

Real-Time FTIR-ATR Spectroscopy of Photopolymerization Reactions

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Summary : Real-time FTIR-ATR spectroscopy was used to study radical photopolymerization reactions. Investigations on various acrylate systems deal with the effect of temperature on the kinetics of the polymerization reaction and the characterization of the depth profile of the conversion of double bonds. Moreover, first results on the photoinitiator-free photopolymerization of acrylates by exposure to short-wavelength UV radiation will be reported. The potential of the method will also be demonstrated in simulations of various irradiation regimes in technical UV curing processes.

Introduction

UV-initiated photopolymerization of multifunctional monomers and oligomers is one of the most efficient methods to produce coatings from polymeric materials. It allows the almost instantaneous transformation of the liquid resins into highly crosslinked solid polymer coatings simply by short exposure to intense UV radiation in the presence of a photoinitiator. Besides the high cure speed, light-induced polymerization has a number of other favorable features such as solvent-free formulation, low energy consumption, ambient temperature operation, and high quality as well as tailor-made properties of the final products. Due to its distinct advantages, UV curing has become an established technology and has found a large variety of commercial applications mainly in the coating industry and in printing, but also in the manufacture of adhesives, in photolithography, and for dental restorative materials.^[1-3]

The steady development of the UV curing technology required experimental methods which allow monitoring of the fast photopolymerization reactions in real time. At first, photo-DSC was used for such investigations. However, this technique suffers from serious drawbacks such as a long response time of the calorimeter and a low thermal conductivity of most of the samples which strongly limits time resolution. Real-time FTIR (RTIR) spectroscopy is not concerned by such limitations. It offers the adequate time resolution and the analytic capabilities for observation and analysis of photoinitiated curing reactions. After the initial work by DECKER^[4] using

a modified dispersive IR spectrometer, the method became very popular and was widely used during the last decade.^[5-13] Most of the research efforts have been focused on basic investigations on the kinetics and the mechanism of photopolymerization reactions.^[5-7] However, RTIR spectroscopy was also used for the characterization of the reactivity of newly developed monomers,^[12] oligomers, and photoinitiators.^[8,11,14-16]

Nowadays, RTIR spectroscopy is well-accepted as a versatile and powerful technique for quantitative monitoring of UV-initiated curing processes which proceed on a millisecond time scale. Due to its high time resolution, curing experiments can be designed and performed under experimental conditions which are quite close to those in technical coating and printing processes. So, simulation of such real curing processes in the analytical laboratory becomes possible, and RTIR spectroscopy can be used as an easy and efficient tool for their optimization. Simulation may cover fields such as the development of coating formulations, the design of suitable irradiation conditions, the determination of the required irradiation dose, or the effect of other parameters during UV curing (temperature, inertization, etc.).

However, with respect to the study of photopolymerization reactions, the usual transmission FTIR spectroscopy suffers from the disadvantage that the sample is held vertically in the beam of the spectrometer. Therefore, the reactive formulation has to be of sufficiently high viscosity or it must be enclosed, e.g. between UV-transparent polymer foils, in order to ensure that the thickness of the layer remains constant during the duration of the experiment. This results in serious restrictions for investigations at increased temperatures, with extensive inertization, or with formulations of low viscosity.

Such limitations can be avoided by recording the IR spectra in attenuated total reflection. The ATR technique permits the thin sample layer to be studied horizontally, i.e. in the orientation direction which is also used in most technical UV curing plants. Moreover, it simplifies sample handling and the geometry of the irradiation. In the present study, a horizontal diamond ATR unit is used for sampling. Such a device has some further fundamental advantages for the investigation of photopolymerization reactions. Due to the small surface area (2×2 mm) of the crystal it can be homogeneously irradiated. After curing, the crosslinked sample can be easily detached from the diamond simply by scratching it away. Furthermore, measurements can be carried out at increased temperature.

The potential of real-time FTIR-ATR spectroscopy in the investigation of radical photopolymerization reactions will be demonstrated in this study for several specific problems such as the effect of temperature on the polymerization kinetics, the characterization of the depth of cure pro-

file, photoinitiator-free UV curing of acrylate monomers and oligomers, and the simulation of technical irradiation regimes. Most of the investigations were performed on samples from technical applications.

Experimental

Infrared spectra were recorded in real time with a Digilab FTS 6000 FTIR spectrometer. The spectrometer is equipped with a MCT detector and achieves a maximum temporal resolution of 11 msec at a spectral resolution of 16 cm^{-1} . Samples were studied with the ATR technique using a single reflection diamond ATR unit ("Golden Gate", Graseby Specac) which is heatable up to 200°C .

UV irradiation was performed with an Osram HBO 103 W mercury arc lamp equipped with a water filter for blocking infrared radiation. Neutral density filters and a 313 nm metal interference filter (Andover Corp.) were used optionally in order to vary the light intensity and to provide monochromatic light, respectively. Irradiation at 222 nm was carried out with a small KrCl^* excimer lamp.^[17] The UV radiation is focused on the surface of the diamond. Its intensity at the position of the sample was measured by a SiC detector. A shutter (Vincent Ass.) which is controlled by the spectrometer computer serves for exact synchronization between UV exposure and IR spectra recording. Additionally, it allows variable irradiation regimes such as continuous, multiple, or flash-like irradiation procedures. A detailed description of the experimental setup is given in Ref.^[13]

The thickness of the sample on the diamond is determined by covering it with a quartz plate which has a depression in its lower side. Depth profiling of the conversion can be performed by using various quartz plates with gaps ranging from 4 to $20\text{ }\mu\text{m}$ which were made by ion beam etching. Layers thinner than $4\text{ }\mu\text{m}$, e.g. printing inks, were prepared by printing the sample with a thickness of 1 to $2\text{ }\mu\text{m}$ on a UV-transparent substrate such as polypropylene foil which is laid on the diamond. Thicker coatings were drawn on the ATR crystal by using small drawing bars.

