On-line Monitoring of the Acrylate Conversion in UV Photopolymerization by Near-Infrared Reflection Spectroscopy

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Summary: Near-infrared (NIR) reflection spectroscopy was used to determine the conversion in acrylate coatings after UV photopolymerization in order to test it as a method for process control in UV curing. A probe head was developed which is adapted to the specific requirements of UV curing and which is linked to a photodiode array spectrometer by an optical fiber. Reflection spectra from thin acrylate layers which were taken in intervals down to the millisecond range have shown an excellent signal-to noise ratio. Quantitative conversion data show good correlation with results from independent reference methods (FTIR, HPLC). Following thesebasic investigations, it was demonstrated that NIR reflection spectroscopy can be used for on-line monitoring of the acrylate conversion in thin coatings. Some examples of such investigations in pilot scale are presented.

Keywords: curing of polymers; photopolymerization

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 on almost any substrate. Besides the high productivity, photoinitiated polymerization has several other important advantages such as solvent-free formulation, low consumption of energy, operation at ambient temperature, and high quality of the final products. Consequently, it has found a large number of commercial applications mainly in the coating industry, but also in printing, adhesive processing, and in numerous other applications.[1,2]

The functional properties of UV-cured coatings strongly depend on the final conversion of the acrylic double bonds which is achieved after UV curing. For instance, scratch and abrasion resistance depend on the hardness of the layer which is directly related to the degree of cure. Coatings for exterior applications have to show a high resistance against weathering which can be only achieved if the conversion is largely completed. Insufficient conversion also increases the soluble fraction which can be extracted from the coating which is one of the most critical

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parameters for packaging materials (e.g. for sensitive goods such as foods, pharmaceuticals etc.). A sufficient conversion is also indispensable for further processing of the coating, e.g. with respect to wipe resistance.

On the other hand, the extent of the conversion depends on numerous influencing variables such as the spectral distribution and the intensity of the incident UV light, the duration of exposure (corresponding to the speed of the web or the conveyor), the composition and the homogeneity of the reactive formulation, the ambient conditions during irradiation (temperature, inertization, etc.) and other factors. Whereas some of them can be easily controlled even under the conditions of technical UV curing, this is hardly possible for effects like ageing, pollution or failure of UV lamps, differences between various batches of the lacquer formulation, or other unexpected influences.

For an efficient process control, instant and continual data on the degree of cure right after UV irradiation are indispensable. However, up to now no analytical method of measurement is available which allows on-line monitoring of the conversion of the acrylic double bonds during operation of a coating machine. In the past, various methods such as fluorescence probe techniques [3] have been tested for this purpose but none of them was found to be suitable for on-line measurements in a production process.

An appropriate measuring method must have high sensitivity since conversion has to be determined in thin layers with a thickness in the range of some microns. It must be able to record data at a high sampling rate because of the usually high web speeds used in UV curing. Moreover, a high reproducibility and reliability of the data is required.

In this study it will be shown that near-infrared (NIR) reflection spectroscopy complies with these requirements. It provides the proven capabilities of vibrational spectroscopy for the analysis of polymers and an excellent signal-to-noise ratio. In particular, the double bonds in acrylates and methacrylates appear as an isolated band at 1620 nm in the NIR spectrum. Moreover, powerful chemometric methods are available which may support quantification considerably. Time resolution and sensitivity of NIR spectroscopy are high enough to enable the monitoring of the conversion after UV curing under typical production conditions in real time. Finally, instrumentation is inexpensive, rugged and reliable which is advantageous for use in technical processes.

Experimental

NIR Reflection Spectrometer

A NIR spectrometer system was developed which is adapted to the specific needs of UV curing. It is based on a modified commercial spectrometer unit (Kusta 4004 from LLA) and a tailor-made probe head which is linked to the spectrometer by an optical fiber. The tungsten halogen lamp as light source is integrated in the probe head. A UV filter cuts off the short-wavelength part of the lamp emission and prevents this way postpolymerization of the acrylate layer induced by the probe light. Spectral resolution is achieved by a holographic concave grating. A fast indium gallium arsenide photodiode array with 256 elements and a minimum integration time of 56 μs provides the high time resolution and the sensitivity which is necessary for on-line monitoring. It covers a spectral range from about 1530 to 2000 nm. Reflection spectra are measured against a ceramic plate as reflectance standard which is attached to the probe head.

