NIR-Laser Based Detection of the Photopolymerization State of Acrylate Coatings Suitable for *In Situ* Measurements

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ABSTRACT: The present article describes a method for the determination of the radical photopolymerization conversion of acrylic coatings suitable for an *in situ* monitoring during the coating process. Acrylate based coatings are increasingly used in many kinds of industrial coating processes, because of advantages of the solvent-free application process. The applied method is based on 1620 nm light absorption of the acrylate. To overcome the disadvantages of a common NIR spectrometer, only the diffuse reflection of the relevant discrete wavelength at 1620 nm and of a reference wavelength is measured. A sophisticated sensor setup including an optical spatial filter and lock-in amplified signal processing is used to achieve a sufficient signal to noise ratio. The capability of the sensor to discriminate between polymerized and unpolymerized coatings on metal substrates down to a coating thickness of 16 μm is demonstrated. Furthermore, the information on polymerization from larger depth in TiO_2 pigmented coatings is investigated. The results can be analytically modeled in analogy to the Lambert–Beer's law, resulting in a detection limit of a maximum pigment concentration of 15 wt % with 100 μm coating thickness. The presented sensor design is suitable to be used in an industrial production environment for example in screen printing applications as a monitoring and quality control tool. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 3494–3500, 2012

Key words: photopolymerization; coatings; infrared spectroscopy; sensors; monomers

INTRODUCTION

Online quality control in UV curing processes of multifunctional acrylate coatings is crucial to ensure film properties like sufficient double-bond conversion, adhesion, and surface hardness. The development of small, robust, and contact-free sensor systems in industrial environments is a technical challenge. Recent studies for online determination of the degree of conversion have used real time infrared spectroscopy (RTIR),[1] conventional near infrared spectroscopic (NIR) systems with common halogen light sources,[2–4] or more recently microdielectrometry.[5] Additionally, photo differential scanning calorimetry is an extensively used technique.[6] However, none of these techniques are amenable for high throughput applications due to low sampling rates. An emerging technique utilizing a reliable high throughput NIR-sensor system may be in demand, capable of conversion control of photopolymerizing coatings on different substrates.

Distributed feedback lasers (DFB) are widely used for gas sensing, fluorescence measurements, and chemical compound analysis.[7] The optical output power and wavelength selectivity of the lasers available on the market have been considerably increased in recent years. These lasers are now able to collect information out of the complete layer volume, rather than close to the surface, as conventional halogen sources do. Gaining conversion information of layers directly adjacent to the substrate-coating interface can be crucial for the coating adhesion and therefore for the quality of the final product.

