Process Control of UV and EB Curing of Acrylates by In-line NIR Reflection Spectroscopy

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Introduction

Though UV curing has become an established technology since many years there are still some problems which are not yet solved in a satisfactory manner. One of them is the search for a simple but nevertheless powerful and reliable method for the quantitative determination of the degree of cure of a coating after UV curing in the running coating line. The immediate and continual availability of such data is, however, an indispensable precondition for an efficient process and quality control of UV and EB curing processes since the degree of cure is the most important objective parameter which largely determines all other functional properties of a coating such as scratch and abrasion resistance, weathering resistance, the content of extractables etc. Moreover, also for further processing of the coating a sufficient degree of cure is required : for example, wipe resistance must be attained before stacking or winding. On the other hand, the degree of cure which is achieved during irradiation depends on a large number of factors such as spectral distribution and intensity of the incident UV light (or the electron current in EB curing), line speed, composition of the reactive formulation, temperature, inertization and others. Whereas some of them can be easily controlled, this is hardly possible for effects like ageing or pollution of the UV lamps, differences between various batches of the formulation, precipitation of fillers or the photoinitiator, or other unexpected influences. Hence, the compliance of the actual level of the conversion of a coating in a production line with the requirements determined by the specific application has to be controlled continuously in order to be able to respond to process variations and to avoid this way rejects. In the past, various analytical methods have been tested for this purpose but for different reasons none of them was found to be suitable for in-line measurements in a production environment [1]. For instance, fluorescence techniques [2] require the addition of fluorescence probes which are hardly commercially available and which may interfere with the properties of the cured coating. Ion mobility spectroscopy [3] is limited to the detection of volatile compounds (such as 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. An appropriate measuring method ideally should determine the degree of cure directly. It must have high sensitivity since measurements have to be done on thin layers with a thickness in the range of some microns. It must be able to supply data at a high rate because of the typically high web speeds used in UV and EB curing. Moreover, a high reproducibility and reliability of the data is required.

Near-infrared (NIR) spectroscopy provides the proven analytic capabilities of vibrational spectroscopy and an excellent signal-to-noise ratio. In particular, the double bonds in acrylates and methacrylates can be observed directly as a strong and isolated characteristic overtone band at 1620 nm. Due to the developments of the photodetector technology during the last decade, time resolution and sensitivity of diode array spectrometers are high enough for in-line monitoring of the degree of cure under the typical conditions of a running coating line. Such multichannel spectrometers are compact, rugged and comparatively cost-effective. Moreover, because of the good transmission of quartz glass in the near-infrared optical fibers can be used which allows spatial separation of spectrometer and probe head which is advantageous for both easy integration of

the instrument in a coating line and for remote monitoring. Due to the power of NIR spectroscopy, it is widely used for process control in the chemical industry and in other commercial applications [4-7].

In UV and EB curing both transparent and opaque coatings and substrates have to be characterized. Therefore, measurements were performed in reflection.

Procedure

A near-infrared reflection spectrometer system was developed which is adapted to the specific needs of UV and EB curing. It consists of a modified commercial spectrometer unit (Kusta from LLA) and a separate tailor-made probe head which is linked to the spectrometer by a fiber-optic cable.

The spectrometer is based on a holographic concave grating and a fast linear photodiode array as detector. The thermoelectrically cooled InGaAs detector with 256 elements covers a spectral range from 1530 to 2000 nm and provides the time resolution (minimum integration time per spectrum : 56 µs) and the sensitivity which is necessary for in-line monitoring.

The 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, a diffusor plate is used to suppress interferences which occur when thin transparent foils of optically high-grade polymers are studied. Reflection spectra are measured against a ceramic plate as reflectance standard which is also attached to the probe head.

Fig. 1 shows the prototype of the NIR spectrometer which was used for the investigations in this study. In this photo, the probe head is mounted on a frame for use in the lab. In Fig. 2, the commercial instrument Kusta 4004 P is shown.