Usually, UV irradiation was carried out in air. However, only the oxygen dissolved in the sample is relevant for inhibition of the reaction when the sample is covered by a quartz plate. Alternatively, samples can be irradiated in an inert atmosphere by flushing the sample compartment of the spectrometer with dry nitrogen.

Results

Depth Profiling of the Conversion

One of the main objectives in the UV curing of coatings and printing inks is to attain both a high degree of conversion at the surface and in the bulk of the layer. Good surface cure is easily obtained when a photoinitiator with high extinction for the incident UV radiation is added in sufficient concentration to the formulation. In order to achieve good through cure of the coating UV light has deeply to penetrate into the layer. However, the absorption of the photoinitiator leads to an attenuation of the incident light resulting in a screening of the deeper-lying layers from UV light. The inner filter effect causes a gradient of the conversion which can lead to poor adhesion to the substrate and may have a negative impact on the final properties of the coating. FTIR-ATR spectroscopy offers the opportunity for quantitative depth profiling of the conversion which can help to avoid curing and adhesion problems. The depth of penetration d_p of infrared radiation into a sample is given by^[18]

$$d_p = \frac{\lambda}{2\pi (n_1^2 \sin^2 \theta - n_2^2)^{1/2}} \quad (1)$$

where λ corresponds to the wavenumber of a vibrational band, n_1 and n_2 are the refractive indices of the ATR crystal and the sample, respectively, and θ is the angle of incidence. Due to the finite depth of penetration of the IR probe signal from the diamond into the sample conversion is analyzed only in a thin layer of about 1 μm from the surface of the crystal regardless of the total thickness of the coating. By variation of the thickness, the depth profile of the degree of cure can be studied.

The self-screening of the photoinitiator was studied on an UV-curable pressure sensitive adhesive which bears copolymerized photoreactive groups (benzophenone) in the side chain.^[19] The adhesive properties of the acrylic resin strongly depend on the degree of crosslinking^[20] and its homogeneity over the profile of the coating. Fig. 1 a shows the kinetics of the UV curing of the adhesive at the bottom of coatings of different thickness in the range between 10 and 120 μm . It is obvious that the inner filter effect of the benzophenone groups leads to a rapidly increasing retardation of the reaction with increasing thickness of the coating.

From the conversion curves, depth profiles of the conversion are obtained. In Fig. 1 b, a number of such profiles after different times of irradiation are plotted. A marked gradient of the conversion is observed. This indicates predominance of surface cure and a lack of through cure of the coating in particular if it is exposed to UV light for short times only. With increasing duration

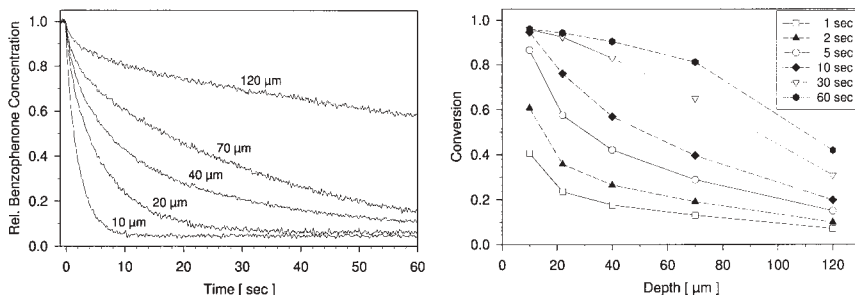


Fig 1. UV curing of a pressure sensitive adhesive with copolymerized photoreactive groups : (a) Conversion at the bottom of layers of different thickness (left) and (b) temporal development of the depth profile of the conversion (right).

of the UV irradiation, the polymerization front slowly moves into the coating. The inhomogeneous through cure was found to affect the adhesive properties of thick coatings which has to be compensated by irradiation with higher UV doses.^[20]

In most UV-curable formulations, the content of photoinitiator is not predetermined by the degree of copolymerization as in case of the adhesive. So, through cure of a coating can be improved by selection of a suitable photoinitiator and variation of its concentration.^[21,22]

Except from the photoinitiator, substantial attenuation of light can also be caused by other components in the formulation which have a high extinction coefficient for the UV radiation used for curing. In Fig. 2, the effect of an UV stabilizer on the depth profile of the conversion in an acrylate-based clear coat is shown. Polymeric coatings for outdoor applications have to be protected against photochemical degradation by the solar ultraviolet radiation. The weathering resi-

