Determination of the UV-curing degree of thin films by crosslinking byproducts of reacted photo initiators in the UV-A & VIS-region of the spectra with actual polymerization degrees obtained from NIR-readings

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Abstract

The importance of an inline determination of the UV-curing degree during production increases. Practical offline techniques like i.e. the acetone rub test are in use to ensure a sufficient production process. The scientific crosslink between these test results and the actual polymerization degree is hardly given. This study shows a validated crosslink between established laboratory NIR analysis and UV-VIS readings. In conclusion it is shown that for practical application all necessary data can be acquired with industrial inline VIS spectral photometers.

Introduction

The usage of UV-curing inks and coatings increased significantly, in the recent past. PIRA released in 2014 a market survey that indicates growth rates of up to 60% within the next five years (PIRA, 2014).

In the context of these growth rates the industry asks for reliable technologies to check the UV-curing degree inline and during production. Unfortunately, there is no control technology available that fulfills the industry's requirements for inline polymerization degree inspection. On a practical scale, only offline tests help the operator to check the polymerization degree (Stropp, 2009).

Reliable laboratory methods are known to determine the actual polymerization degree. These methods base on FFT (Fast Fourier Transformation) analysis of IR (infrared) spectral data or on measurements in the NIR (near infrared) region of the electromagnetic spectra (Rauh et al., 2015).

First in this study, a detailed analysis of two typical photo initiators (PIs) is carried out for multiple radiation doses. On the basis of high resolution UV-VIS (ultraviolet & visible) spectral measurements, the resulting absorption and reflection spectra are analyzed regarding emerging reaction products.

Second, selected coating variants containing different PIs and monomer / oligomer ratios are applied to a substrate and irradiated with several radiation doses. These samples are again measured using a UV-VIS spectral photometer. Next, these samples are measured and analyzed on the basis of NIR measurements to gain information about the actual polymerization degree.

Finally, the crosslink between secondary reaction products of typical PIs and the actual polymerization degree is presented and discussed. These byproducts show a certain absorption in the close UV and visible spectra and are therefore linked to the well-known "yellowing" of UV cure able inks and coatings (Schär et al., 2015) (Segurola et al. 1999, p. 39).

State of the scientific knowledge

The principle of photo polymerization

The basic principles of radical based photo polymerization, as well as the chemical properties of associated substances in UV-curing inks and varnishes, are well known and documented (Slugovc, 2011) (Schwalm, 2006).

In principle, at the beginning of a radical induced polymerization, PIs decay under the influence of UV radiation in start radicals "R·", shown in figure 1. During the start phase of the photo polymerization these radicals break C=C double bonds of binders (such as tri(propylene glycol) diacrylate (TPGDA)) to reactive diluents and initiate a chain reaction. During the growth phase split up C=C double bonds are continuously attached to the polymer chain without losing their radical character. This chain reaction continues until the "activated" chain reacts with another radical and the process is terminated this way.

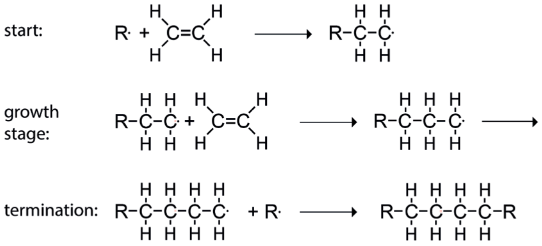

Figure 1: Stages of the radical polymerization process
Experimental study for determination of the actual curing degree of coatings with UV radiation

The absorption of a photon with a suitable energy (hv) by a PI molecule results not directly in the creation of a free radical. First in this process, the PI molecule shifts by absorption to an excited singlet state (S_1), shown in figure 2. The PI molecule stays in this state only for 1ns up to 0.1ms. During this time, the excited PI molecule relaxes back to the ground state (S_0) by emitting heat or photons (fluorescent effect). Similarly, it is possible that the singlet state can be transformed to the favorable energetic triplet state (T_1). This triplet state has a lifetime of up to several ms, which is significantly longer compared to the singlet states life time. Coming from the triplet state (T_1), the PI relaxes either again to the ground state (S_0) or it disintegrates into free radicals. The number of free radicals that are created depends on the type of PI.

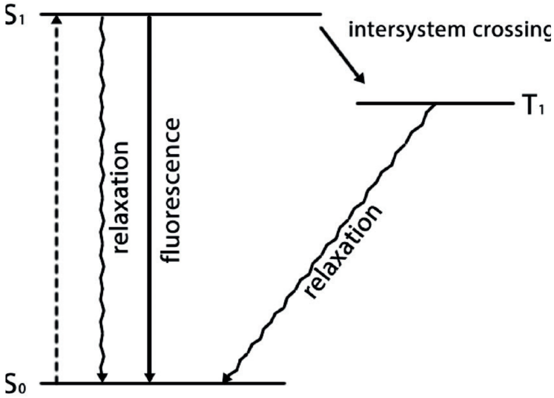

Figure 2: Excitation- and relaxation-processes of PIs

The rate of free radical creation can be calculated by using equation 1 (cf. Eq1), if the absorption behavior of a PI is well known.

$$r_i = \Phi_i I_a \qquad \text{(Eq1)}$$

with:

r_i as the rate of free radical creation

Φ_I as the quantum yield of the reaction

I_a as the absorbed radiation dose

The radiation dose (I), which is available for polymerization at a depth x of a coating, can be calculated with the Lambert-Beers law (cf. Eq2).

$$I = I_0 e^{-\alpha x c} \qquad \text{(Eq 2)}$$

with

I_0 as the incoming radiation power

I as the available radiation power

α as the natural molar extinction coefficient

c as the molar concentration of the absorbing substance

x as the path length of the radiation

It is not only relevant how many free radicals are created but also the deletion process of these radicals: In case the mentioned ratio becomes negative, the polymerization stops, because more radicals are terminated than created. If at this point in time, all C=C double bonds are broken and chained to a polymer and all involved PI are exhausted, the curing degree would be 100% (Pieke, 2009).
Actually, this case of a 100% completed polymerization is in practice not achievable: the PI concentration in the recipe is for process safety higher than required, or free radicals are trapped in the more and more cured mass and cannot participate in the ongoing polymerization process.
Summarized, the creation of new free radicals depends on several parameter that can be influenced by, for example:

- PI concentration
- radiation dose
- reactivity of the PI
- quantum yield of the reaction of the PI

A simplified visualization of the polymerization process is given by Figure 3.