Samples

Acrylate formulations were applied to substrates such as polyethylene foil, paper or panels from medium-density fibreboard (MDF). Application and curing were performed on various pilot plants at IOM. Irradiation was carried out with industrial mercury arc UV lamps (Fusion, IST) or by a LEA electron beam (EB) accelerator operated at 180 kV (IOM).[2,4] Details are given below for each specific experiment.

Analytical Studies

Samples for analytical laboratory studies were drawn on polyethylene or polypropylene foils with drawing bars and subsequently irradiated with an IST lamp under nitrogen. In order to cover a wide range of conversions, the concentration of the photoinitiator (acylphosphine oxide; Lucirin TPO-L from BASF), the power of the UV lamp and the speed of the conveyor were varied.

FTIR spectra in the mid-infrared were recorded in transmission using a Digilab FTS 6000 spectrometer. A DTGS detector was used because of the better linearity of its response in comparison to a MCT detector. The acrylate band at 1405 cm^{-1} which is assigned to the CH_2 scissor deformation[5] was evaluated.

The soluble fraction in the coatings was determined by HPLC using a Shimadzu LC-10 system equipped with a diode array detector and a RP 18 column. A mixture of water and acetonitrile was used as eluent. Extraction was performed in an ultrasonic bath. The calibration was based on the chromatograms of the unirradiated sample.

Results

Investigation of Thin Acrylate Coatings by NIR Reflection Spectroscopy

In a number of previous works, NIR spectroscopy was used to follow the conversion of acrylic double bonds in the bulk or solution polymerization of methyl methacrylate and other methacrylates. [6-13] Some authors report the investigation of (meth)acrylate photopolymerization reactions by NIR spectroscopy. [14-18] However, in contrast to the present work, investigations were performed on thick samples (mostly dental composites) with a thickness between 1 and 6 mm. In the past, NIR spectroscopy was only little used to study thin coatings because of its relative low sensitivity compared to other techniques in vibrational spectroscopy. However, in preliminary investigations of this study it could be shown that the sensitivity is nevertheless high enough to detect and to analyze acrylate coatings with a thickness of just a few microns. As an example, spectra of an acrylate coating with a thickness of 10 µm on a polyethylene foil before and after UV photopolymerization are shown in Fig. 1.

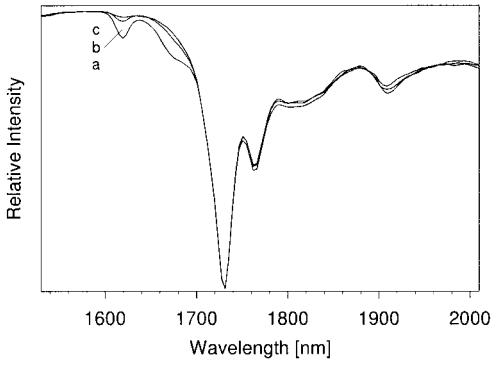

Fig. 1. NIR reflection spectra of a 10 µm acrylic clear coat on a 30 µm LDPE foil before (a) and after UV irradiation with 10 (b) or 600 mJ/cm² (c), respectively

Generally, in UV curing a wide variety of coatings and substrates is used. In order to establish an universal method which can be used for the analysis of clear and pigmented coatings on transparent or opaque substrates measurements are performed in reflection. Strictly speaking, the term *reflection* is correct for opaque samples only (e.g. paper, white pigmented coatings, etc.). When a clear coat on a transparent polymer foil has to be characterized the incident light is transmitted through the sample and then scattered back from the ceramic reflector. Since this setup combines transmission and reflection it is often called *transflection*. [19-21] In the present work, both transparent and opaque coating and substrate materials are studied in various combinations. So, for simplification the term *reflection* will be used throughout this study.