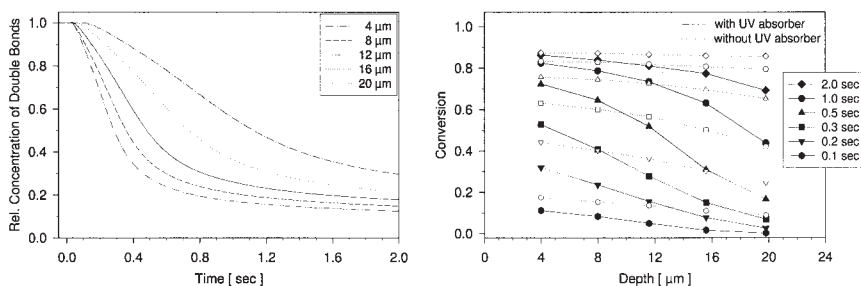


Fig. 2. Effect of an UV absorber on the depth of cure profile in TPGDA (photoinitiator : 0.5 wt.-% morpholino ketone, UV absorber : 2 wt.-% hydroxyphenyl triazine) : (a) Conversion curves (left) and (b) depth of cure profiles (right).

stance can be increased by the addition of UV stabilizers, which is typically a combination of an UV absorber and a radical scavenger. However, the UV absorber has a negative effect on the photopolymerization reaction (in contrast to most scavengers) since it competes with the photoinitiator for the available UV light.

It is evident from Fig. 2 b that the through cure of the acrylate coating suffers from the attenuation of the incident light by the hydroxyphenyl triazine used as UV absorber. This is related to its high molar extinction coefficient at 313 nm which is in the same order like that of the photoinitiator ($1.9 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ vs. $1.7 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$). The filter effect of the UV absorber efficiently prevents penetration of the UV radiation into the coating which leads to a marked gradient of the conversion of acrylic double bonds. Moreover, the UV absorber was found to slow down the polymerization rate with increasing depth in the coating.^[22] The incomplete polymerization at the bottom of the coating can cause poor adhesion to the substrate which is crucial for coatings in exterior applications.

Particularly strong screening of the incident UV light is observed in highly pigmented systems such as printing inks. In order to obtain sufficient hiding power and a high color density of the cured inks, up to 20 wt.-% pigments have to be added to the binder formulation.^[23] However, pigments do not only absorb radiation but also reflect and scatter light which strongly limits the penetration of UV light into the printed layer.

Besides white-pigmented systems,^[22] the curing of black printing inks is one of the most difficult problems in UV photopolymerization. Pigmentation is mainly based on carbon black which is well-known for its strong absorption of the light in nearly the complete spectral region. Consequently, almost the total incident UV radiation is absorbed close to the surface of the print, and only very few light reaches its deeper-lying layers which can cause insufficient drying of the printing ink and a lack of adhesion to the substrate.

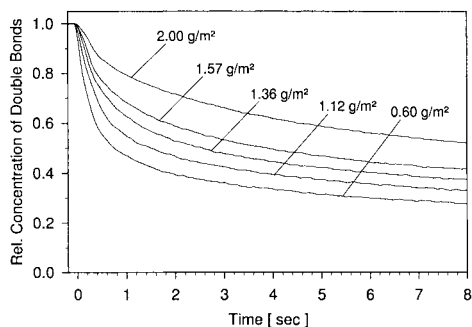


Fig. 3. UV curing of a commercial black-pigmented printing ink with monochromatic light (313 nm, 60 mW/cm², 8 wt.-% photoinitiator). The thickness of the printed layers is given as grammage.

In Fig. 3, the UV curing of thin layers of a commercial black printing ink is shown. Irradiation was performed with monochromatic radiation with a wavelength of 313 nm to simulate the emission of a XeCl* excimer lamp at 308 nm.^[24] Two morpholino ketone photoinitiators which both have high extinction at this wavelength^[15] were added at a total concentration of 8 wt.-% to the printing ink. Despite of the self-screening of the photoinitiators, such high concentrations are necessary in order to achieve sufficient curing of the print. The thickness of the layers printed on polypropylene foil is given as grammage which roughly corresponds to its thickness in microns.

Both the conversion of double bonds and the cure speed of the various prints strongly depend on the thickness of the layer. After short irradiation times in the range which is typical in printing, differences of the degree of cure up to 25 % are observed. Even after 8 sec exposure to UV light, the conversion in the 0.6 g/m² layer does not exceed 72 %. This clearly reflects the pronounced screening of the deeper-lying layers of the print from UV light due to the mighty absorption of the black pigment.

Effect of Temperature on Photopolymerization Reactions

One of the advantages of the UV curing technology is that it can be carried out at ambient temperature. Nevertheless, in practice curing is often performed at increased temperatures. The layers to be cured are heated by the infrared part of the radiation from the mercury arc lamp or by the release of the reaction enthalpy. Moreover, external heating may be necessary in order to reduce the viscosity of a formulation for proper application to the substrate.

In most thermally induced polymerization reactions, an increase of temperature leads to an increase of both the reaction rate and the ultimate conversion. Similar behavior has also been observed in photoinitiated radical polymerizations where the reaction steps are the same like in thermally initiated reactions except of the initiation step. In the past, several investigations have been performed by photo-DSC in order to study the effect of temperature on the kinetics of the photopolymerization of acrylates and methacrylates.^[25-28] Whereas the maximum polymerization rate can be easily obtained from DSC measurements if appropriate experimental conditions, e.g. with respect to light intensity and photoinitiator concentration, have been chosen, it is quite difficult to determine the induction period by this method due to its limited time resolution.