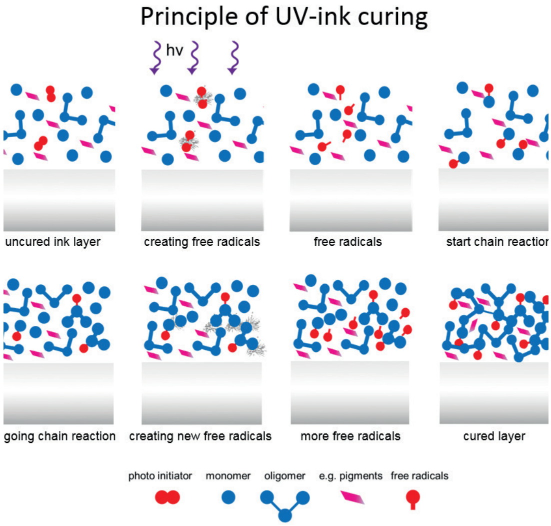

Figure 3: Principle of photo initiator induced polymerization

Figure 4 gives an overview about the structure of typical used photo initiators and related main applications (cf. figure 4). We focus in this study on the first two types.

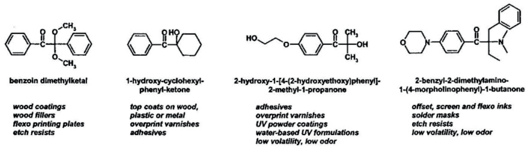

Figure 4: Structure of typical photo initiators and their main application areas (Dietliker et al. 2004, S. 78)

Approaches to determine the photo polymerization degree

It is important to distinguish between the actual polymerization degree and the resulting adhesion of the applied ink or varnish. While the adhesion is important for the quality of the final print product and the production process, the actual polymerization degree is crucial for migration critical applications, such as food packaging. Established test methods to check the polymerization degree can be split into spectral based methods and manual methods. Therefore, this chapter is split into two parts.

IR and NIR analysis of acrylic polymerization degrees:
On a laboratory scale IR spectroscopy based analysis can be used to determine the actual polymerization degree.
For example, by utilizing FTIR spectroscopy in ATR (attenuated total reflection) mode the polymerization degree can be determined at 810 cm^{-1} if calibrated against 1720 cm^{-1} (Rauh et al., 2015). However, ATR-measurements of solid state samples cannot be done inline. Furthermore, this contact technique requires repeated cleaning of the ATR-crystal to avoid sample cross contamination and is therefore not well suited for measurements of semi polymerized samples. *Scherzer* showed on a pilot scale that the acrylate polymerization can be monitored inline with NIR spectroscopy at 1620nm for clear layers (Scherzer et al. 2004, S. 151), but the signal to noise ratio has shown to be critical in many cases.
The TPGDA photo polymerization process includes the free radical induced breaking of the vinyl group (R–CH=CH2) double bonds resulting in a cross-linking polymerization of TPGDA monomers and thus increases with decreasing double bond concentration. Thus, the degree of acrylate coating polymerization can be described quantitatively as a function of the C=C double bond concentration, which can be determined spectroscopically. With a TPGDA molecular weight of 300.35g/mol and a density of 1.036 g/cm^3 (BASF, 1996) the specific double bond concentration of a 6µm thick TPGDA layer is $2.5 \cdot 10^{18} cm^{-2}$ and decreases to about zero in the fully polymerized coating.
IR and NIR absorption measurements with quantitative analysis are widely used for concentration measurements of chemical compounds and of specific functional groups of compounds and mixtures. These analytical methods are based on quantum theoretical principles, relating specific quantum energies of absorbed photons to specific molecule excitation energies. The excitation energies are quantum energies in form of vibrational modes of oscillating molecules or sub-structures of molecules, e.g. functional groups. For coating and solid state applications the fundamental vibrational modes can be described in a simplified manner by symmetric or asymmetric stretching vibrations due to bond length variations and several bending vibrations due to bond angle variations.
Beside these fundamental vibrations, also combinations of vibrational modes and configurations of neighboring atoms influence the absorption spectra. However, the absorption spectra of chemical compounds allow a qualitative relation of absorption lines to functional groups and quantitative measurements. Typical fundamental vibrational modes correspond to IR wavelengths above 2.5µm (< 4000cm^{-1}) to more than 25µm (< 400cm^{-1}).

Excitations with higher quantum energies, due to overtone oscillations modes, result in relatively weak NIR absorptions at wavelengths above 0.8µm. This is related to approximately double or multiple quantum energies of the fundamental modes (Günzler, 1975, pp. 20-31).