Fig. 1 : Prototype of the NIR spectrometer
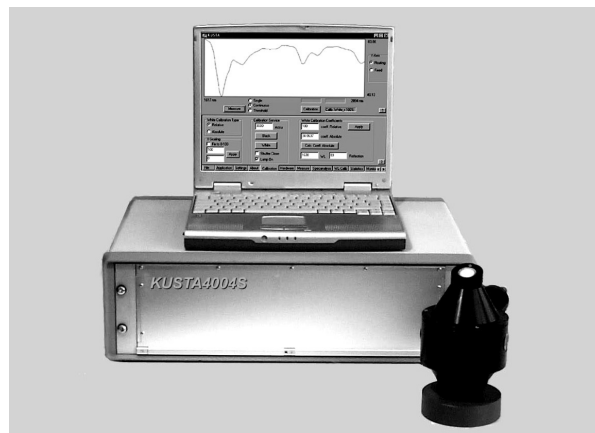
Fig. 2 : NIR spectrometer Kusta 4004 P

The capability of NIR reflection spectroscopy to monitor the degree of cure was tested with a wide variety of acrylate formulations and substrates. Proprietary acrylate formulations to be used as scratch resistant, decorative, adhesive, or protective coatings were coated on polymer foils, paper, wood, MDF panels etc. Application and curing were performed on various pilot plants at IOM. Irradiation was carried out either with mercury arc UV lamps (Fusion, IST) or by a LEA electron beam (EB) accelerator operated at 150 kV (IOM) [8].

Results and Discussion

Due to the relative low absorption coefficients in the near-infrared NIR spectroscopy is commonly used to study batch processes or at least thick layers in the range of millimeters or centimeters [9-13]. However, it could be shown in this study that one even can obtain spectra of good quality from coatings with a thickness of some microns which are typical for radiation curing processes when they are taken in reflection with an instrument with sufficient sensitivity. Fig. 3 shows spectra of 10 µm thick acrylic clear coats on polyethylene foil before and after UV curing. It is obvious that the acrylate band at 1620 can be clearly seen in the spectra.
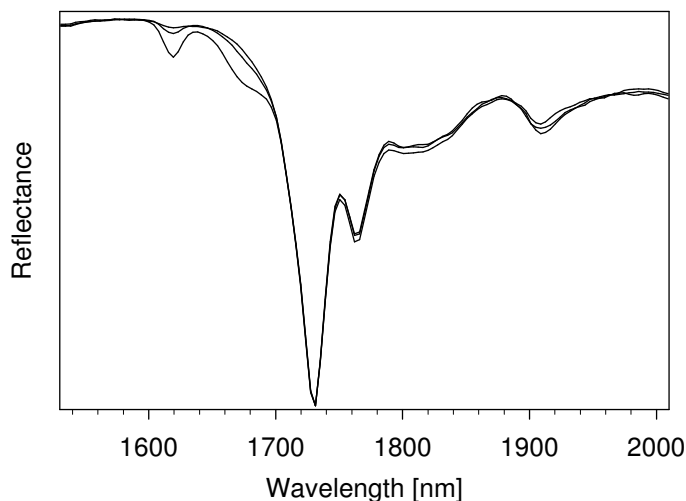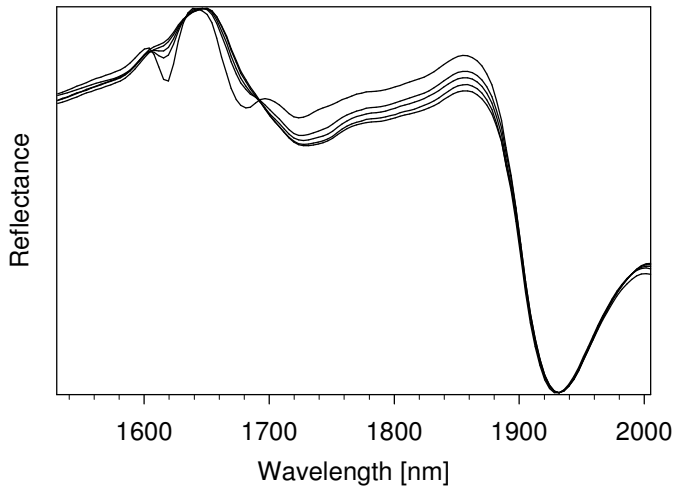

Fig. 3 : NIR reflection spectra of 10 µm thick acrylic clears coat on 30 µm LDPE foil before and after UV irradiation with different doses

When thin transparent foils of optically high-grade polymers such as OPP or PET are used as substrate whose thickness is in the range or only little higher than the wavelength of the probe light (i.e. foils up to about 20 µm), so-called interference fringes appear which completely mask the spectrum and prevent any analysis, at least if clear coatings have to be characterized. This problem was solved by the diffuser plate and by careful adjustment of the tilt of the probe head against the sample [14]. Both together completely suppress the interferences and thus enable the determination of the degree of cure in clear coatings on such foils.