When thin transparent foils of optical high grade polymers such as polypropylene or polyester 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 ~ 20 μm), interference fringes appear which completely mask the spectrum and prevent any analysis if a clear coating is applied to the foil (see Fig. 2a). This problem can be overcome by (i) using a diffuser plate which is mounted between probe head and sample, and by (ii) a tilt of the optical path of the incident and reflected light versus sample and reflector. Both together suppress the interferences very efficiently (see Fig. 2b) and enable this way the determination of the conversion in clear coatings on thin transparent polymer substrates.

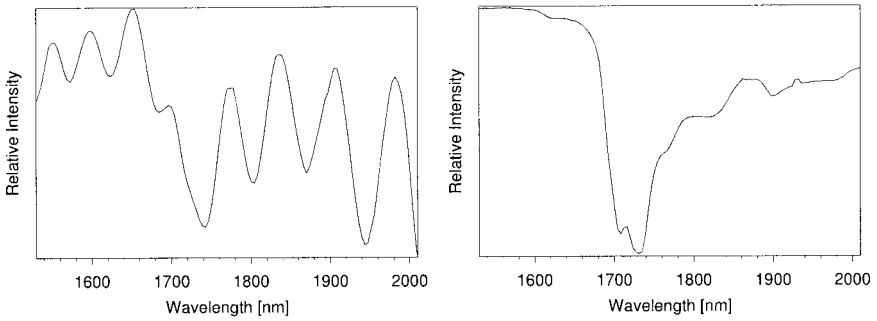

Fig. 2. NIR reflection spectra of a 10 μm acrylic clear coat on 19 μm oriented polypropylene (OPP) foil after UV radiation: (a) without diffuser plate (left) and (b) with diffuser plate (right)

Quantitative Analysis of the Acrylate Conversion

Quantitative analysis in NIR spectroscopy is usually performed by using sets of well-defined calibration samples and sophisticated chemometric evaluation methods (PLS, PCR, etc.). [19-22] Basically, this procedure is also applicable in UV photopolymerization and produces excellent results if suitable calibration samples with an exactly known conversion are available. However, the specific preparation of UV-cured coatings with a predetermined conversion is difficult to achieve in most cases, and the careful characterization of cross-linked polymers is usually a labor-intensive task. Therefore, it should be often hardly possible to use chemometric methods routinely in process and quality control of UV curing, in particular if the coating applications for which the conversion is to be monitored are changing frequently.

Alternatively, the conversion can be directly determined by using Beer's law. In the near-infrared spectrum of acrylates and methacrylates appears a characteristic band at 1620 nm which is due to the first overtone of the C-H stretching vibration in the acrylic double bond. [23] Because of its isolated position in the spectrum it is well suited for band integration. Certainly, this method is not as sophisticated as the chemometric techniques. However, with respect to the routine analysis of photopolymerized coatings it has the important advantage that calibration is performed simply by recording spectra from the uncured layer.

In the present study, both chemometrics and band integration were used for quantitative analysis. Besides the PCR technique, a wavelet transformation algorithm [24] was used as an additional chemometric method. In contrast to PCR, calibration can be performed with just one calibration sample which could be the acrylate coating before irradiation.

Quantification of the Conversion using PCR

The efficiency of PCR as an analytical tool for quantification of the conversion in photopolymerized acrylate coatings is demonstrated for 5 µm thick layers on a 19 µm foil from oriented polypropylene (OPP). A number of samples were prepared whose degree of cure differs to a large extent. The conversion of acrylic double bonds was determined by FTIR spectroscopy. Some of the samples were selected for calibration of the PCR method. After the calibration procedure, the conversion in all the samples was analyzed by NIR spectroscopy and compared to the results from FTIR spectroscopy (see Fig. 3).