The concentration of C=C double bonds can be related directly to the vibrational modes at 1410cm^{-1} and at 810cm^{-1} (Pieke, 2009). Since the concentration of the carbonyl group (…C=O) does not change during polymerization the normalization of acrylate IR spectra can be carried out. Therewith, using the strong absorption band of the carbonyl group C=O double bond which is in the range of 1715 -1740cm^{-1} for the C=C configuration of glycol acrylates (Günzler, 1975, p. 203) and at 1730cm^{-1} for TPGDA according to figure 5.
Transmission measurements of IR spectral absorbance have been carried out with a Mattson Galaxy FTIR spectrometer with coated polymer samples. However, the polymer substrate material of the samples was not suited for the concentration determination due to its significant absorptions at 1410cm^{-1} and 810cm^{-1} due to C=C double bonds, which inhibit a precise concentration determination.
Alternatively, the degree of acrylate coating polymerization can be determined in the NIR range. The breaking of the vinyl-group double bonds during polymerization can be described as the disappearance of =CH2 groups with hydrogen unsaturated carbon (unsaturated CH2 groups) which are converted to -CH2 groups with hydrogen saturated carbon (saturated CH2 groups). This conversion can be used for the NIR measurement of this chemical reaction.
Unsaturated CH2 groups have stretch modes in the wave number range above 3000cm^{-1} and specifically, the vinyl group asymmetric stretch mode is generally in the range of 3075 - 3090cm^{-1}. Whereas, the saturated CH2 groups have stretch modes in the wave number range below 3000cm^{-1} according to the spectral interpretation of Smith (Smith, 1998, pp. 44-46). The unsaturated CH2 groups of TPGDA in figure 5 are represented by relatively weak absorption peaks of stretch modes at about 3055cm^{-1}, 3087cm^{-1}, 3114cm^{-1}, and 3126cm^{-1}. According to Smith, the absorption peak at about 3087cm^{-1} is related to the asymmetric stretch mode. This asymmetric stretch mode relates to a first order overtone mode at about 6172cm^{-1} which causes a relatively weak NIR absorption at about 1620nm. Due to the polymerization related conversion of unsaturated CH2 groups to saturated CH2 groups this absorption and the three other mentioned absorptions shift to below 3000cm^{-1} and may alter their magnitude. The shift relates to a NIR absorption shift from about 1620nm to below 1667nm. Measurements of the NIR absorption at about 1620nm before polymerization and its decrease with increasing polymerization due to the conversion related overtone shift, have been carried out. This has been done with an IndiSpectro NIR sensor system concerning coated paper samples to determine the degree of polymerization (cf. figure 6).

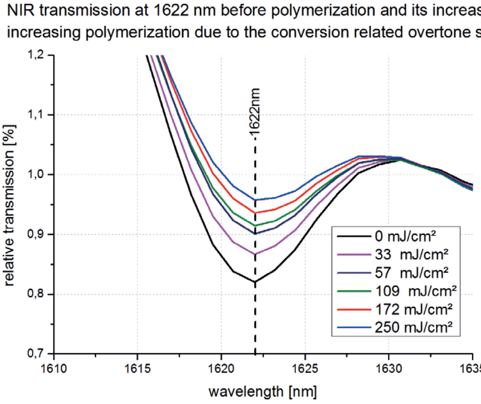

Figure 6: Relative NIR transmission spectra with the overtone absorption peak of unsaturated CH2 groups before polymerization and at various ultraviolet radiation doses.

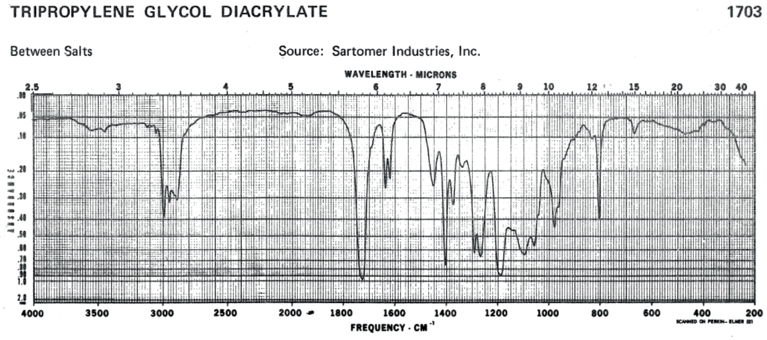

Figure 5: Spectral absorbance of TPGDA over wave number (lower abscissa) and wave length (upper abscissa) from transmission measurements (Sadtler, 1980)

Manual UV-curing degree check methods:
A brief overview about manual & semi-manual polymerization degree test methods, like acetone rub test, methyl ethyl ketone rub (MEK) test and talcum test, is given by *Stropp* (cf. Stropp, 2009).
A very popular method is the acetone rub test. Hereby, 0.2ml of acetone is applied on a cured layer. After 10 seconds of reaction time a cotton fabric is used to remove the acetone with "only a little pressure". A visual inspection has to be correlated to a scale that ranges from "no visible alteration" to "destruction of the test area" (cf. Stropp 2009). This test can only be done offline. Furthermore, it is highly depending on the executing person (e.g. pressure, speed, …) and the used type of cotton fabric.
The MEK rub test is very similar to the acetone test application and also the talcum test bases on a visual inspection concerning how much talcum stays on the surface after removing the powder with a cotton fabric.
An additional, on visual inspection based method is the "grid cutting test": A grid is carved into a cured surface and the damage that occurs to the surface due to placing and removing an adhesive tape has to be classified.

UV-curing induced yellowing effects
Next to the actual desired free radicals, which are products of PIs that were broken open by UV radiation to start the polymerization process, several other "unwanted" byproducts are created. Thereby, the type of byproduct depends on the type of PI (cf. Segurola et al. 1999, S. 40) and the actual chemical reaction.
These byproducts do not support the actual polymerization process, but show a temporary increase of the absorption in the close UV-VIS range of the spectra.
This effect is subject of intense research of *Segurola* (Segurola et al. 1999, S. 44) and *Studer* (Studer und Königer 2001, S. 32), because the resulting "yellowing effect", that is visible to the bare eye, is unwanted. The CIE-Lab* system is used to describe the yellowing of varnish coatings and *Segurola* used ΔE values to describe the degree of yellowing, while *Studer* described differences on the basis of Db* values. Moreover, *Segurola* and *Studer* do not describe if their measurements have been done directly after the curing or after a timeframe, after which the temporary yellowing effect has come down to a stable condition.