The ATR technique is well suited for studies on the effect of temperature. Diamond and tungsten carbide from which the mount of the ATR crystal is made have a high heat conductance.

Thus, good thermal contact between sample and ATR unit is guaranteed, and the polymerization reaction proceeds under almost isothermal conditions.^[13]

Aqueous urethane acrylate dispersions are increasingly used in industry, e.g. for wood coatings and in exterior applications. Due to their low viscosity they can be applied by spray application. After evaporation of the water physical dry solid films are obtained which have to crosslinked to attain the optimum properties, e.g. solvent resistance. UV curing can be performed at elevated temperatures in order to achieve better conversion. Fig. 4 shows the effect of temperature on the kinetics of the photopolymerization of a coating from an urethane acrylate. The acrylate dispersion with a photoinitiator which is compatible with water was coated onto the diamond by a drawing bar and dried by blowing nitrogen over the sample.

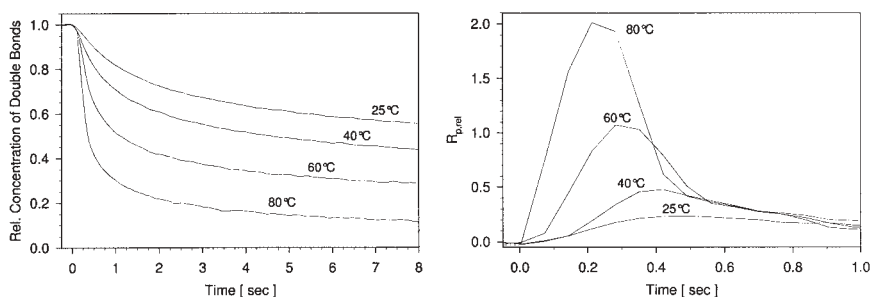


Fig. 4. Effect of temperature on the photopolymerization of a dried film from an urethane acrylate dispersion (Laromer 8949, 4 wt.-% photoinitiator) : (a) Conversion curves (left) and (b) polymerization rates (right).

The temperature during irradiation has a strong effect on the polymerization rate and the degree of cure. An increase of temperature leads to a softening of the dry solid coatings and results in a considerable increase of the molecular mobility. Therefore, the curing reaction proceeds much faster and results in a distinctly higher conversion. The difference between the conversion at ambient temperature and at 80°C almost amounts to 50 %. In Ref.^[29] it has been shown that an increase of temperature during the photopolymerization of such dried urethane acrylate films is much more effective with respect to the conversion than the addition of higher amounts of the photoinitiator. Therefore, if drying of the coatings in a technical process is carried out at elevated temperature, UV curing should succeed immediately.

Except of the better conversion of the acrylic double bonds, an increase of temperature also accelerates the photopolymerization during the initial stage of cure, i.e. the reaction rate strongly

increases with temperature (Fig. 4 b). In Fig. 5, the temperature dependence of the maximum of the polymerization rate $R_{p,max}$ is given as Arrhenius plot. From the slope in this plot, an overall activation energy E_A of the photoinitiated polymerization of the urethane acrylate of 33 kJ mol^{-1} is obtained. For various acrylates, overall activation energies from about 7 to 38 kJ mol^{-1} have been reported.^[25,27,28] The value calculated for the urethane acrylate fits in the range of those observed for highly viscous acrylate systems.

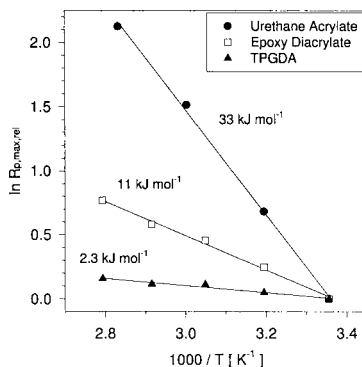


Fig. 5. Arrhenius plot of the maximum polymerization rate of some acrylates.

Fig. 5 also shows the Arrhenius plots of two other acrylates, i.e. tripropylene glycol diacrylate (TPGDA) and a viscous epoxy diacrylate oligomer on the basis of bisphenol A.^[30] Their activation energies are much lower than that of the urethane diacrylate. It was shown in Ref.^[30] that the overall activation energy of acrylates is closely correlated with the temperature dependence of their viscosity, i.e. an increase of the polymerization rate with increasing temperature is largely due to the change of viscosity. TPGDA has a low viscosity at 25°C (15 mPas) which decreases by less than one order of magnitude up to 85°C . In contrast, the viscosity of the epoxy diacrylate (7500 mPas) falls by more than two orders of magnitude between 25 and 85°C . No viscosity can be determined for the urethane acrylate film since it is solid before photopolymerization. Nevertheless, it is evident that the larger the decrease of viscosity with rising temperature the higher is also the increase of the mobility of the acrylate groups, and consequently, the higher is the activation energy of the photopolymerization of the respective acrylate system. In contrast to mercury arc lamps, excimer lamps^[3,24] do not emit infrared radiation and cause, therefore, no heat transfer to the substrate or a printing machine. Therefore, the XeCl^* excimer