This article presents a new DFB laser based approach to sense the acrylic conversion of photopolymerized coatings with thicknesses between 16 and 100 μm, like printing or wood coating applications,[8] respectively. The C-double bond concentration of the acrylic coating is determined by measuring the absorption of the connected C—H overtone oscillation. Furthermore, the system inherent information depth of the polymerization in clear and pigmented coatings is analyzed. The experimental setup is designed to detect the combined diffusely reflected laser light from the substrate and from the coating. A spatial filter is used for blocking the directly reflected light from the coating surface, which does not contain any information on the acrylic conversion.
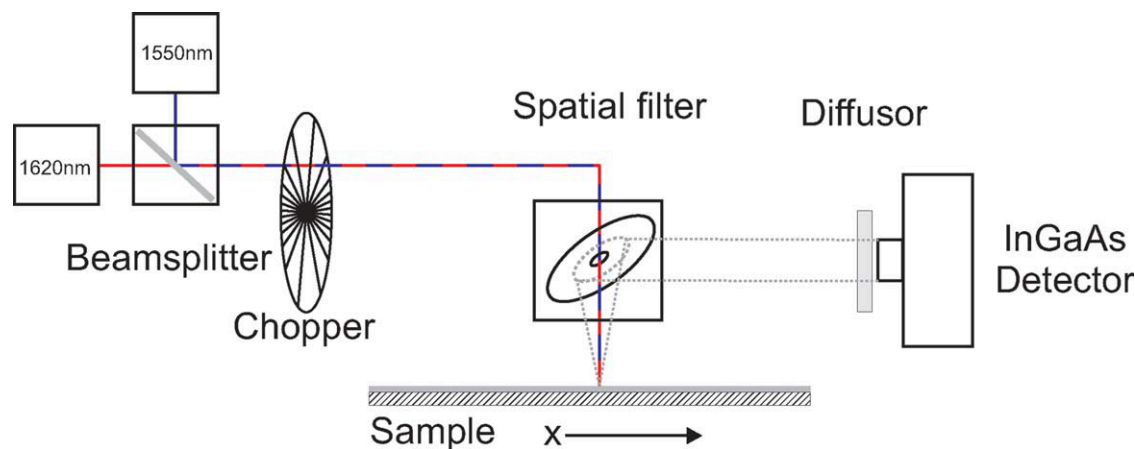
Figure 1 Setup of the measuring system consisting of two laser sources (1620 nm DFB laser, 1550 nm Fabry-Perot laser source), light chopper, spatial filter (pinhole mirror), and InGaAs detector diode. The coated substrate is placed orthogonal to the incident laser light. The diffuse reflected light from the sample is guided via the spatial filter on to the detector diode and processed by using a lock-in amplifier triggered by the light chopper. The sensor is designed for collecting only the diffuse reflected light from the substrate and/or coating. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Here presented results are the outcome of the laboratory based sensor development, and the acquired data is still *ex situ*, but the optical design and measurement principle has been already adapted to an industrial sensor system measuring the acrylic conversion *in situ*. The solved technical challenges as outlined in these experiments will allow quality control of acrylate coatings suitable for industrial high throughput processes.

EXPERIMENTAL

Materials

Four different types of multifunctional acrylate coatings were prepared and investigated.

The clear coating for the sensor measurements and photometric verification is composed of modified epoxy acrylate resin (LAROMER LR9019, 75 wt %) and tri(propyleneglycol)diacrylate (LAROMER TPGDA, 25 wt %) were purchased from BASF Laromer. The white pigmented coating is made by dispersing 2, 5, and 10 wt %, respectively, of titanium dioxide (TiO$_2$, KRONOS 2059) in the clear formulation. The average size of the TiO$_2$ pigments has been determined to a diameter of 2 μm from scanning electron microscopy. In all samples the photoinitiator Phenylbis(2,4,6-trimethyl benzoyl) phosphine oxide (IRGACURE 819, 3 wt %) from Ciba Specialty Chemicals is used with a high ratio of 3 wt % to ensure a maximum of polymerization.

Sample preparation, coating application and UV irradiation:

The substrates of all samples are identical steel panels from Q-Labs (Type QD-23.5, 50 × 90 × 2 mm^3,

steel, and smooth). Thereby all panels have equal physical properties concerning reflectivity and wettability. All formulations are applied using spiral ductors from MTV-Messtechnik with various nominal lamination strengths. The UV radiation is generated by using a medium pressure mercury lamp (IST Metz GmbH, Germany) with an irradiance of 6.5 kW/m^2 at the sample surface. After all samples have been irradiated for 10 s, the thickness of each sample is measured with a DualScope® from Fischer.

Experimental setup of the sensor system

The measuring system shown in Figure 1 combines two laser sources one with the emission at 1620 nm (DFB laser, 8 mW optical output power purchased from Sacher Lasertechnik, Germany) and the other at 1550 nm (5 mW optical output power from Thorlabs GmbH) via a beam splitter. The collimated laser light is guided through a pinhole mirror (spatial filter) onto the coated samples. The back scattered diffuse light from the samples is selected by the spatial filter and reflected to an indium gallium arsenide diode (InGaAs), used for detection (Teledyne Judson Technologies). To enhance signal stability a Teflon diffuser in front of the diode is applied. For increase of the signal to noise ratio, a lock-in amplifier (Model 5207/5208 form Signal Recovery) is used in combination with a chopper, operated at 1 kHz, and positioned in the optical pathway.