Methods
Used materials

Substrates: Two substrates are considered in this study:

1. The fiber based substrate "ProNatur" is chosen for the spectral analysis because of its low absorption, even in the UV region of the spectra.
2. A typical HDPE (high density poly ethylene) foil with a typical absorption in the UV range.

The spectra of both substrates are shown in figure 7 (cf. figure *7*).

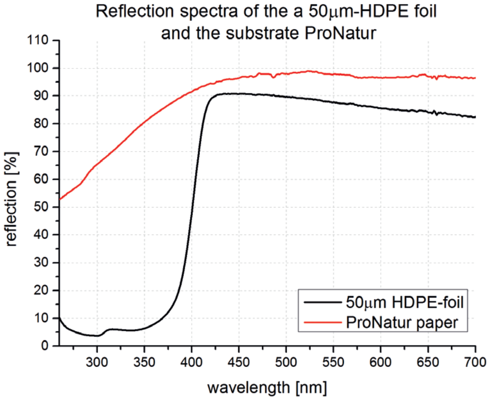

Figure 7: Reflection spectra of a 50mm-HDPE foil and the fiber-based substrate „ProNatur" in the wavelength range 250-700nm

Varnish components and application: The following two PIs and the two agents for diluting and binding were mixed for laboratory UV varnishes. For the reproducible application of layer thicknesses of 6mm and 12mm to the substrate, wire rods were used.

- "Irgacure 184" of the a-hydroxy-alkylphenones group
- "Irgacure 369" of the a-aminoalkylphenones group
- TPGDA (CAS: 42978-66-5) a diluting agent
- DPGDA (CAS: 57472-68-1) a diluting agent
- "LEO10801" (polyester acrylates) a binding agent

Table *1* gives a brief overview over created and analyzed mixtures and layer thickness combinations. In total, 120 coatings form a data base. In the results we focus on two very conclusive combinations.

Table 1: Used substances and concentration ranges

Photoinitiator [name]	**Concentration [%]**	**binding agent [name]**	**binding agent [%]**	**diluting agent [name]**	**diluting agent [%]**	**Layers [µm]**
Irgacure 184	1, 2, 4, 8, 16	LEO 10801	9 - 29	TPGDA, DPGDA	70 - 90	6, 12
Irgacure 369	0.5, 1, 2	LEO 10801	9 - 29	TPGDA, DPGDA	70 - 90	6, 12
Esacure One	1, 2, 4	Only solved in acetone				

Devices

Laboratory UV-curing station: For the actual curing a laboratory UV-curing station "AKTIPRINT Mini" from the company *Technigraf* is being used. This device allows to control the radiation intensity and the time of exposure.
Furthermore, radiation doses resulting from combinations of radiation intensity and time of exposer have been determined by utilizing TESA UV strips (Tafelmeier, 2008).
Figure *8* shows that the absorption spectra of the TESA strip correlates very well with the relative spectral power distribution of the curing lamp.

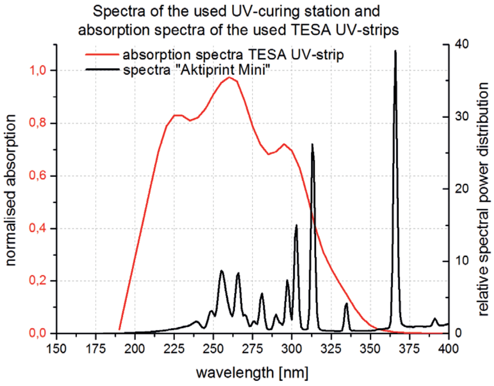

Figure 8: Absorption spectrum of the TESA UV strips in comparison to the relative spectral power distribution of the used UV-curing station "Aktiprint Mini"

UV-VIS Spectrometer: A UV-VIS laboratory reflectance spectrophotometer "MultispecPro" of Tec5 GmbH is used to obtain detailed spectral readings of 1nm bandwidth between 250nm and 780nm with a 45°/0° degree geometry. The illumination is realized by a 200W high pressure xenon lamp.

NIR Spectrometer: The spectral transmission measurements with coated paper substrates were carried out with the IndiSpectro® sensor of BST ProControl. The used wavelength range is 0.95µm up to 1.70µm with a resolution of 5nm. The radiation direction is perpendicular to the substrate with a 0°/0° degree geometry.

Results & Discussion

To communicate our results, this chapter is organized as follows: First we focus on the scientific background of the reaction of (pure) PIs due to radiation using UV-VIS analysis. This identified yellowing occurs comparable with laboratory varnishes (PIs with mentioned additives) and prepares the next step to show the correlation of UV-VIS based results and NIR based results for the determination of the actual polymerization degree. Finally, the crosslink of actual NIR determined polymerization degrees with effects observed in the visible spectra is shown.