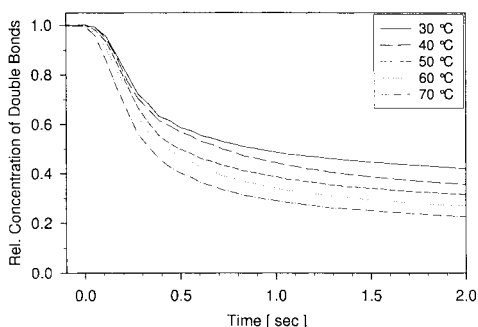


Fig. 6. Effect of temperature on the UV curing of a magenta-pigmented printing ink with monochromatic light (313 nm, 50 mW/cm², photoinitiator : 1 wt.-% morpholino ketone).

lamp with an emission at 308 nm can be successfully used in printing,^[31] in particular when heat-sensitive substrates such as polyethylene foil should be printed. On the other hand, the heat transfer from a mercury lamp to the printing ink might accelerate its curing and increase the conversion. In order to test the effect of temperature on the cure speed of a printing ink, thin layers of an ink with magenta pigmentation were irradiated at various temperatures (Fig. 6).^[32] Irradiation was performed with monochromatic light with a wavelength of 313 nm which was generated by filtering out an intense line of the mercury lamp.

Whereas the conversion of the acrylic binder in the printing ink increases by 20 % on rising the temperature from 30°C to 80°C, heating has only moderate impact on the cure speed. An overall activation energy of 6 kJ mol⁻¹ was calculated from the polymerization rate. This is in accordance with the typically low viscosity of (flexo) printing inks.^[23]

It is apparent from Fig. 6, that temperature has also an influence on the induction period of the photopolymerization reaction. The induction period t_i is due to the inhibition of the radical polymerization by oxygen. Triplet states and radicals are strongly attacked by oxygen leading to quenching and the formation of peroxy radicals, respectively. Polymerization just starts when the oxygen concentration decreased below a level where the side reactions do no longer compete with initiation. The acrylate layers in the present study are covered by the quartz plate. Therefore, the induction period is determined only by the oxygen which is initially dissolved in the acrylate. Diffusion of atmospheric oxygen into the layer is prevented by the quartz plate.

The excellent time resolution capabilities of RTIR spectroscopy and the exact synchronization between shutter and spectrometer enable the determination of the duration of the induction period. The effect of temperature on t_i was studied on TPGDA with 1 wt.-% benzyl dimethyl ketal (BDMK) as photoinitiator (Fig. 7 a). Samples were irradiated at various temperatures with monochromatic light. Evidently, the induction period considerably decreases on heating. The

quantitative dependence of t_i on temperature is plotted in Fig. 7 b. Similar relations between t_i and temperature were also found for other acrylate / photoinitiator systems.^[30] Regardless of the specific system, the induction period decreases with increasing temperature.

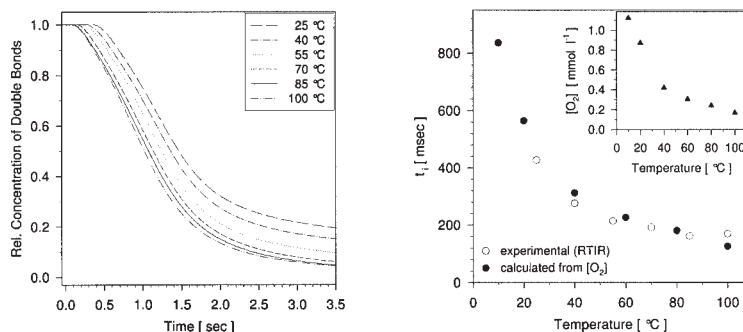


Fig. 7. Photopolymerization of TPGDA / 1 wt.-% BDMK at various temperatures by irradiation at 313 nm with 65 mW/cm²: (a) Conversion curves (left) and (b) temperature dependence of the induction period (right). Experimental data from RTIR spectroscopy are compared to values calculated from the solubility of oxygen in TPGDA (inset).

The drop of t_i with increasing temperature is supposed to be due to a decreasing solubility of oxygen in the acrylate. Therefore, the oxygen concentration $[O_2]$ in TPGDA was determined in dependence on temperature (see inset in Fig. 7 b).^[33] In fact, the solubility of oxygen in TPGDA strongly decreases with increasing temperature.

The oxygen which is initially dissolved in the mixture has to be consumed before polymerization can start. Hence, from the rate of radical generation which depends on the light intensity absorbed in the sample the induction period can be calculated by^[33]

$$t_i = \frac{[O_2]}{\Phi_i I_o (1 - \exp(-2.303 \varepsilon [PI] d))} \quad (2)$$

where Φ_i is the initiation quantum yield of the photoinitiator, I_o the intensity of the incident UV light, ε the molar extinction coefficient of the photoinitiator at the irradiation wavelength, $[PI]$ its concentration and d is the optical pathlength of the light corresponding to the thickness of the sample.

The temperature dependence of t_i in TPGDA / 1 wt.-% BDMK was calculated from the oxygen solubilities in the inset of Fig. 7 b by using Eq. (2). The initiation quantum yield of BDMK was

reported to be 0.44.^[34,35] The calculated t_i values are plotted together with the experimental data from RTIR spectroscopy in Fig. 7 b. It is obvious that the calculated induction periods fit quite well to the experimental data. The close correlation of both sets of data clearly indicates that the decay of the induction period with increasing temperature is solely due to the decreasing oxygen solubility in the acrylate.