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 (see Fig. 4) 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 absorb in this spectral region. Moreover, there are no restrictions with respect to the color of the pigment except of black pigments. The reflectance of black coatings is too low to get a signal with sufficient intensity. A special example of pigmented coatings is given in Fig. 5. It shows NIR spectra of layers of various UV-cured varnishes for automotive applications containing metallic effect pigments which were sprayed on zinc-plated metal plates.

In principle, NIR reflection spectroscopy is also suited for UV-curable printing inks as systems with a particularly high degree of pigmentation. However, in most printing applications the applied
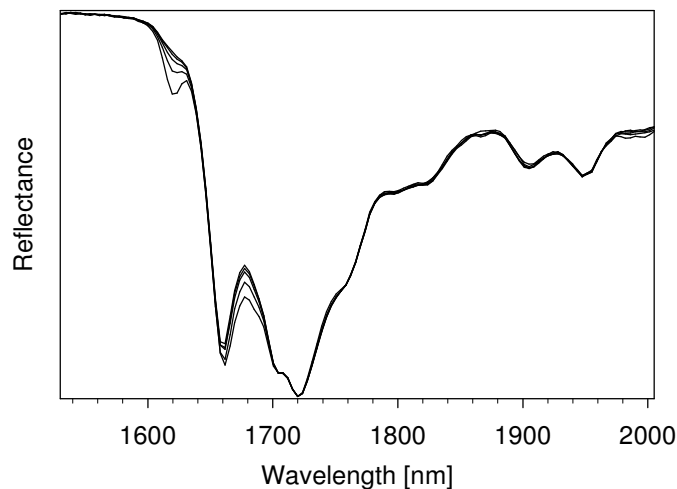
Fig. 4 : NIR reflection spectra of 30 μm thick clear coats on 120 g/m² white paper before and after irradiation with different UV doses
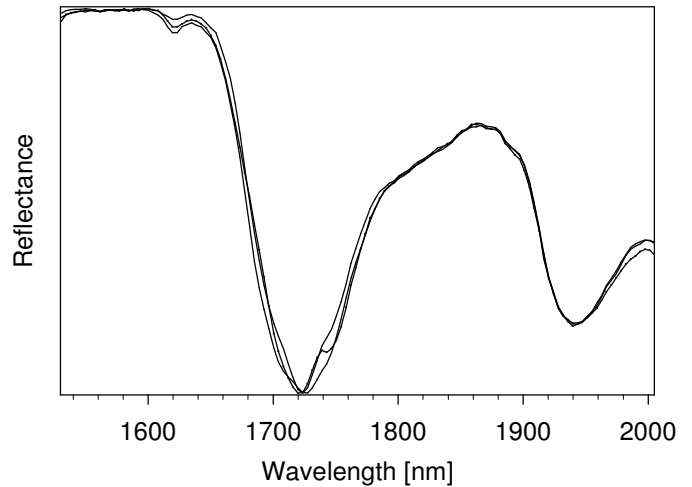
Fig. 5 : NIR reflection spectra of various experimental lacquer formulations with metal-effect pigments after UV irradiation

thickness of the layer is very low (typically 1-2 microns) which presently makes an exact quantification difficult. However, it is expected that a further increase of the sensitivity of the NIR instrument might improve its capability to follow the drying of printing inks.

Another potential application of monitoring the degree of cure by NIR spectroscopy are coatings on wood and panels from medium-density fiberboard (MDF) to be used for furniture and flooring. When wood panels have to be characterized one has to regard the effect of the wood grain which may cause different reflectance of the substrate and different penetration of the lacquer into the wood. The latter, in particular, may lead to low reproducibility of the signal of the acrylic

Fig. 6 : NIR reflection spectra of 200 μm thick layers of an acrylic hot-melt for PSA applications on 100 μm PET foil before and after irradiation with different UV doses

double bonds since it leads to an inhomogeneous thickness of the coating. This problem can be overcome by averaging of the NIR signal over the cross-section of the wood panel.