Reaction of PIs due to irradiation

For an analysis of PIs, without being in contact with oligomers and monomers, the PIs "Irgacure 184" and "Irgacure 369" have been solved in acetone and were applied using an Eppendorf pipette with a constant volume (20 microliters) to the substrate "ProNatur" (cf. chapter Methods).
For reasons of simplified interpretation both, absorption as well as reflection spectra are plotted next to each other, where needed. Please notice that mainly data obtained regarding the PI "Irgacure 184" are discussed in detail since the PI "Irgacure 369" shows in many aspects a comparable behavior, which is presented for concept validation.
Figure 9 (top-left) shows the absorption spectra and figure 9 (top-right) the reflection spectra of the PI "Irgacure 184" for several concentrations (1%, 2%, 4%, 8%, 16%) in a wavelength range of 225nm to 600nm without being irradiated with an UV curing lamp (0mJ/cm^2). The PI shows thereby a strong absorption behavior for all concentrations, especially at 260nm (up to 0.6 for the 16% concentration). Another, medium-strong absorption band can be found at 340nm (up to 0.32 for the 16% concentration). Thereby, this specific PI shows only a low absorption of 0.008 (reflection: 96.84) for the 1% concentration or rather 0.023 (reflection: 94.993) for the 16% concentration in the visible part of the spectra at 420nm and above.

In contrast, figure 9 (bottom-left) shows the absorption spectra and figure 9 (bottom-right) the reflection spectra of the PI "Irgacure184" for the same concentrations as discussed above for a radiation dose of 250mJ/cm². Comparable spectra to the un-irradiated samples are obtained. But at a closer look, especially an increased absorption in the wavelength range of 310nm to 450nm for all concentrations is found. This effect becomes even more obvious in the related reflection spectra (cf. figure 9 (bottom-right)). While the obtained maximum reflection difference of the un-irradiated sample at 420nm is -1.85%, a reflection difference of -4.89% can be found for the irradiated sample. This can be interpreted as a shift of bands, indicating the creation of reaction products (cf. chapter "UV-VIS-based analysis of UV-curing ink-systems") by an irradiation induced decomposition of the PI. In conclusion, the pure PI "Irgacure 184" shows upon irradiation a certain yellowing (absorption at 420nm) that can be used to identify weather the PI has been reacted or not with common spectrometers.

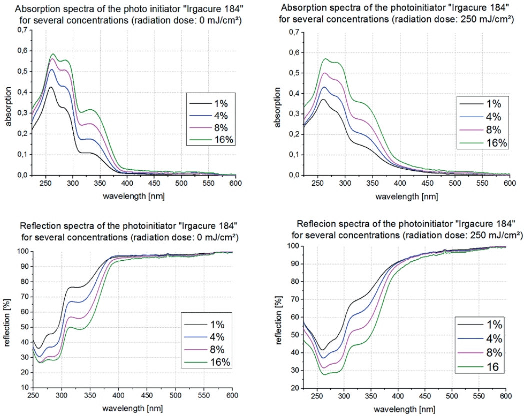

Figure 9: Absorption and reflection spectra in the wavelength range 225nm – 600nm for concentrations of 1%, 4%, 8% & 16% of the PI "Irgacure 184". Absorption spectra with a radiation dose of 0mJ/cm² (top-left). Absorption spectra with a radiation dose of 250mJ/cm² (top-right). Reflection spectra with a radiation dose of 0mJ/cm² (bottom-left). Reflection spectra with a radiation dose of 250mJ/cm² (bottom-right)

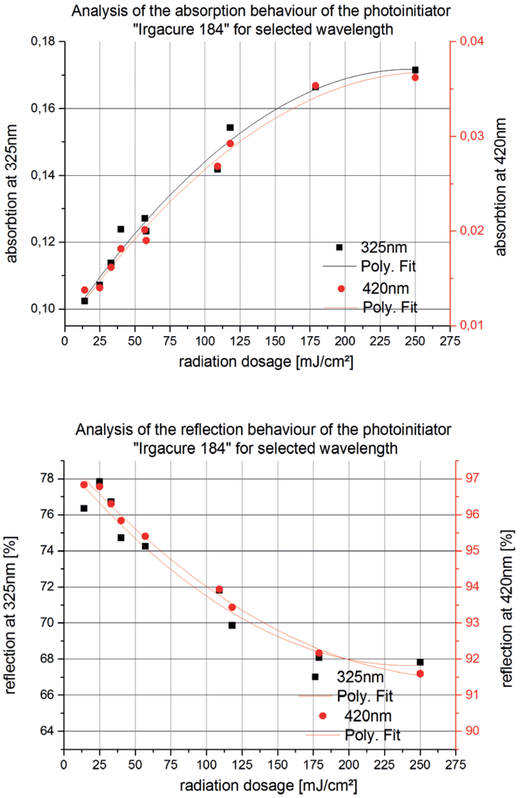

Figure 10: Comparison of obtained absorptions of the photo initiator "Irgacure 184" at 325nm and 420 for several radiation doses (top). Comparison of obtained reflections of same photo initiator and same wavelengths (bottom).

Next, figure 10 (top) shows the dependency of the actual radiation dose and the obtained change of absorption spectra for two wavelengths: 325nm (main absorption in the UV-range) and 420nm (significant absorption in the visible range of the spectra). In contrast, figure 10 (bottom) shows the corresponding data on the basis of reflection values. For both wavelengths significant and correlating changings in the signal can be obtained. Furthermore, readings at 325nm correlate very well with readings at 420nm. Only in term of intensity, readings at 420nm are weaker but still very significant. Anyhow, it can be seen, that with an increasing radiation dose a saturation can be found in both considered wavelengths. This indicates that no more reaction products of the PI are created due to decomposition.

