does not represent a real decay of the conversion. This result shows that the conversion can only be monitored with one probe head if it can be guaranteed that the thickness of the layer does not change during the coating process. In most technical coating processes, it is, however, almost impossible to eliminate fluctuations of the thickness of the layer which will lead to apparent changes of the conversion.

The two setups with one or two probe heads, respectively, were then used for in-line monitoring of the acrylate conversion in

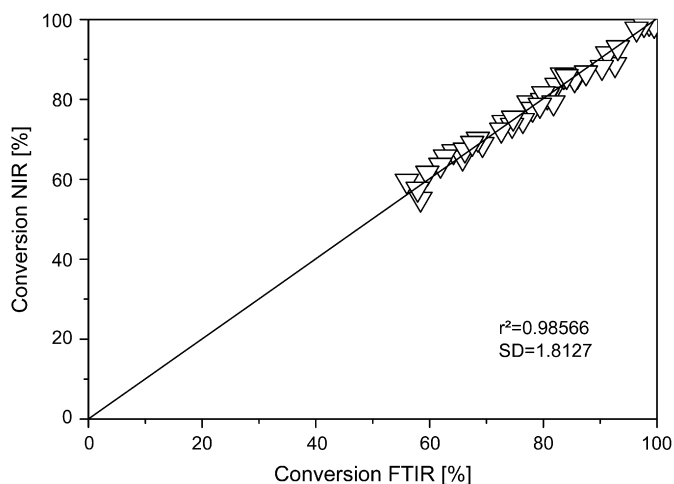


Fig. 4. Conversion in 10 μm acrylate coatings: comparison of values obtained from NIR reflection spectra by band integration with reference data from FTIR transmission spectroscopy.

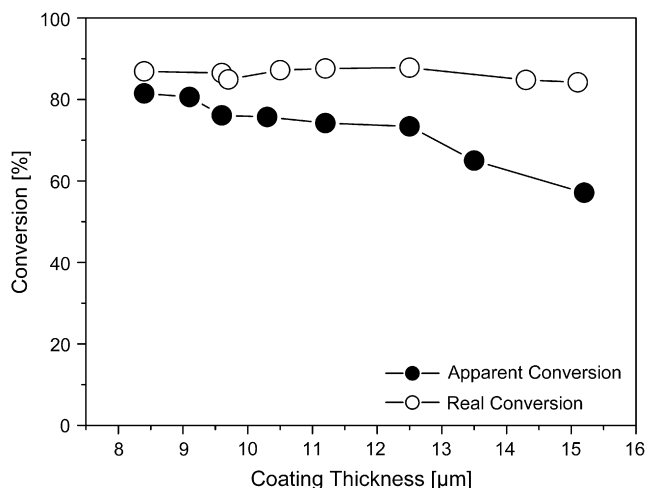


Fig. 5. Conversion in clear acrylate coatings with (\circ , 2 probe heads) and without (\bullet , 1 probe head) correction of the varying thickness of the coating.

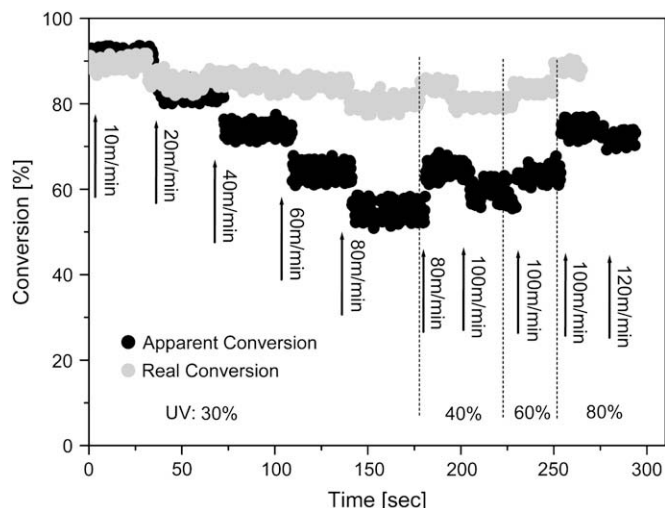


Fig. 6. In-line monitoring of the conversion in clear acrylate coatings with one (●) or two (●) NIR probe heads, respectively.

a coating process which was carried out at various line speeds and UV intensities. Quantitative evaluation of the data was performed by band integration. A record of a typical test trial is shown in Fig. 6.