A more recent development in UV curing technology are acrylic hot-melts for pressure sensitive adhesives (PSA) [15]. Their adhesive properties, i.e. peel strength and shear strength, are well-known to respond very sensitive even on small changes of the conversion [16]. Both overcure and undercure of the layer have a strong detrimental effect, in particular on the peel strength. NIR reflection spectroscopy offers a unique possibility to monitor the actual degree of cure and to ensure a constantly high quality of the product. Fig. 6 shows spectra of 200 µm thick layers of an acrylic hot-melt applied to polyester foil before and after irradiation with different UV doses.

Calibration of the method

Quantitative analysis of the NIR spectra can be basically performed by two different ways : by using chemometrics or by band integration. In most technical applications of NIR spectroscopy, it is used in combination with sophisticated chemometric methods such as PLS or PCR [7,17] which require large sets of well-defined samples for calibration. However, the specific preparation of UV- or EB-cured coatings with a predetermined conversion is hardly to achieve, and the careful characterization of cross-linked polymers is a rather labor-intensive task. Therefore, chemometric methods can be only reasonably used for process and quality control in UV and EB curing when complex analytic problems have to be solved and when these processes run without changes for a long time.

In contrast, in most other coating applications where fast and easy operation is required and where again and again varying coating jobs have to be handled it will be hardly possible to apply the time-consuming and costly chemometric methods routinely. As a simple but in most cases practicable alternative the integration of the acrylate peak at 1620 nm can be used. The degree of cure is determined from the ratio of the band areas in the spectra of the cured and the uncured layer, respectively. Calibration is performed simply by recording some spectra of the wet coating as reference. However, one basic requirement has to be fulfilled in this case : correct and reliable conversion data are only achieved when the thickness of the coating is constant throughout the entire calibration and measurement process.

In the present work, quantitative analysis of the NIR spectra was done by peak integration only. In order to check, if the results obtained in this way from the NIR spectra actually reflect the correct degree of cure in the coatings they were compared with data from two independent reference methods. Acrylate layers were drawn on polyethylene foil and subsequently irradiated under nitrogen. 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 belt were varied. Each coating was then studied by NIR reflection and FTIR transmission spectroscopy as well as HPLC. FTIR spectra were recorded using a Digilab FTS 6000 spectrometer. The acrylate conversion was obtained from the intensity of the band at 1405 cm^{-1}. For HPLC measurements, extraction of the coatings was performed with a mixture of water and acetonitrile. The soluble fraction was analyzed with a Shimadzu LC-2010 system using a RP 18 column. The calibration was based on the chromatograms of the unirradiated sample.