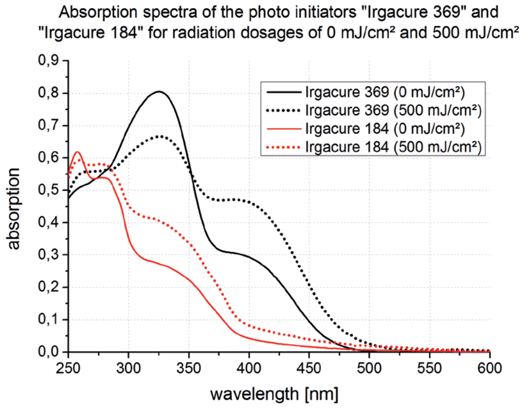

Figure 11: Absorption spectra of "Irgacure 369" and "Irgacure 184" for radiation doses of *0mJ/cm² and 500mJ/cm²*

For reasons of completeness, figure 11 shows the absorption spectra of the PIs "Irgacure 184" and "Irgacure 369" in the uncured state and a maximum radiation dose of 500mJ/cm^2 in comparison.

Finally, these findings are considered for an in depth analysis on the basis of actual varnishes, including mentioned PIs mixed with monomers and oligomers, in the next chapter.

Correlation of UV-VIS & NIR for deriving the actual polymerization degree out of UV-VIS data

As already pointed out, it is the goal of this study to find for thin UV varnish layers a correlation between PI byproducts appearing in the visible spectra and the actual polymerization degree that can be measured in the NIR range. Therefore, in the next chapter two laboratory UV varnish formulations (based on the PIs "Irgacure 184" and "Irgacure 369", respectively) are analyzed in depth on a UV-VIS basis, in a first step (cf. chapter "UV-VIS based analysis of UV-curing varnishes").
Following, NIR-spectra of the same samples are used to analyze the actual polymerization degree (cf. chapter "Crosslinking of actual NIR analysis determined polymerization degrees with effects observed in the visible spectra").
Finally, both examination results are linked together to obtain a crosslink between the PI induced yellowing effect and the actual polymerization degree.

UV-VIS based analysis of UV-curing varnishes

Photo Initiator "Irgacure 369": Figure 12 shows the absorption spectra (250-600nm) of a laboratory varnish applied to the substrate "ProNatur" for several radiation doses. The varnish formulation contains 1% of the PI "Irgacure 369", 80% of the diluting agent "TPGDA" and 19% of a binding agent "LEO10801" for a 6mm thick layer. This particular varnish shows already for a radiation dose of 14mJ/cm^2 an intense peak absorption at 325nm. Another peak, with a moderate intense absorption is found at 400nm, which is located in the visible region of the spectra. This particular absorption band is very broad and reaches up to 500nm, even in the uncured state.
By increasing the radiation dose, an increase of absorption occurs for wavelengths at 300-550nm. Therewith, the absorption of the 400nm band is even further broadened, leading to a red-shift. This red-shift provides a very significant yellowing due to an intensive absorption in the visible region of the spectra.
By performing a multi-peak analysis of the minimal irradiated (14mJ/cm^2) and the maximum irradiated sample (500mJ/cm^2) the spectra can be deconvoluted (cf. figure 13). This analytical technic provides data about individual absorbing components of samples. By comparing figure *13* (left) and figure *13* (right) it is found that certain chemical structures related to the absorption band at 330nm are reduced due to irradiation, while other structures related to the absorption bands at 260nm and 410nm are intensified. Basically, increasing bands intend newly formed products due to photon initiated decomposition of PIs.

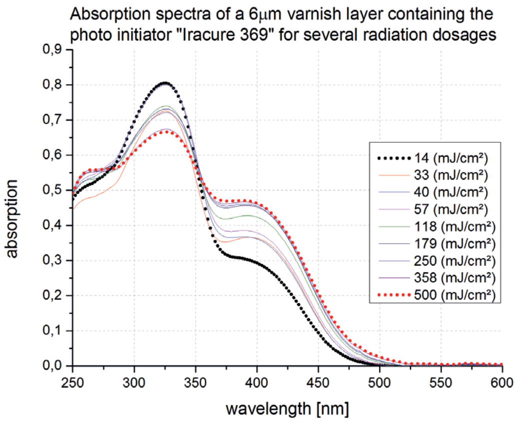

Figure 12: Absorption spectra of a 6mm varnish layer containing 1% of the photo initiator „Irgacure 369" solved in 80% "TPGDA" and 19% "LEO10801" for several radiation doses

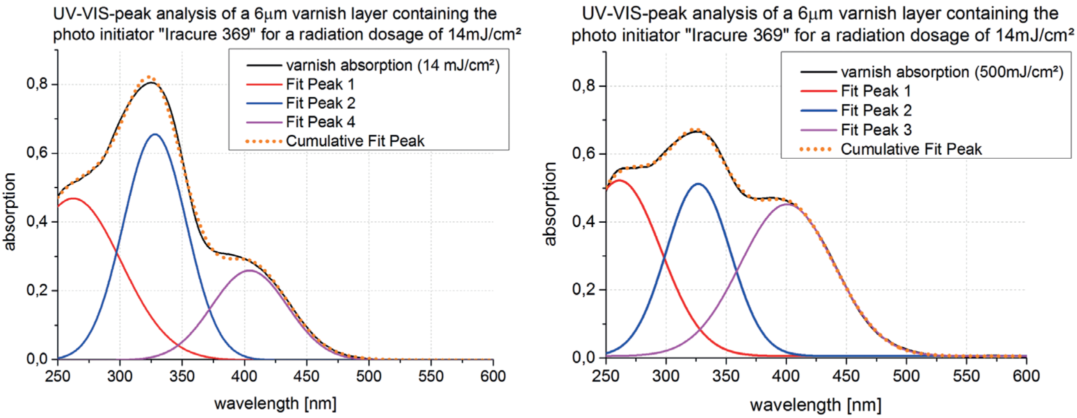

Figure 13: UV-VIS analysis of the absorption spectra of a 6mm varnish layer containing 1% of the photo initiator „Irgacure 369" solved in 80% "TPGDA" and 19% "LEO10801" for radiation doses of 14mj/cm^2 (left) and 500mJ/cm^2 (right)

Photo Initiator "Irgacure 184": Figure 14 shows the absorption spectra (250-600nm) of a laboratory varnish for several radiation doses, consisting of 4% of the PI "Irgacure 184", 77% of "TPGDA" and 19% of "LEO10801" for a 6mm thick layer again applied to the substrate "ProNatur". This particular varnish shows already for a radiation dose of 14mJ/cm^2 an intense double-peak absorption at 250-280nm. Another peak, with a moderate intense absorption is found for 325nm that is *not* located in the visible region of the spectra. This particular absorption band shows just like the PI "Irgacure 369" a broad absorption that also reaches up to 500nm even in the uncured state but in this case with a low absorption of 0.04 at 420nm and decreasing above.