At first, the speed of the web was stepwise increased at constant irradiance. During the second stage, both the power of the UV lamp and the line speed were alternately varied up to 120 m min^{-1} at the end of the trial. After each change of dose, an almost immediate response of the conversion was observed, which shows that the NIR method is sufficiently fast for in-line monitoring.

In case only one probe head was used for monitoring, the changes of the coating thickness, which were induced by the increasing web speed, lead to an apparent decrease of the conversion. This is due to the fact that the reference data of the uncured layer, which were taken in advance, are only correct for the thickness at the beginning of the experiment. Consequently, the pronounced decay of the conversion is largely an artifact.

However, if the conversion is determined from a pair of spectra which were recorded immediately before and after UV irradiation, the influence of thickness changes is completely eliminated. Accordingly, the trace, which was recorded with two probe heads, shows much less variation of the conversion, particularly during the first stage of the trial made up of speed changes only. In contrast, changes of the irradiance are clearly reflected in the conversion data. These results correlate quite well with the findings shown in Fig. 5.

3.2.2. Pigmented systems

The UV curing of white-pigmented coatings is one of the most difficult problems in photopolymerization. On the one hand, sufficient pigment has to be added to the binder formulation to achieve a good hiding power. On the other hand, the pigment particles prevent the penetration of UV light into the deeper layers of the coating. In particular titanium dioxide, which is used as pigment in most white lacquer formulations, shows only a narrow spectral window around 400 nm where UV light can penetrate into the coating. The resulting conversion gradient may cause serious curing problems including the loss of adhesion to the substrate.

Titanium dioxide does not absorb significantly in the near-infrared part of the spectrum [18]. This allows for monitoring of the acrylate conversion in coatings containing titania in the same manner as for clear coatings. Thus, in-line monitoring may help to optimize the curing conditions of the curing process. Coatings

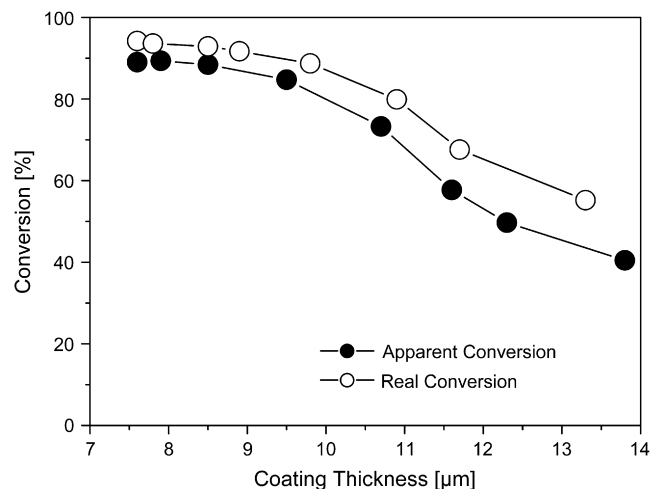


Fig. 7. Conversion in white-pigmented acrylate coatings with (○, 2 probe heads) and without (●, 1 probe head) correction of the varying thickness of the coating.

pigmented with 10 wt% TiO_2 were investigated in this paper. The application of pigmented formulations by roll coating may lead to similar changes of the thickness of the layer as in the case of clear coats. Therefore, analogous monitoring trials using one or two probe heads, respectively, were carried out with the white-pigmented acrylic formulation as well. Fig. 7 summarizes the experimental results.