All samples were placed on the sample stage and measured several times by constantly moving the stage ±10 mm in the *x*-direction with a velocity of 20 mm/s.
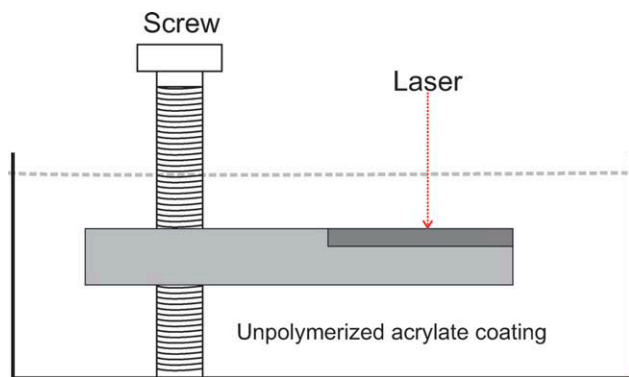
Figure 2 Illustration of the measuring device used for the depth profiling of the clear and pigmented formulations. The tray is filled with the liquid formulation up to a defined mark. By turning the screw a substrate is moved vertically through the formulation, thus decreasing the coating thickness from 4000 μm down to nearly zero. Unintended volume changes in the tray are avoided in this configuration and can be neglected. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Depth profiling of clear and pigmented unpolymerized acrylate formulations

The penetration depth of the sensor system into the acrylate system is measured by using a substrate probe mounted on a boom. The boom is moved stepwise through the acrylate resin filled tray up to the surface of the liquid coating, see Figure 2. The setup ensures a constant resin volume in the tray to minimize measurement errors of the layer thickness. The setup adjusts the film thickness with a resolution of 85 μm/step.

Spectroscopic validation measurements

To verify the sensor signal, comparative measurements on all samples were performed with a spectrophotometer (Lambda1050 from Perkin–Elmer) in the spectral range from 1500 to 1700 nm including the measuring wavelength at 1620 nm where absorption changes with proceeding acrylic polymerization. All measurements were carried out in reflection with an integrating sphere from LabSphere. To enhance signal strength the diffuse as well as the direct reflection of the incident beam are used together. The resolution of the spectrophotometer is set to 1 nm.

RESULTS AND DISCUSSION

Verification of the C=C double bond conversion using the C—H stretch overtone

A comparison of the spectroscopic data from unpolymerized and polymerized samples of a clear coating in Figure 3 verifies the absorption band at 1620

nm of the terminal double bond C—H oscillation overtone of the acrylate group.[9,10] The change in absorption of this C—H oscillation is a direct measure of the degree of polymerization and accordingly an indicator for remaining acrylic C-double bonds in the coating. Furthermore, an overall attenuation of the reflection is observed, as a result of the coating shrinkage in combination with a change of the refractive index,[11,12] and a change in molecular scattering. Consequently, a discrete measurement of the absorption at 1620 nm is only possible by compensating for these changes.

In the spectral range between 1500 and 1600 nm no absorption bands of the acrylic formulation are observed or reported. Therefore a normalization of the C—H stretch absorption of the C-double bond is realized by recording the back scattered light from an additional 1550 nm laser diode, additionally to the 1620 nm laser light as shown in Figure 1.

Comparison of the discrete laser measurement with a spectrophotometric reference

Samples coated with 16, 35, 67, and 96 μm clear formulations, respectively were measured before and after UV curing using the earlier described experimental setup. The radiant quotients $Q = \frac{I_{1620nm}}{I_{1550nm}}$ of signal intensities are plotted in Figure 4, as well as the radiant quotient differences between unpolymerized and polymerized samples normalized to the range of
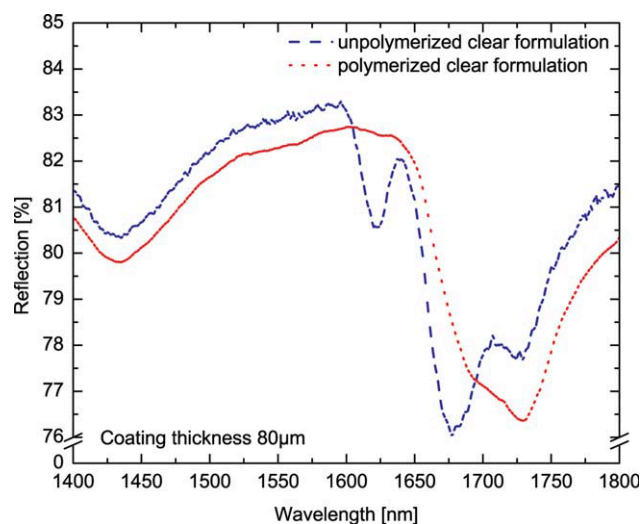