For increasing radiation doses an increase of absorption at the wavelengths range 300-550nm is found. Therewith, the absorption of the 325nm band is even further broadened, leading to a red shift. This red-shift leads to a low yellowing due to a low absorption in the visible region of the spectra. By performing a multi-peak analysis of the minimal irradiated (14mJ/cm^2) and the maximum irradiated sample (500mJ/cm^2) the spectra is again deconvoluted (cf. figure 15). By comparing figure 15 (left) and figure 15 (right) it is found that certain chemical structures related to the absorption band at 250nm are reduced due to irradiation, while others are intensified (related absorption bands at 275 & 340nm). Again, increasing bands indicate newly formed products due to photon initiated decomposition of the PIs.

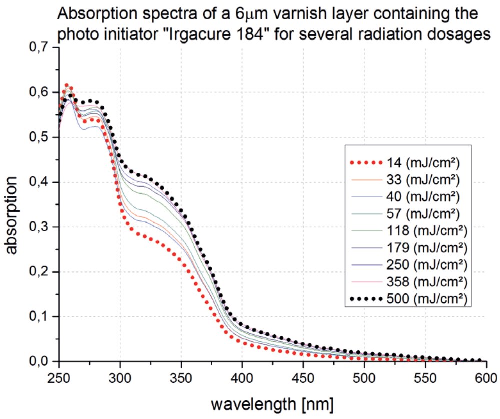

Figure 14: Absorption spectra of a 6mm varnish layer containing 4% of the photo initiator „Irgacure 184"solved in 77% "TPGDA" and 19% "LEO10801" for several radiation doses

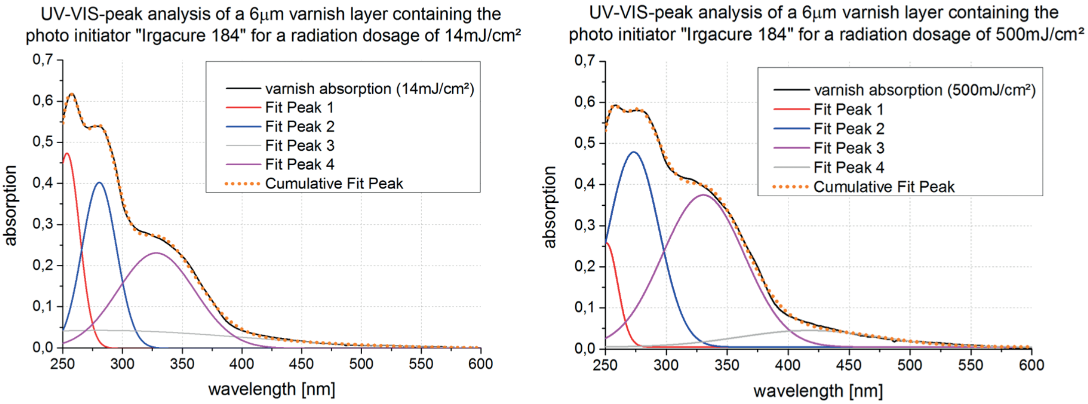

Figure 15: UV-VIS peak analysis of the absorption spectra of a 6mm varnish layer containing 4% of the photo initiator „Irgacure 184" solved in 77% "TPGDA" and 19% "LEO10801" for radiation doses of 14mj/cm^2 (left) and 500mJ/cm^2 (right)

Crosslinking of actual NIR analysis determined polymerization degrees with effects observed in the visible spectra

The black data points in figure 16 show the absorption of the PI "Irgacure 369" based varnish at 420nm for several radiation doses. It is found that the absorption increases from 0.25 to 0.4 in the range of 0 – 179mJ/cm^2. This effect is, as already described in chapter "Reaction of PIs due to irradiation", related to the decomposition of the PIs. For higher radiation doses no additional absorption is observed, which indicates that all PIs are decomposed.

In contrast, the red data points in figure 16 show the actual normalized absorption change obtained from NIR-readings at 1622nm. This wavelength is known to show an overtone shift which is directly correlated to the actual polymerization (cf. chapter "IR- and NIR-analysis of acrylic polymerization degrees"). It is found, that a significant absorption change occurs for low radiation doses (0 – 118mJ/cm^2), indicating that acrylates are being polymerized. For higher radiation doses no more change in absorption is observed, indicating that the polymerization was already completed. Both datasets combined show a significant correlation. It can be concluded that the actual polymerization is completed if no more absorption change is observed in UV-VIS readings at 420nm.