In Fig. 7, the conversion data which were obtained from the NIR spectra are plotted vs. the results from FTIR spectroscopy and HPLC, respectively. It is obvious that there is a close linear correlation between the data from the two spectroscopic methods over the complete range of conversion studied. Whereas the results exactly correspond to each other at lower conversion NIR spectroscopy slightly underestimates the degree of cure in comparison to FTIR spectroscopy at higher conversion which might be probably due to baseline effects in one or both methods.
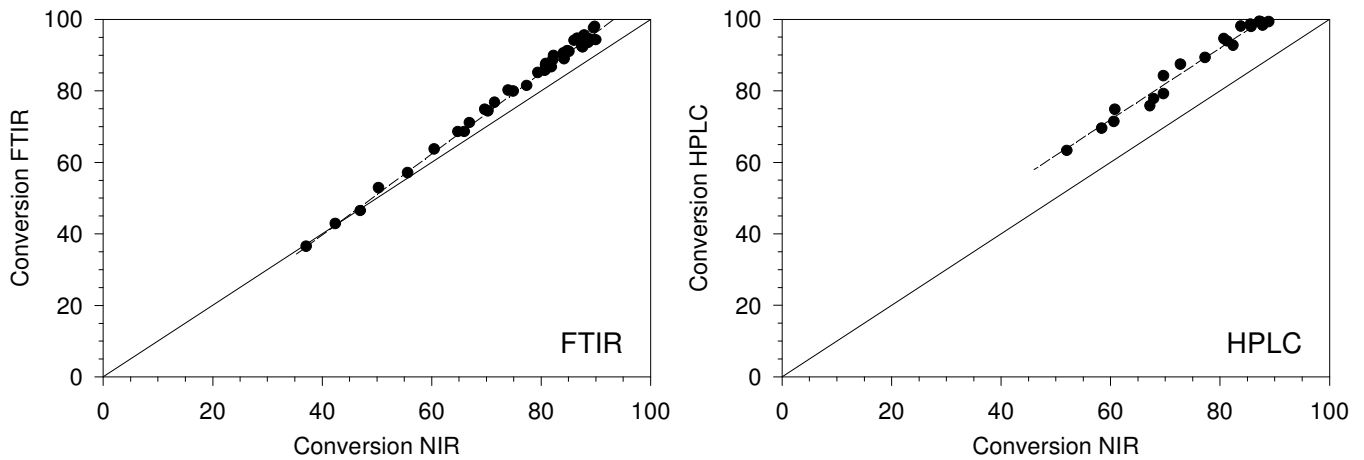
Fig. 7 : Comparison of the conversion determined by NIR reflection spectroscopy with reference data from FTIR transmission spectroscopy and HPLC, respectively, for 10 µm acrylic clear coats on 30 µm LDPE foil

The conversion calculated from the HPLC data was found to be apparently 12 to 15 % higher than that from NIR spectroscopy. This offset is due to basic differences between both analytical methods and is well-known from other investigations. Whereas vibrational spectroscopy generally detects all remaining acrylic double bonds in a sample, chromatography only analyzes the extract which means that only monomers and oligomers with low molecular weight which are still soluble are detected. Pendant double bonds which are already linked to the forming polymer network cannot be observed. For this reason, chromatographic methods generally pretend an apparently higher conversion than spectroscopic ones.

Nevertheless, the results in Fig. 7 prove that NIR reflection spectroscopy can be reasonably used to predict the degree of cure in acrylate coatings after UV or EB curing.
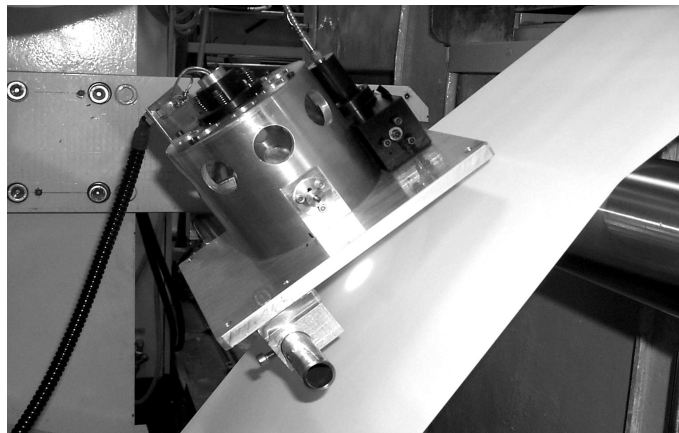

**Fig. 8 :** NIR probe head mounted above the paper web in a roll coating machine at IOM

In-line Monitoring of the Degree of Cure in Pilot Scale

For in-line monitoring of the degree of cure in acrylate coatings on flexible substrate materials such as polymer foils and paper the probe head was mounted above the web of a roll coating machine at IOM behind the outlet of the UV lamp or the EB accelerator (see Fig. 8). For the characterization of clear coats on OPP and PET foils the probe head was tilted against the web in order to suppress interferences.