Regardless of the method of measurement, the conversion was found to decrease with increasing thickness of the coating. This result reflects the limited penetration of UV light into the subjacent layers which leads to a conversion gradient. Due to the higher penetration depth of NIR radiation, the NIR spectrum represents an average conversion across the profile of the coating. Consequently, a conversion gradient within the layer is reflected by a lower total conversion in the spectrum.

The comparison of the two measuring methods shows that, similar to the findings in Fig. 5, a difference between the apparent conversion and the conversion, which was corrected for the variation of the coating thickness, was also observed for pigmented coatings. However, this difference is much smaller than in clear coats. This shows that the real effect on the conversion caused by

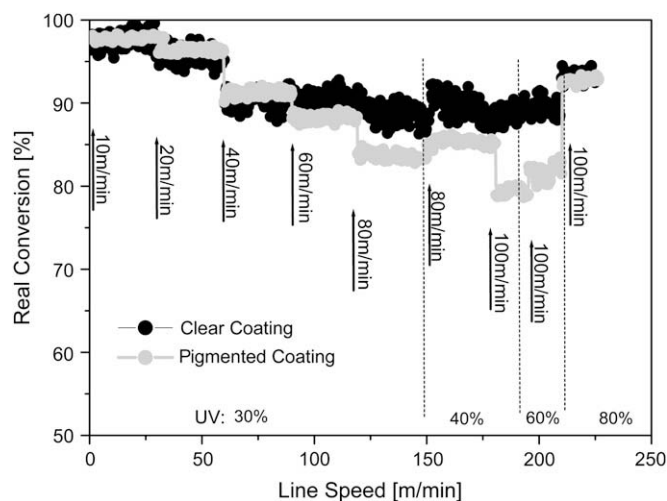


Fig. 8. Comparison of the in-line monitoring of the corrected conversion in clear and white-pigmented acrylic coatings on OPP foil.

the gradient of the light intensity within the coating dominates over the error, which is introduced by the measuring procedure.

In order to study the effect of the pigments on the penetration of the UV radiation and hence on the acrylate conversion in more detail, in-line studies were carried out on both a clear and a pigmented formulation with equal binder composition and with the same photoinitiator concentration (1.5 wt%). Both trials were performed with two NIR probe heads in order to eliminate the effect of fluctuations in thickness caused by changes of the web speed. Results are compared in Fig. 8.

In both systems, an instantaneous response of the conversion after each change of the irradiation dose is observed. With increasing line speed, i.e. with decreasing dose, the conversion more and more decreases. However, at line speeds higher than 60 m min^{-1} the decay of the conversion is distinctly stronger in the pigmented system than in the clear coat. This is due to the fact that the increasing thickness of the coating at higher line speeds and the pigmentation lead to a stronger gradient of the conversion within the layer.

4. Conclusions

In this study, it was demonstrated that NIR reflection spectroscopy can be effectively used for process control in UV curing of thin polymeric coatings. The method is able to monitor important process parameters such as the actual conversion after UV irradiation in real time. Quantitative analysis of a part of the NIR data was based on multivariate calibration models. Alternatively, a simple band integration method was used for the determination of the conversion, which is based on the overtone of the C–H stretching vibration of the acrylic double bond at 1620 nm.

In most technical coating processes, the thickness of the applied layer may change unintentionally, e.g. if the line speed is changed. Such thickness changes strongly affect the accurate determination of the conversion and thus preclude its analysis by use of chemometric models based on the PLS1 algorithm. In the present study, the correct conversion was determined by recording spectra both before and after UV irradiation using two NIR probe heads. In this way, it was possible to follow the conversion in clear and pigmented systems with high precision and unaffected by fluctuations

of the coating thickness. The time resolution of the method and the precision of the results were found to be sufficient for both process and quality control.

Further investigations are directed towards the inclusion of both the acrylate conversion and the coating thickness into a combined chemometric model using the PLS2 algorithm. This approach will intrinsically compensate for the effect of thickness changes on the conversion. Moreover, it will allow for the simultaneous prediction of both parameters.

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