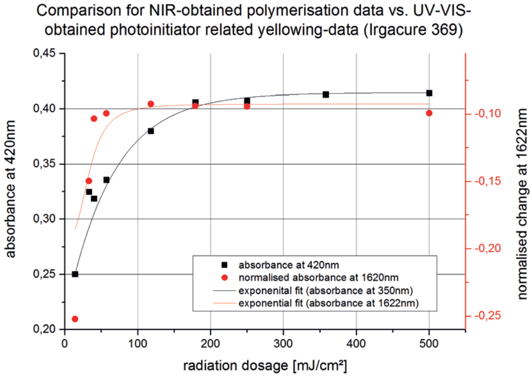

Figure 16: Comparison of NIR-overtone shifts at 1622nm and obtained absorptions at 420nm for several radiation doses of a varnish containing the PI "Irgacure 369"

The black data points in figure 17 show the absorption of the "Irgacure 184" based varnish at 420nm for several radiation doses in combination with NIR-obtained readings for 1630nm. A comparable behavior, just like for the PI "Irgacure 369" is obtained.

Again, both datasets combined show a significant correlation. Also for this example, it can be concluded that the actual polymerization is completed if no more absorption change is observed in UV-VIS readings at 420nm.

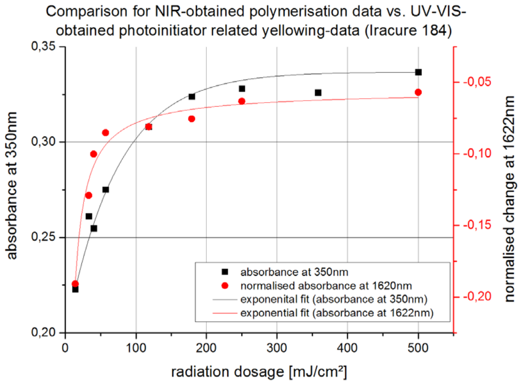

Figure 17: Comparison of NIR-overtone shifts at 1622nm and obtained absorptions at 420nm for several radiation doses of a varnish containing the PI "Irgacure 184"

Practical significance

Several industries ask for a reliable technology to check the UV-curing degree of thin layers during production and inline. Since there is currently no established inline technology available to check the actual polymerization degree, the presented indirect approach offers a practical solution for the first time: The yellowing effect can be identified with commercial inline spectral photometers and the crosslink between this identification of the (unwanted) photo initiator byproduct and the actual polymerization degree of a complete varnish has been shown (cf. chapter: "Crosslinking of actual IR-spectrally determined polymerization degrees with effects observed in the visible spectra", figure 17 & figure 18).

Identifying the yellowing effect requires a sufficient signal-to-noise ratio at relevant wavelengths. 350nm and 420nm were identified to be most relevant with several varnishes and the laboratory substrate "ProNature" (cf. Figure 7) but especially typical foils and many paper substrates show a strong absorption below 380nm. Fortunately, most of the white and transparent substrates have minor absorptions in the visible wavelength range above 380nm, where also commercial photometers are sensitive. Therefore, the identified effect at 420nm is most important for the practical realization.
Particularly, the temporary characteristic of the yellowing effect is of practical significance, because an UV color system has to avoid a permanent color shift due to curing. Figure 19 (left) shows this temporary characteristic: Spectra of a commercial varnish before curing (black), immediately after curing (red) and 1440 minutes later (blue). The related reflection values at 420nm for 0, 30, 60, 120, 180, 240, 1200, 1750, 2400 minutes after curing (cf. Figure 18 (right)) verify this declining yellowing.

But since this effect is temporary and therefore without any negative impact on the desired production result, it helps to do a reliable inline polymerization check immediately after curing. These fundamental findings allow to think about a camera based 100% inspection of the UV-curing degree with a sufficient illumination in combination with a sufficient sensor sensitivity in the identified wavelength range.

Outlook

The indirect check of the polymerization degree already works with several transparent varnish substrate combinations, even if the used PIs are known to show only a very

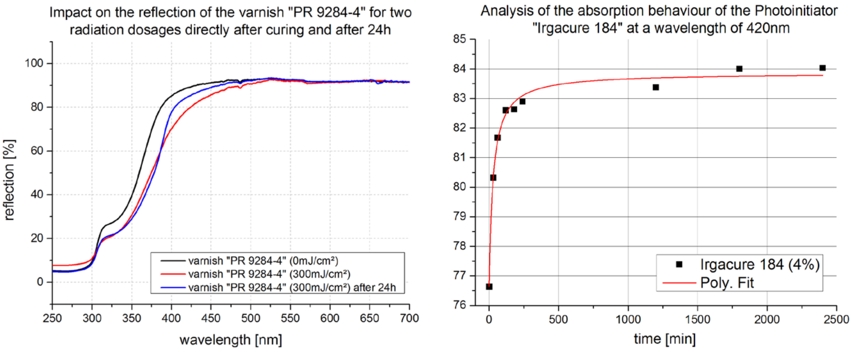

Figure 18: Reflection of the commercial varnish „PR 9284-4" (including the PI "Irgacure 184") of one identical varnish sample: Black for the sample being uncured, Red for cured state immediately measured after curing and Blue for the cured sample but measured 1440min after curing (left). Reflection of the PI "Irgacure 184" at 420nm for a radiation dose of 300mJ/cm^2 over a period of 2400min (right).

limited yellowing. This holds true, even if pigmented inks are involved that have a low absorption at 420nm. But the mentioned temporary effect with an explicit more intensive characteristic may help to specify special recipes for PIs in pigmented inks to achieve a sufficient signal-to-noise ratio. Up to now, the aim in ink formulation was to eliminate this yellowing effect in all states of production. But with this new fundamental knowledge, it will be possible to check the polymerization degree and handle the related temporary color shift. Even now, this optical effect should be considered and compensated. This is especially important in process control, because spectral data generated immediately after curing is found to be significantly different (1.55 ΔE) to the data that is obtained 24 hours after production. In future research additional PIs- and concentrations will be analyzed to refine the presented method. Furthermore, pigmented UV-curable color-systems will be analyzed as well.

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