Figure 3 Spectral reflection of the clear formulation (25% TPGDA and 75% Epoxyacrylate) with 3 wt % Irga-Cure819 and a coating thickness of 80 μm. The blue line shows the unpolymerized state with the absorption at 1620 nm. The red line shows the polymerized spectra devoid of the 1620 nm absorption. The formulation was coated on a steel panel from Q-Labs and irradiated for 10 s. The spectral data was acquired using a spectrophotometer from PerkinElmer and an integrating sphere from LabSphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
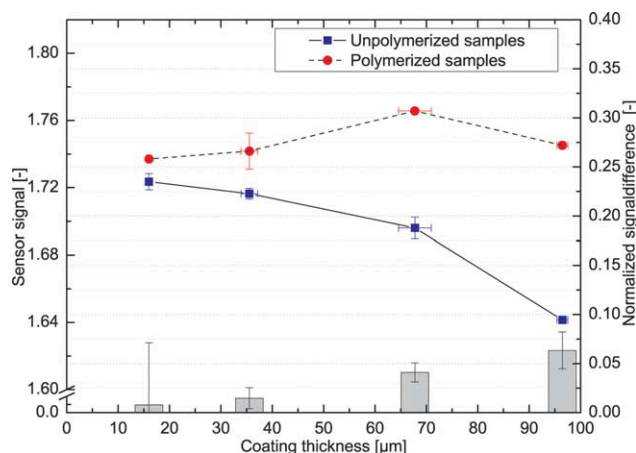
Figure 4 Experimental signal result from unpolymerized and polymerized samples acquired by the discrete laser spectroscopic measuring system. Left ordinate shows the absolute radiant quotient of the sensor system. The bar chart (right ordinate) shows the signal difference of the coatings before and after UV curing. The error bars are the standard deviation of five independent samples. The coating thickness of each measurement was determined after curing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 5 Measured signal results from unpolymerized and polymerized samples obtained by the spectrophotometer. Left ordinate shows the absolute radiant quotient of the sensor system. Right ordinate and bar chart shows the signal difference of the coatings before and after UV curing. The coating thickness of each measurement was determined after curing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

[0,1]. The decay of the 1620 nm overtone absorption is clearly seen in Figure 4, from an increasing radiant quotient Q. The decrease in absorption and increase in the radiant quotient Q is directly connected to the degree of conversion, as mentioned before. The relative signal differences increase with the coating thickness from 0.7 to 6.3%. The given errors are determined by computing the standard deviation over five different samples at each thickness. In Figure 5 the same five samples were measured in the spectrophotometer to verify the acquired data from the sensor system. According to the above described method, the discrete spectral intensities at 1620 and 1550 nm of the spectrophotometer were used to calculate the radiant quotient Q of both polymerized and unpolymerized samples.