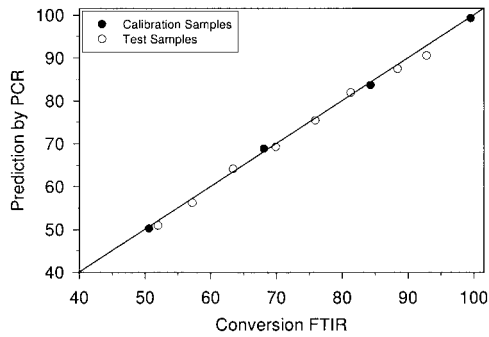

Fig. 3. Comparison of the conversion in 5 µm acrylate layers on a 19 µm OPP foil predicted by PCR from NIR reflection spectra with reference data from FTIR spectroscopy

The results clearly show the capability of PCR to predict the conversion of double bonds even in thin acrylate coatings from NIR reflection spectra on the basis of a previous calibration of the method with several well-defined samples. If calibration samples can be provided, PCR is the most powerful of the 3 methods used in this study to extract quantitative conversion data from NIR spectra.

Quantification of the Conversion according to Beer's Law

In contrast to the indirect determination of the conversion from chemometric techniques like PCR where the exactness of the NIR results depends on the precision of the reference method, the integration of the acrylate band directly leads to quantitative results. In order to ensure that the data obtained by NIR spectroscopy in this way actually reflect the conversion of the sample correctly, they were compared with results from independent reference methods (FTIR spectroscopy and HPLC). Again, samples with a wide range of conversions were prepared. The comparative analytical investigations were performed with the same samples for each of the three methods.

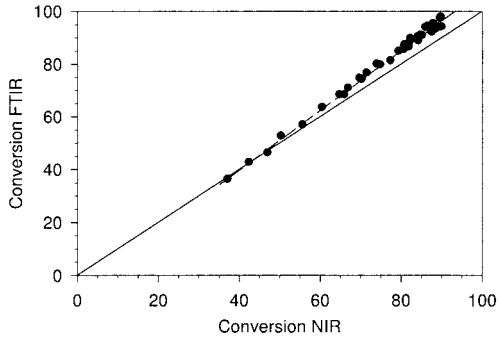

Fig. 4. Comparison of the conversion in 10 µm acrylic clear coats on a 30 µm LDPE foil determined by NIR reflection spectroscopy vs. the conversion determined by FTIR transmission spectroscopy

In Fig. 4, the conversion in 10 µm thick layers of acrylate on a 30 µm LDPE foil obtained by NIR spectroscopy is plotted vs. results determined with FTIR spectroscopy. An excellent linear correlation between both spectroscopic methods over the complete conversion range studied was found. At very high conversion NIR spectroscopy slightly underestimates the degree of

cure in comparison to FTIR spectroscopy. Nevertheless, the results prove that NIR reflection spectroscopy can be reasonably used to predict the conversion in thin acrylate layers after UV photopolymerization even with a simple evaluation according to Beer's law.

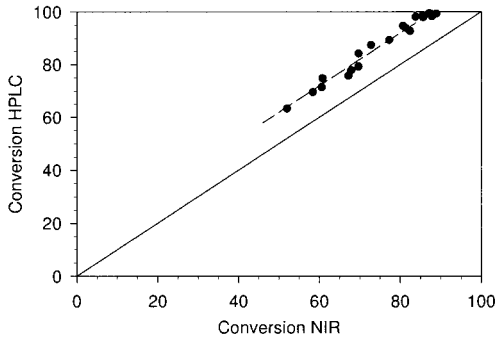

Fig. 5. Comparison of the conversion in 10 µm acrylic clear coats on a 30 µm LDPE foil determined by NIR reflection spectroscopy vs. the conversion determined by HPLC

The corresponding plot of the conversions determined from HPLC and NIR spectroscopy, respectively, is shown in Fig. 5. In general, the conversions derived from HPLC seem to be about 12 to 15 percent higher than those from NIR spectroscopy. However, this offset is due to basic differences between both experimental methods and is well-known from other investigations. Spectroscopy detects all remaining acrylic double bonds in the sample. In contrast, chromatography only analyzes the soluble fraction which means that only monomers and oligomers with low molecular weight which are still soluble are detected whereas pendant double bonds which are already linked to the forming polymer network cannot be observed. Consequently, chromatographic methods generally pretend an apparently higher conversion than spectroscopic ones.