Data on the initiation quantum yield Φ_i are available for some photoinitiators only. A rough estimation of Φ_i can be obtained from the determination of the induction periods by RTIR spectroscopy and the solubility of oxygen in the acrylate under investigation. Some data which were determined this way are reported in Ref.^[33]

Photopolymerization Without Photoinitiators

In photopolymerization, photoinitiators are required for rapid and efficient initiation of the polymerization reaction. The basic principle of any photoinitiator consists of two main steps : i) absorption of the incident photons associated with an electronic excitation of the initiator molecule, and ii) generation of initiating species from the excited states with a high yield.

The introduction of excimer lamps with an intense short-wavelength emission (e.g. the KrCl⁺ excimer lamp which emits at 222 nm)^[3,36] opens up new possibilities for the initiation of the photopolymerization of acrylates. Like most other organic compounds, acrylates strongly absorb radiation with a wavelength shorter than about 220 to 240 nm. The molar extinction coefficient of an acrylate at 222 nm depends on its specific chemical structure and may approach the order of typical extinction coefficients of photoinitiators (see Tab. 1). So, acrylate molecules can be directly excited when they are exposed to radiation from a KrCl⁺ excimer lamp.

Tab. 1 : Molar extinction coefficients of acrylates at 222 nm.

Acrylate	ϵ [l mol ⁻¹ cm ⁻¹]
TPGDA	740
HDDA	480
polyethylene glycol diacrylate	630
aromatic polyester acrylate	8370
silicone acrylate	380

RTIR spectroscopy was used for probing if the excitation of the acrylate also leads to the generation of radicals and if the rate of generation is sufficient for the initiation of the polymerization. Irradiation with a small KrCl⁺ excimer lamp with an intensity of 12 mW/cm² at the diamond surface was performed in inert atmosphere in order to avoid any side reactions of the radicals with oxygen which would completely suppress the polymerization reaction. Fig. 8 a shows the conversion of double bonds in layers of TPGDA, hexanediol diacrylate (HDDA), a polyethylene glycol diacrylate (PEG-DA), an aromatic polyester acrylate and a silicone acrylate.

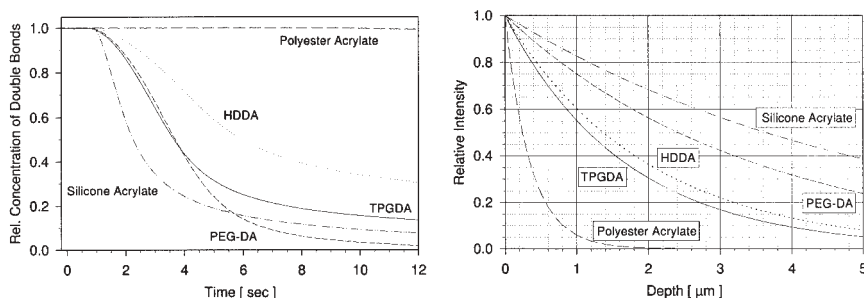


Fig. 8. Photopolymerization of various acrylates without photoinitiator by irradiation at 222 nm (12 mW/cm², thickness of the layers 4.5 μm) : (a) Conversion curves (left) and (b) depth of penetration of the UV light into the coating (right).

Surprisingly, a quite fast photopolymerization which proceeds to high conversion is observed for most of the acrylates. Aliphatic acrylates with low extinction are quite reactive whereas no conversion is detected in the aromatic polyester acrylate. These results mainly reflect the different penetration of the short-wavelength UV radiation into the coatings (see Fig. 8 b). The aliphatic monomers and oligomers absorb only moderately at 222 nm, and the light reaches more or less deep layers. In contrast, due to the high extinction coefficient of the aromatic polyester acrylate the UV light penetrates only about 1 μm into the coating. Such surface curing of coatings with a thickness of 4.5 μm cannot be observed by RTIR-ATR spectroscopy since the infrared light penetrates only 1 to 2 μm into the sample, and the analysis of the conversion is limited, therefore, to the thin layer at the bottom of the coating. However, if thin films with a thickness of ~ 300 nm are deposited on the diamond from solution moderate conversion is observed also for the aromatic oligomer.

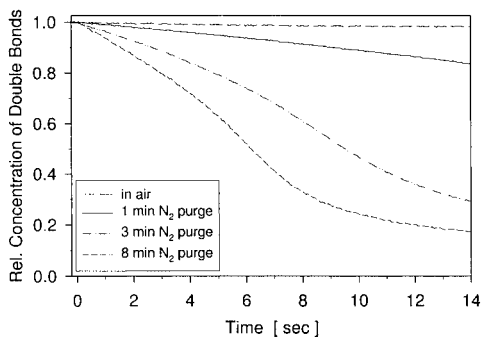


Fig. 9. Effect of nitrogen purging on the kinetics of the photopolymerization of TPGDA without photoinitiator by irradiation with 222 nm (thickness of the coatings : 1 μm).

The detrimental effect of oxygen on radical photopolymerization is well known from curing processes performed with photoinitiators. However, since the radical concentration in the photoinitiator-free systems studied here is very much lower they are even much more sensitive to oxygen and require careful inertization. The effect of the duration of flushing the sample with nitrogen on the kinetics of the directly initiated photopolymerization of TPGDA is shown in Fig. 9. Without or with insufficient inertization, the concentration of surviving radicals is too low for significant conversion. Only when most of the oxygen is purged out, polymerization rate and conversion more and more increase.