In Figure 4 the measured data of the discrete sensor system shows an unexpected maximum at the coating thickness of 67 μm. This maximum is a result of the scattering of the laser light in the coating layer, deflected from the incident light path. This radiant quotient value is saturated at a distinct point controlled by the layer thickness. Beyond this layer thickness, the light propagation does not change anymore; a stable equal light distribution is reached. The recurring radiant quotient decrease at higher thickness values in the unpolymerized state is because of the occurrence of more acrylic C—H compounds respectively, thus resulting in an increased absorption at 1620 nm. The surface reflection of the system can be neglected in this case, due to the system inherent blocking of the direct reflected laser
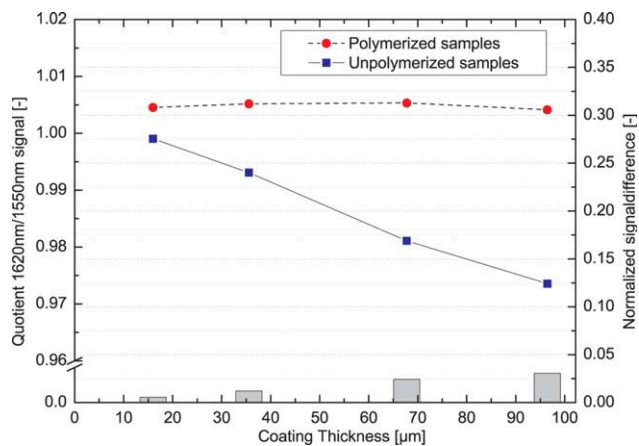
light. The data measured by the spectrophotometer in Figure 4 does not show this maximum in the radiant quotient. It was gathered by integrating the whole half space of the reflected light from the sample. That incidence is again proofed by comparing the relative signal differences between the polymerized and unpolymerized data of each measuring system. The signal difference range of the discrete sensor system is notably higher, because of the blocking of the direct reflected light. The result indicates one advantage of the laser sensor system concerning the possible conversion detection sensitivity with increasing coating thickness, see Table I.

The measurement with the spectrophotometer is performed without motion of the sample. The standard deviation of the spectrophotometer is due to the high precision of the device and the comparable large beam spot (20×30 mm^2) and thus large spatial integration of the sample areas negligible and not displayed. The results of these verification

TABLE I
Summary of Radiant Quotient Q Differences of the Discrete Laser System and the Reference Spectrophotometer

Coating thickness (μm)	Difference of the discrete laser system signal (%)	Difference of the spectrophotometer signal (%)
16	0.785 ± 0.633	0.552
35	1.471 ± 1.080	1.210
67	4.096 ± 0.976	2.424
96	6.332 ± 1.881	3.055

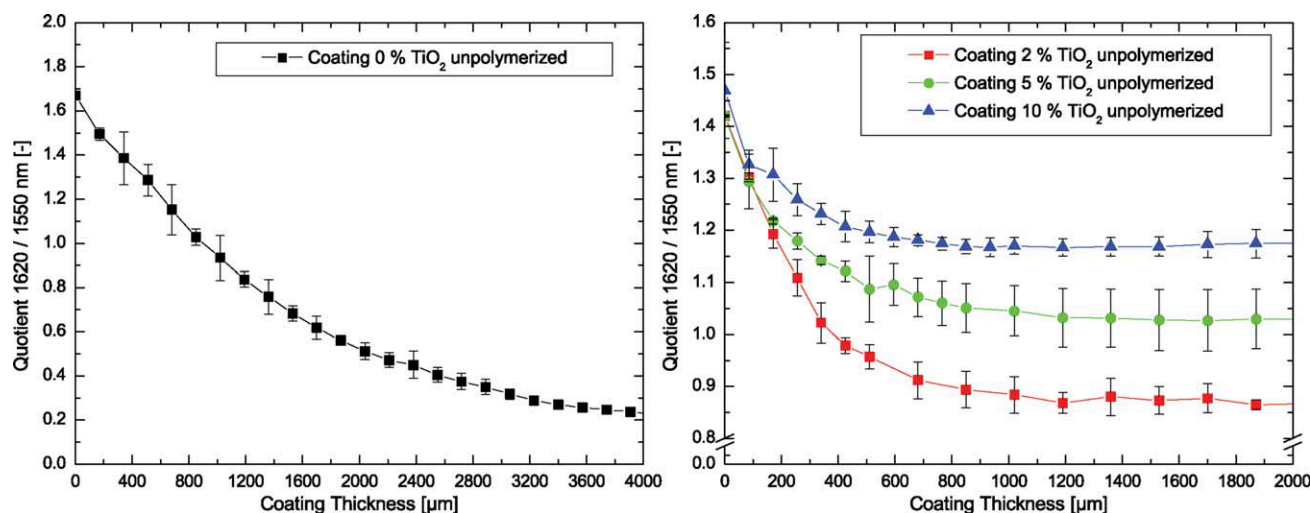High relative signal amplitudes by the discrete laser system are observed.