On-line Monitoring of the Conversion

The NIR spectrometer was fitted to several pilot-scale curing lines for the coating of web materials and panels, respectively. During operation, reflection spectra from thin acrylate coatings were taken in arbitrary intervals down to the millisecond range depending on the requirements of the specific application. The conversion was followed in various clear and pigmented acrylate coatings on transparent or opaque substrates such as polymer foils, paper, wood and MDF panels, etc. Some selected examples of such investigations will be discussed in this paragraph.

Coatings on Web Materials

For on-line monitoring of the conversion of acrylate coatings on paper and polymer foils the NIR probe head was mounted above the web of a roll coating machine behind the outlet of the UV lamp (or the electron beam accelerator). A typical example of on-line monitoring of the conversion is shown in Fig. 6. A clear acrylate formulation containing 1 wt.-% Lucirin TPO-L as photoinitiator was coated on a decor paper with a coating weight of 10 g/m² and subsequently irradiated by a Fusion F-600 UV lamp. NIR spectra were continuously recorded with an integration time of 824 µs and at a rate of 72 spectra/min.

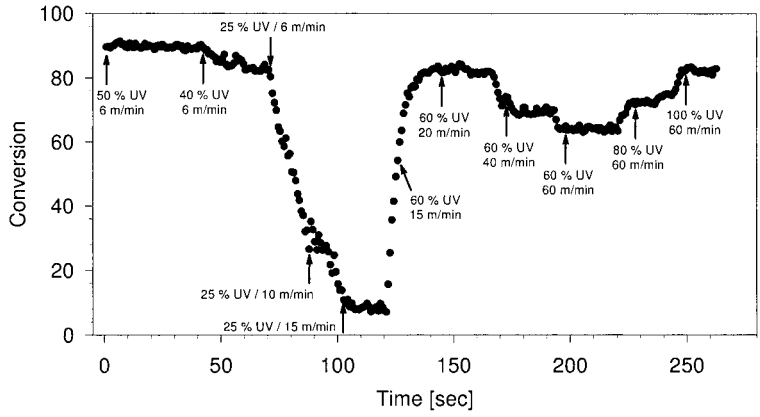

Fig. 6. On-line monitoring of the conversion in a 10 g/m² acrylic clear coat on decor paper after UV curing with a Fusion F-600 UV lamp with variable power (given in percent of the maximum power) and at various web speeds

In order to vary the irradiation dose, both the power of the UV lamp and the web speed were varied during UV irradiation. Each change is marked by an arrow in Fig. 6. According to the resulting dose, the degree of cure increases or decreases. Any change of the web speed leads to an immediate change of the conversion whereas changes of the power of the UV lamp can be observed after a delay only since the response of the lamp itself is much slower than that of its electronic control. Except of some outliers, the scatter of the conversion data is less than ± 2 % at web speeds up to 60 m/min. Even higher web speeds up to 100 m/min and higher recording rates for the NIR spectra were successfully tested.

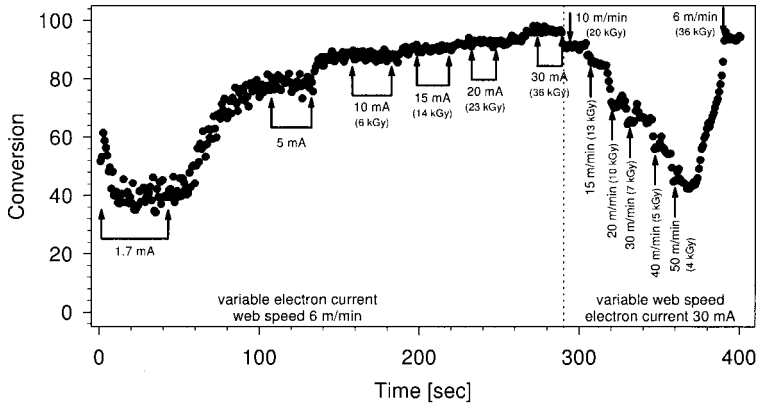

Fig. 7. On-line monitoring of the conversion in a 10 g/m² acrylic clear coat on decor paper after EB curing with variable electron current and at various web speeds