A possible mechanism of the direct initiation of acrylates was proposed on the basis of laser photolysis experiments and accompanying quantum chemical calculations.^[17] Probably, initiation proceeds via a triplet state located at the vinyl group which adds to another double bond forming a biradical.

In pilot scale curing trials, thin layers of various acrylates without photoinitiator were cured with 222 nm UV radiation under inert conditions at web speeds up to 30 m/min depending on the specific acrylate.^[17] A thinkable application of photoinitiator-free photopolymerization could be, for example, the curing of silicone acrylate release coatings which are generally applied in very thin layers (0.3 to 3 μm) only.

Simulation of Irradiation Processes in Technical UV Curing

In technical UV curing processes, coatings to be cured are exposed to the intense ultraviolet light for very periods of time only. Depending on the speed of the web, the irradiation time per UV lamp is in the range of some milliseconds in printing up to 1 second, e.g. in wood coating. Therefore, multiple irradiation of the coating by a number of UV lamps in succession may be required in order to achieve sufficient conversion.

RTIR spectroscopy can be used to simulate such pulse irradiation sequences.^[13,29] Due to its high time resolution and the short response time of the shutter (4.5 msec), the conversion of the reactive groups can be followed on a time scale of milliseconds which corresponds to typical conditions in printing. Flash-like or multiple irradiation procedures can be carried out with the shutter, and pulse duration and interval may be easily adapted to a particular technical situation. The duration of the short UV pulse corresponds to a certain speed of the web or conveyor, and the pulse interval stands for the distance between successive UV lamps. So, RTIR spectroscopy becomes an efficient tool for the design and the optimization of the irradiation conditions in technical curing (number, spatial arrangement, spectral output, and power of the UV lamps), the determination of the required irradiation dose, or the effect of other process parameters such as temperature or inertization. Examples of the simulation of specific irradiation patterns by RTIR spectroscopy are given in Figs. 10 and 11.

Fig.10. Conversion of acrylic double bonds and polymerization rate in a magenta-pigmented offset printing ink during irradiation with a series of pulses of monochromatic UV light (pulses of 50 msec with an interval of 200 msec, 313 nm, 50 mW/cm²).

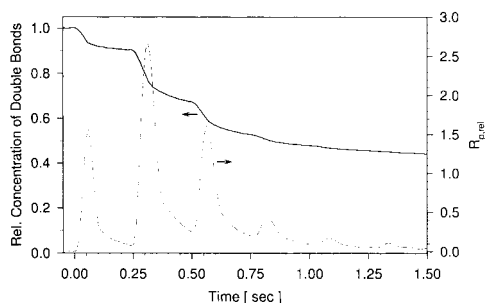


Fig. 10 shows the multiple irradiation of an offset printing ink with magenta pigmentation and a morpholino ketone photoinitiator with a series of monochromatic UV pulses of 50 msec in an interval of 200 msec. Three UV pulses are necessary for sufficient conversion of the double bonds in the acrylic binder of the ink whereas further pulses have only minor effect. If one considers the fourfold irradiance of commercial 50 W/cm XeCl⁺ excimer lamps in the curing plane (200 mW/cm²) as compared to that used here, which leads to the double polymerization rate (according to $R_p \sim I_0^{0.5}$ ^[4,13]) and consequently halves the required irradiation time, a maximum printing speed of 240 m/min can be estimated for a curing unit with three excimer lamps. Obviously, most of the conversion occurs after the end of each of the UV pulses due to postcuring. The effect of postcuring is well-known in radiation curing. In Ref.^[13] it has been shown that the dark reaction may amount up to 80 % of the total conversion after irradiation of acrylate systems with short UV flashes.

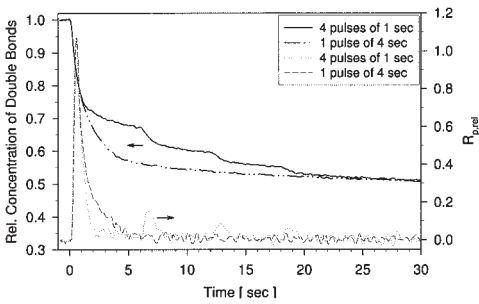


Fig.11. UV curing of dried films from an urethane acrylate dispersion with 4 pulses of 1 sec (interval 5 sec) or with 1 pulse of 4 sec (acrylate : IRR 424, 4 wt.-% photoinitiator) : Con- version and polymerization rate.

A simulation of UV curing at much lower speed of the conveyor (about 10 m/min) is shown in Fig. 11. A dried film from an urethane acrylate dispersion was irradiated by either one UV pulse with a duration of 4 sec or a sequence of 4 pulses of 1 sec. In both cases the same degree of cure is achieved after a total exposure of 4 sec. This indicates that the final conversion only depends on the total irradiation dose applied to the coating but not on the specific irradiation regime.^[29]

The polymerization rates calculated from the two cure profiles are also plotted in Fig. 11. The initial rate is independent of the duration of the UV pulse. In the multiple irradiation scheme, the first pulse, corresponding to one UV lamp, accounts for the major part of the final conversion. The contribution of the other lamps is much smaller or even negligible.