Figure 6 Acquired signals by using the experimental setup described earlier. Left figure shows the clear unpolymerized formulation, right side shows the Ti0$_2$ pigmented unpolymerized formulations. All curves show an exponential decay according to the Lambert–Beer law. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

measurements are in great accordance to the results shown in Figure 4. The high standard deviation of the laser sensor systems on different samples is caused by the comparable rough steel substrates. Measurements performed on different uncoated substrates like paper or PVC indicates a lower standard deviation by one magnitude. Furthermore, an even more controlled coating application like printing processes will provide fewer errors.

We now consider the relevance of our laboratory setup with respect to the transfer of the sensor system to an industrial application. Because of the laser spot size of 2 mm and the short integration time of 1 ms in the lab setup and half a millisecond in the industrial setup, respectively, the differences in stage velocity only lead to negligible deviations in the size of the spatial integration area (stage velocities of 20 mm/s and 250 m/min; swept over area of 2 and 4 mm, in the lab and industrial case, respectively). Except for the discussed velocity difference, the measurement principle and process will be identical in an industrial application. Therefore a transfer of the laboratory results to the industrial application is appropriate.

Information on conversion from larger depth by the discrete laser sensor

The main advantage of using lasers as light sources, in comparison with halogen light sources, are their high beam intensities, which enhances the depth of penetration into an acrylate coating. For this reason, gathering integral information of the polymerization reaction from the substrate coating boundary up to the surface is possible.[13]

Four different unpolymerized acrylate formulations were analyzed by using the depth profiling tool described earlier. Because of the necessary movement of the experimental setup, only unpolymerized samples were measured. The results are assumed valid for the polymerized case as well, due to a coating shrinkage of only 5–8% after polymerization in comparable formulations,[14] which will be neglected. The clear coating showed a signal change from 4 mm coating thickness downwards, whereas a signal change of the TiO$_2$ pigmented formulations started at 2 mm. The radiant quotient of the two laser beam signals are plotted in relation to the coating thickness of the clear and pigmented formulations (Fig. 6). All radiant quotients show an exponential decay with increasing coating thickness, according to the Lambert–Beer law.[15] By comparing the signal strength at 0 μm of the clear formulation according to Figure 6 with that of Figure 4, it is ensured that the remaining coating thickness on the small boom substrate is less than 20 μm. The TiO$_2$ pigmented formulations show three different decay slopes as well as different minimum signals. The pigmented formulations data were normalized for a detailed comparison and determination of the actual penetration depth. The normalization into the range of[0,1] is computed by $y' = \frac{y - y_{\mathrm{mean}}}{y_{\mathrm{SD}}}$ with y_{sd} = standard deviation of y. The normalized data y' is shown in Figure 7.