Similar investigations were also performed with electron beam curing (see Fig. 7). The same acrylate formulation (however, without photoinitiator) was applied to decor paper with a thickness of 10 g/m². NIR reflection spectra were recorded under the same conditions like in Fig. 6. Again, the irradiation dose was varied stepwise. At first, the electron current was varied whereas the web speed was kept constant at 6 m/min. Later, the web speed was increased at constant electron current. The beginning and the end of each phase with constant dose are marked by arrows. The time in-between is needed to set the new irradiation conditions. It can be clearly seen from the data obtained by NIR spectroscopy that any change of the irradiation dose results in an immediate change of the conversion.

The results in Figs. 6 and 7 show that near-infrared reflection spectroscopy is able to detect variations of the conversion in thin acrylate coatings on paper or polymer webs in a running coating line with sufficient time-resolution.

Coatings on Panels

Except for web-like materials, NIR spectroscopy was also used to monitor the conversion in photopolymerized acrylate coatings on panels. For this, the probe head was mounted above the conveyor of a panel coating line. After leaving the outlet of the UV lamp, the panels directly passed through the probe beam of the NIR spectrometer. A typical result of on-line monitoring of the conversion is given in Fig. 8.

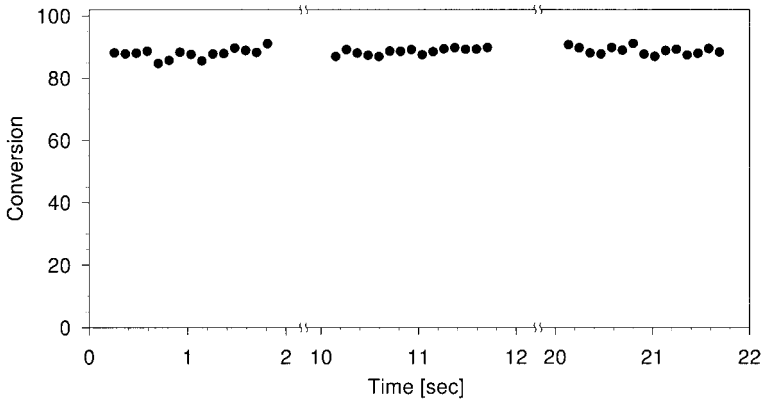

Fig. 8. On-line monitoring of the conversion in 40 g/m² acrylic clear coatings on MDF panels with a length of 30 cm after UV curing with an IST lamp at 10 m/min

MDF panels with a length of 30 cm were coated with a 40 g/m² clear coat containing 0.5 wt.-% Lucirin TPO-L as photoinitiator. UV irradiation and NIR measurement were performed at a speed of the conveyor of 10 m/min. In order to get enough spectra per panel, the rate of spectra recording was set to 9 spectra/sec.

Fig. 8 shows the conversion for a number of successive panels. Ones again, it is apparent that the conversion can be determined very rapidly and with high reproducibility. So, NIR spectroscopy has been proven to be able to follow the acrylate conversion on both web materials and individual objects such as panels or plates.

Conclusions

In this study, it was shown that near-infrared reflection spectroscopy can be successfully used for on-line monitoring of the conversion in thin acrylate coatings after photopolymerization. It is able to follow the conversion in clear and pigmented coatings on transparent or opaque substrates such as polymer foils, paper, cardboard, wood, MDF, etc. Thus, for the first time there is a practicable analytical method available which could be applied for process and quality control in technical UV and EB curing.

It was demonstrated in both laboratory and pilot scale investigations that conversion data can be recorded with high reproducibility, high reliability and with sufficient time resolution. The accuracy of the conversion data from NIR spectroscopy was verified by comparison with two in-

dependent reference methods. Moreover, a chemometric and a simple integration method which is less time-consuming were tested for evaluation of the NIR spectra. Despite of the higher efficiency of the former one, the latter may be used when minor deviations at higher conversion can be accepted. There is only one basic requirement which has to be generally fulfilled : correct and reliable conversion data are only achieved when the thickness of the coating is constant throughout the entire calibration and measurement process.

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