The capability of NIR reflection spectroscopy to monitor of the degree of cure in-line was tested in numerous trials. Several clear and pigmented acrylate coatings were studied on various substrates after UV or EB curing. Both the web speed and the power of the radiation source were varied repeatedly during irradiation. Simultaneously, NIR spectra were recorded continuously at rates of 70 or 100 spectra/min. Some typical examples of in-line monitoring of the acrylate conversion are shown in the following figures.
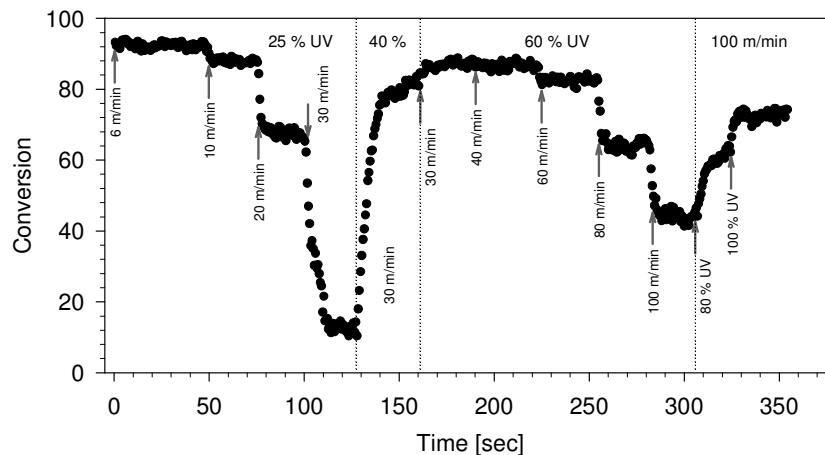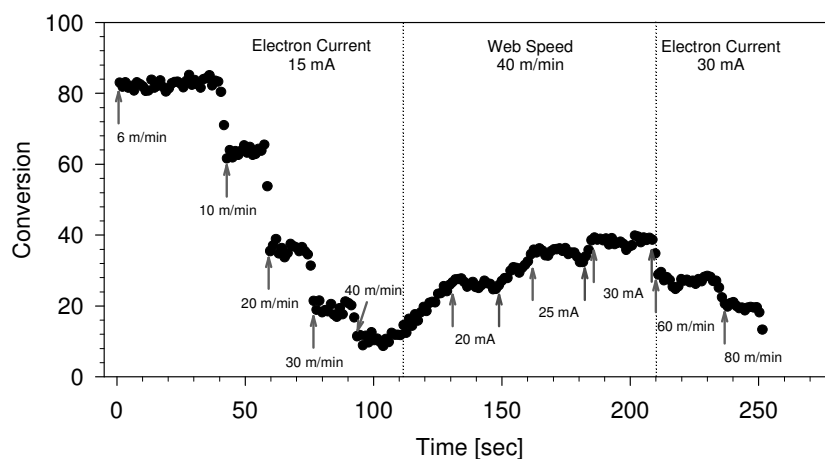

Fig. 9 : In-line monitoring of the degree of cure in a 20 g/m² clear coat on 36 µm PET foil after UV curing with variable power and at various line speeds
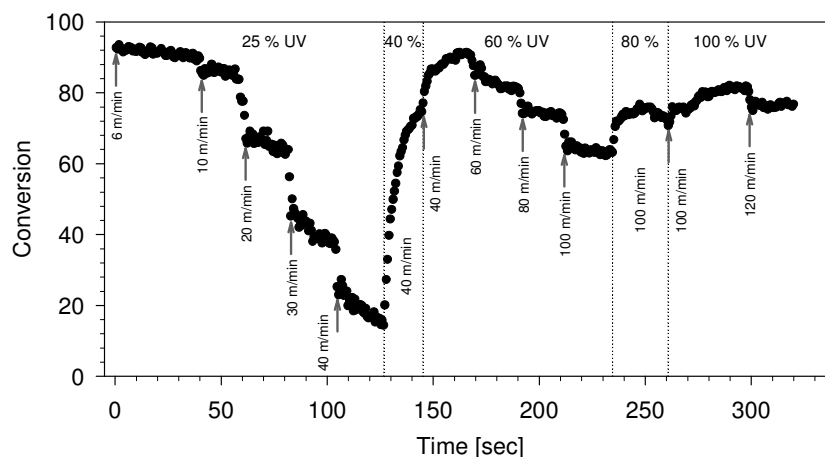
Fig. 10 : In-line monitoring of the degree of cure in a 11 g/m² clear coat on a 60 g/m² white paper after UV curing with variable power and at various line speeds

Figs. 9 and 10 show the in-line monitoring of the degree of cure in clear coats on a transparent polymer foil and on white paper as typical non-transparent substrate, respectively, after UV curing. In order to vary the irradiation dose, the power of the UV lamp and the line speed were varied alternately. The power of the lamp is given in percent of its maximum output. Each change of the irradiation conditions is marked by an arrow. It can be clearly seen that the degree of cure increases or decreases according to the resulting irradiation dose. Any change of the line speed becomes apparent immediately as a change of the conversion. In contrast, changes of the power of the lamp can be observed 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.