The Lambert–Beers law is defined as $I = I_0 e^{-ax}$, with I for the measured light intensity, I_0 for the incident light intensity, α for the absorption coefficient, and x for the light path distance in the material. In analogy to this law, all data were fitted using an exponential decay function $I = I_{\mathrm{off}} + A e^{-\alpha x}$. Where I_{off} represents the intensity offset caused by
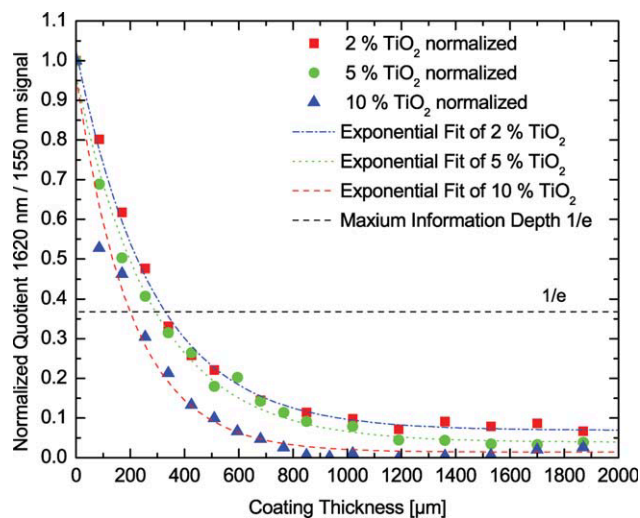
Figure 7 Normalized data of the measured unpolymerized pigmented formulations including the exponential fit of each dataset. The information depth of 1/e is plotted as well. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the unwanted direct reflected light, A the related fitting coefficient (I_0 in the Lambert–Beer law) and I the measured laser light intensity of the 1620 nm absorption. The results are summarized in Table II. All RMS-errors of the least-square fit are below 0.02, which states a good model fit. I_{off}, the undesired direct light reflection, is increasing from 0.01411 to 0.06871, because of the decreasing scattering of less TiO$_2$ particles. The coefficient A with values of 0.92–0.95 indicates some uncertainties in the measurement owed to the remaining of some minor coating on the substrate at a thickness value of 0 μm.

The calculated absorption coefficient α, is due to the nature of the used laser radiant quotient, a difference of the absorption coefficients of 1620 and 1550 nm. The portion of each single coefficient cannot be derived in this experimental setup with respect to the C-double bond conversion and thus the variable 1620 nm absorption coefficient will not be further investigated. However, the acquired absorption coefficients are in the same order of magnitude. Thus, the results are suited for calculating the more important penetration depth of the laser signals.

The determination of the maximum information depth x_{ID} is defined by using the Lambert–Beer law as follows:

$$I = I_0 e^{-ax} \text{ with } x_{ID} = \frac{1}{\alpha} \rightarrow \frac{I}{I_0} = \frac{1}{e}$$

The information depth of the sensor system in 2, 5, and 10% TiO$_2$ pigmented coatings is calculated to 330, 300, and 200 μm, respectively. This gathered information of the coating layer is an integral over all infinitesimal thin layers between the surface and the

substrate, respectively and the maximum penetration point. Any C-double bond or rather C—H ligand interacting with the laser light will be accounted to the signal no matter of depth position. The higher orders causing the offset I_{Off} are neglected. If a reciprocal correlation between the pigment concentration and the penetration depth is assumed, we can extrapolate the data to higher concentrations. The extrapolated result leads to a maximum of 20 wt % concentration of TiO$_2$ at nearly 0 μm.

The analyzed samples with 2–10% TiO$_2$ pigments reflect a common range of pigment proportions used in industrial applications with coating thicknesses of about 60–80 μm, for example anticorrosion coatings. Higher volume concentrations of pigments are only applied within thin coating thicknesses of about 1–2 μm, because of the high absorption of the UV irradiation by the pigments below 380 nm.[16] For example screen ink formulations include about 5% of organic pigments.[17] Especially, in an application area with complex geometries, varying irradiance power on the surface and different coating thicknesses, the information on remaining C-double bonds, which is equivalent to conversion, is most desirable.

Limits and future perspectives

The nature of the presented sensor systems is transmission through a coating and reflection on a substrate. The principle implies the presence of a well-defined coating layer of a few micrometer thickness. Therefore, the current sensor can hardly be used in offset printing applications, where coating thickness is defined by the weight amount of ink per square meter. The marginal use of ink leads to coating thicknesses in the range of 1–2 μm. In offset printing closed coating films are often not formed on surfaces like paper or cardboard.

Future work will be focused on the implementation of an imaging detector unit, which will provide more accurate information of the conversion on complex geometries. The current one-dimensional information of conversion will be complemented by the sample geometry, and thus coating thickness

TABLE II
Exponential Least Square Fitting Results of the TiO$_2$ Pigmented Unpolymerized Formulations Using $I = I_{Off} + Ae^{-\alpha x}$ Analog to the Lambert–Beer Law

Formulation	10% TiO$_2$	5% TiO$_2$	2% TiO$_2$
RMS	0.01913	0.01014	0.00413
I_0	0.01411	0.03876	0.06871
Std deviation	0.01028	0.00914	0.00632
A	0.94448	0.92179	0.95609
Std deviation	0.03088	0.02179	0.01515
α (1/cm)	49.4	35.3	35.3
Std deviation	3.258	1.721	1.167

information, as each sample will be scanned before and after the coating process.