Apart from the duration of the exposure, the irradiation dose is also directly related to the intensity of the UV radiation. Accordingly, if the dose applied to the coating by one UV lamp is to low for sufficient curing at a given web speed, instead of the use of several UV lamps a single lamp of higher irradiance can be used. The effect of UV intensity on both the conversion and the polymerization rate is well-known.^[4,13,37] In Fig. 12, the influence of the UV intensity on the conversion of the photoreactive benzophenone groups in a pressure sensitive adhesive^[19] (see also Fig. 1) is shown.

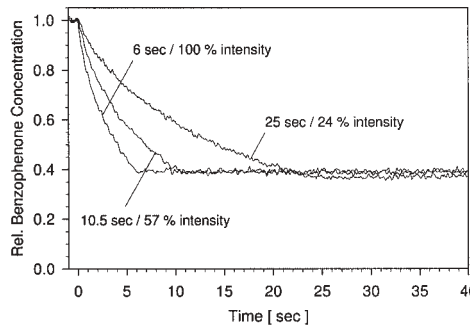
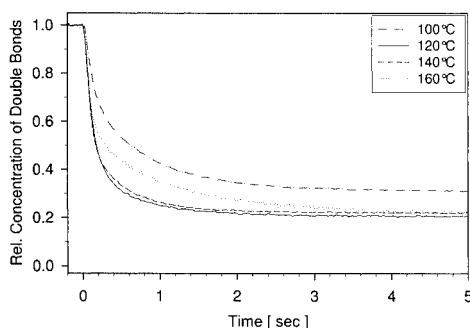


Fig.12. Curing of a pressure sensi- tive adhesive with equal UV doses by exposure to pulses of different duration and with different relative in- tensities.

The conversion rate considerably slows down on decreasing the intensity by neutral density filters. The total UV dose applied to the adhesive is hold constant, i.e. a decrease of the UV intensity is compensated by an accordingly longer pulse length. Again, irradiation with equal doses is found to result in equal conversion. Consequently, conversion is not only independent of the irradiation regime (see Fig. 11) it is also not affected by the dose rate. This was also confirmed by investigation of the adhesive properties of coatings which were cured in pilot scale at various dose rates and UV intensities.^[20]

UV-curable powder coatings become more and more interesting for protective coatings on wood and metal. Whereas thermosetting powders have a narrow processing window since melting of the powder, leveling of the melt, and curing are merging, for UV-curable powders the former two processes are separated from curing. The powders are first melted by infrared irradiation. After achieving the desired leveling, they can be crosslinked by UV irradiation. Curing has to be performed at increased temperature in order to attain a sufficient degree of cure in the otherwise solid coatings. In Fig. 13, the UV curing of a powder formulation based on an acrylated polyester resin^[38] at various temperatures is shown.

Fig. 13. UV curing of a powder coating formulation based on an acrylated polyester resin at various temperatures (Uvecoat 1000, 3 wt.-% photo-initiator).



UV curing at temperatures between 120 and 140 °C was found to be the optimum temperature range for processing. At lower temperature, the system is still too viscous which results in poor conversion. At higher temperatures, competing termination reactions occur which lead to a decrease of the curing rate and probably to some depropagation. A similar decrease of the rate was already observed in the photopolymerization of viscous epoxy acrylates at temperatures above 100°C.^[27,28,30] The findings on the temperature dependence of the UV curing of powder coatings correspond quite well to results by photo-DSC.^[39]

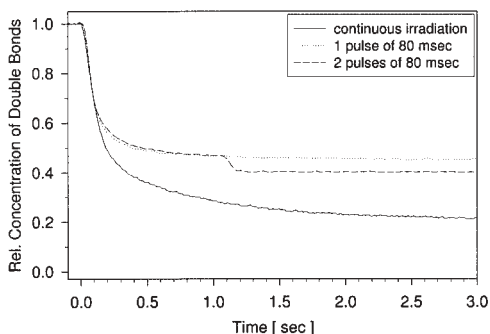


Fig. 14. UV curing of a powder coating formulation with continuous or pulsed irradiation at 140°C.

Curing of the powder coatings at 140°C by irradiation with either continuous or pulsed irradiation is shown in Fig. 14. Coatings were found to cure quite fast. Despite of the short irradiation time, considerable conversion of the double bonds already occurs during the first pulse. The second pulse (or UV lamp) leads to an only insignificant further increase of the conversion.

Conclusions

Real-time FTIR-ATR spectroscopy has proved to be a versatile and powerful tool for the quantitative monitoring of fast photopolymerization reactions. Due to the finite penetration of the infrared radiation from the ATR crystal into the sample it is well suited for depth profiling of the conversion during UV curing of clear and pigmented coatings. In studies at elevated temperatures it was demonstrated, that temperature has a strong effect on the kinetics of photopolymerization. Whereas its influence on the polymerization rate is related to the decrease of viscosity in the specific system, the decay of the induction period with increasing temperature was found to be solely due to the decreasing solubility of oxygen in the acrylate. It was also shown that aliphatic acrylates can be photopolymerized without photoinitiator simply by exposure to short-wavelength monochromatic UV light. Moreover, RTIR spectroscopy was used to simulate various irradiation sequences in technical UV curing processes.

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