At the end of these two trials the monitoring of the degree of cure was performed at lines speeds of 100 or 120 m/min. Even at line speeds, the scatter of the conversion data is low, i.e. it is in the order of about ± 2...4 %. The results show that NIR reflection spectroscopy is able to detect small variations of the degree of cure in thin acrylate coatings even when they have to be analyzed in a running coating line. The time-resolution of the data 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.

Fig. 11 : In-line monitoring of the degree of cure in a 25 g/m² clear coat on 60 µm LDPE foil after EB curing with variable power and at various line speeds

Similar results like in UV curing were also obtained after EB curing. As an example, Fig. 11 shows the monitoring of the conversion in a clear coat on polyethylene foil after EB irradiation under varying conditions. At first, the electron current was kept constant and the line speed was increased stepwise. Later, the electron current was varied at constant line speed. The beginning and the end of each phase with constant irradiation dose are marked by arrows. The time in-between is needed to set new irradiation conditions since increasing the electron current of an EB accelerator takes some time. Any change of the irradiation dose can be directly observed as a change of the degree of cure. Even the gradual increase of the degree of cure during the set-up periods of the electron current can be clearly seen in the conversion chart.
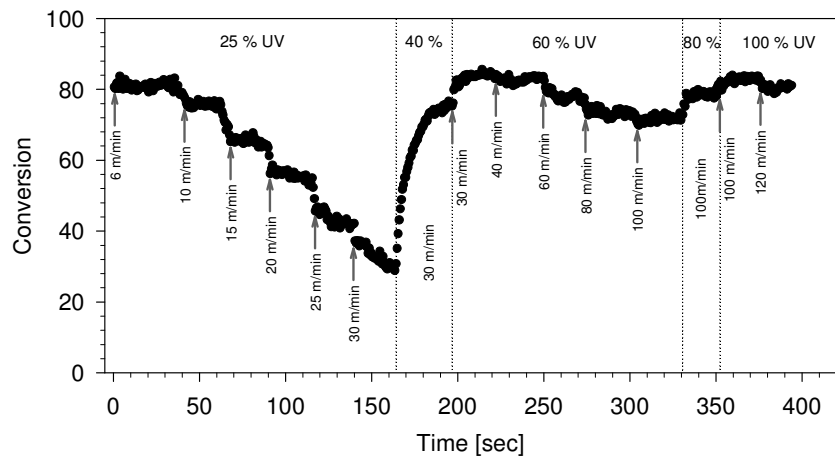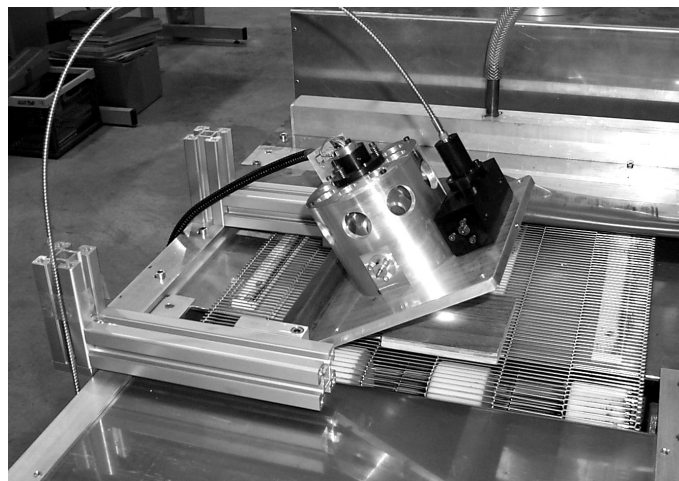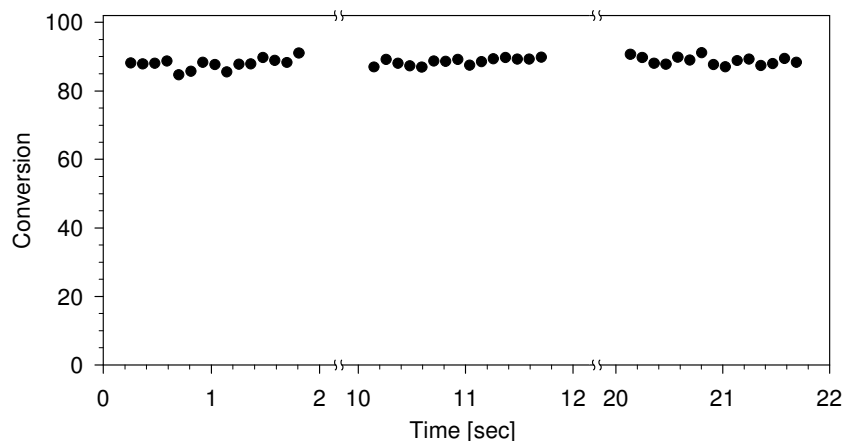
Fig. 12 : In-line monitoring of the degree of cure in a 12 g/m² white-pigmented coating (with 15 wt.-% titanium dioxide) on 19 µm OPP foil after UV curing with variable power and at various line speeds