CONCLUSIONS

This article demonstrates that the discrete laser sensors approach is a feasible technique for the noninvasive monitoring of the acrylic polymerization within layer thicknesses of 20–100 μm. The reflection measurement on the C—H ligand oscillation of 1620 nm and the corresponding reflection at 1550 nm is sufficient to achieve a maximum radiant quotient Q change, respectively, relative signal amplitude of about 6% with a 100 μm coating thickness. The used reference measurements with a spectrophotometer only provide relative signal amplitudes of 3% before and after UV-curing.

Three acrylic formulations with different TiO_2 concentrations were prepared to determine the sensors information depth into the coating resulting in a depth of 200 μm at 10 wt % TiO_2 concentration. The measured information depth is sufficient for most industrial printing and coating applications. Within the assumptions made earlier, pigment concentrations up to 15 wt % are tolerable in 100 μm thick coatings for acrylic C-double bond conversion, detection with the presented sensor principle.

The author is responsible for the contents of this publication.

References

1. Decker, C.; Moussa, K. J Polym Sci Pol Chem 1990, 28, 3429.
2. Lousberg, H. H. A.; Boelens, H. F. M.; Comte, E. P. L.; Hoefsloot, H. C. J.; Smilde, A. K. J Appl Polym Sci 2002, 84, 90.
3. Li, F.; Zhou, S.; You, B.; Wu, L. J Appl Polym Sci 2006, 99, 3281.
4. Scherzer, T.; Mehnert, R.; Lucht, H. Macromol Symposia 2004, 205, 151.
5. Xu, K.; Zhou, S.; Wu, L. Prog Org Coat 2009, 65, 237.
6. Clark, S. C.; Hoyle, C. E.; Jönsson, S.; Morel, F.; Decker, C. Polymer 1999, 40, 5063.
7. Zeller, W.; Naehle, L.; Fuchs, P.; Gerschuetz, F.; Hildebrandt, L.; Koeth, J. Sensors 2010, 10, 2492.
8. Bongiovanni, R.; Montefusco, F.; Priola, A.; Macchioni, N.; Lazzeri, S.; Sozzi, L.; Ameduri, B. Prog Org Coat 2002, 45, 359.
9. Weyer, L. G. Appl Spectroscop Rev 1985, 21, 1.
10. Scherzer, T.; Muller, S.; Mehnert, R.; Volland, A.; Lucht, H. Polymer 2005, 46, 7072.
11. Aldridge, P. K.; Kelly, J. J.; Callis, J. B.; Burns, D. H. Anal Chem 1993, 65, 3581.
12. Heymann, K.; Mirschel, G.; Scherzer, T.;Appl Spectrosc OSA 2010, 64, 419.
13. Pieke, S. Experimentelle Untersuchungen zur effizienten Vernetzung von Oberflächenbeschichtungen mit UV-Strahlung; Karlsruhe: KIT Scientific Publishing 2009.
14. Neo, W. K.; Chan-Park, M. B. Polymer 2007, 48, 3337.
15. Fabbri, F.; Sassaroli, A.; Henry, M. E.; Fantini, S. Phys Med Biol 2004, 49, 1183.
16. Dietliker, K. Radiation curing in polymer science and technology: Photoinitiating systems, Vol.2; Fouassier, J. P.; Rabek, J. F., Eds.; Elsevier Applied Science: London; 1993; Chapter 3, p 155.
17. Leach, R. H.; Armstrong, C.; Brown, J. F.; Mackenzie, M. J.; Randall, L.; Smith, H. G. Eds.; The Printing Ink Manual, 4th ed.; Chapman and Hall: London, 1991.