Fig. 12 shows the in-line monitoring of the degree of cure in a white-pigmented acrylate coating which contains 15 wt.-% titanium dioxide. As already mentioned, pigment particles such as titanium dioxide do not absorb around 1620 nm and hence do interfere with the investigation of the acrylate band in the binder which allows monitoring of the degree of cure in pigmented systems in the same way like for clear coats.

Except for web-like materials, NIR spectroscopy was also used to monitor the degree of cure in acrylate coatings on individual objects such as panels and plates. The probe head was mounted above the conveyor of a panel coating line just behind the outlet of the UV lamp. So, after leaving the lamp, the panels directly pass through the probe beam of the NIR spectrometer (see Fig. 13).

Fig. 13 : NIR probe head mounted above the conveyor of a panel coating and curing line at IOM

Fig. 14 : In-line monitoring of the degree of cure in 40 g/m² acrylic clear coats on MDF panels after UV curing at a line speed of 10 m/min

MDF panels were coated with a clear acrylate formulation. UV irradiation and NIR measurement were performed at speeds of the conveyor from 5 to 30 m/min. In order to get enough spectra per panel, the rate of spectra recording was set to 9 spectra/sec. Fig. 14 shows the degree of cure in coatings on panels which successively pass through the curing line. Evidently, the conversion of the double bonds can be determined with high reproducibility. The time resolution is sufficient for process control : at a line speed of 10 m/min the degree of cure in the coatings is measured every 18 mm. However, if the line is to be operated at much higher speed of the conveyor, the spectra sampling rate can be further increased.

Conclusions

In this study, it was shown that NIR reflection spectroscopy can be effectively used for in-line monitoring of the degree of cure in thin acrylate coatings after UV and EB curing. Thus, for the first time there is a practicable analytical method available which can be applied for process and quality control in technical curing processes.

The newly developed spectrometer which available as Kusta 4004 P from LLA provides the time resolution and the sensitivity which are necessary for such investigations. Its layout with a separate probe head linked to the spectrometer by a fiber-optic cable allows easy installation in industrial coating and curing lines. It was demonstrated in pilot-scale investigations that in-line data can be obtained with high reproducibility and reliability at line speeds of 100 m/min or more. Moreover, it was shown that there is a close correlation between the results from NIR spectroscopy and data from independent reference methods, i.e. the NIR method is able to predict the degree of cure in a correct manner.

With NIR reflection spectroscopy the degree of cure can be studied in clear and pigmented coatings on the basis of acrylates and methacrylates and on most substrates which are typically used in radiation curing, e.g. polymer foils, paper, cardboard, wood, MDF etc. Potential applications comprise many current and future areas where UV and EB curing are or will be used such as coatings for furniture and parquet flooring, decorative, protective and functional coatings on flexible materials, UV-curable adhesives, automotive varnishes etc.

Acknowledgements

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