

# Monitoring of the development of viscoelastic parameters and conversion during UV curing of acrylate formulations by hyphenated photorheometry and near infrared spectroscopy

Tom Scherzer\* and Martin W. Schröder

*Leibniz Institute of Surface Modification (IOM), Permoserstr. 15, D-04318 Leipzig, Germany. \*E-mail: tom.scherzer@iom-leipzig.de, Fax: +49-341-235-2584*

## Introduction

Photorheometry has been developed to follow the rapid changes of the viscoelastic and mechanical properties, which proceed in reactive resin formulations during UV photopolymerisation reactions.<sup>1-3</sup> However, this method cannot provide the information necessary for understanding the chemical reactions that proceed during curing (for example, conversion). The coupling of photorheometry with vibrational spectroscopy<sup>4,5</sup> allows one to monitor both the viscoelastic properties and the extent of the conversion simultaneously. Near-infrared (NIR) spectroscopy is preferred to FTIR spectroscopy in the mid-infrared for various reasons such as thickness limitations in FTIR spectroscopy, and the availability of optical fibres in the NIR range. In most of the previous experimental setups, the upper tool of the rheometer was replaced by a quartz plate, and UV illumination was carried out through the hollow plate holder.<sup>2,4,5</sup> In the present study, the lower plate was made of quartz, which allows both UV irradiation and NIR measurement from the bottom up. NIR spectra were measured in transfection mode using the top plate as reflector for the probe beam.

## Experimental

Dynamic mechanical analysis (DMA) was carried out with a Physica MCR 300 rheometer (Anton Paar), which is equipped with a UV cell. The lower plate of the conventional plate-to-plate measuring system was replaced by a quartz plate, which allows UV irradiation of the sample. The temperature of the sample was controlled by both Peltier heating (or cooling) of the quartz plate and convection heating of the environmental chamber. In the present study, a disposable

aluminium plate with a diameter of 10 mm was used as the upper tool, in order to be able to record strain data during the complete experiment (frequency 20 Hz). The thickness of the sample was 400  $\mu\text{m}$ .

UV radiation was supplied by a Hamamatsu LC-5 spot light source (200 W HgXe bulb, band-pass filter 300 . . . 400 nm), which is linked to the rheometer by a light guide. The end of the fibre was fixed 30 mm below the centre of the quartz plate, which allows homogeneous irradiation of the complete area below the top plate. A scheme of the setup is shown in Figure 1. The intensity of the UV radiation was set to 10  $\text{mW cm}^{-2}$ . Irradiation was carried out under inert conditions by flushing the environmental chamber with nitrogen.

NIR spectra were taken with a Bruker MPA FT-NIR spectrometer, which is equipped with a thermoelectrically cooled InGaAs detector. By use of the chromatography module of the OPUS software package, NIR spectra can be recorded at a sampling rate of 8.5 spectra  $\text{s}^{-1}$  at a spectral resolution of 32  $\text{cm}^{-1}$ . The extent of the conversion was directly obtained from the decrease of the absorption band at 6170  $\text{cm}^{-1}$ , which is assigned to the first overtone of the C–H stretching vibration of the acrylic double bond.

The NIR spectrometer is linked to the rheometer by two optical quartz fibres, which are equipped with collimating lenses (Hellma). The fibre ends are fixed below the quartz plate (see Figure 1). The NIR beam is directed towards the upper aluminium plate of the measuring system. After reflection at this plate, the probe light is collected by the collimator of the other fibre. Synchronisation between the DMA measurement, NIR spectroscopy and UV irradiation is achieved by triggering the start of the collection of NIR spectra as well as the opening of the shutter of the UV lamp by the rheometer software.

Methacryl-grafted silica nanoparticles prepared according to Reference 6 were dispersed into a mixture of a bisphenol A epoxy diacrylate and tripropylene glycole diacrylate (TPGDA) at a level of 20 wt %. An acylphosphinoxide (Lucirin TPO-L) was added as photoinitiator at a concentration of 0.5 % relative to the binder formulation.

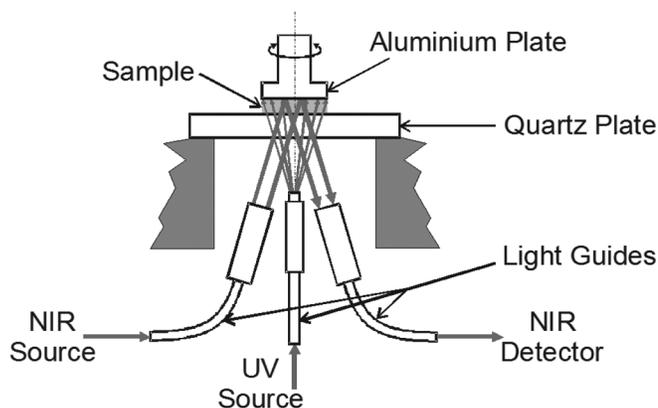


Figure 1. Scheme of the experimental set-up.

## Results and discussion

Temperature is well-known to have a strong influence on the kinetics of UV curing reactions. The evolution of the complex shear modulus upon UV irradiation at various temperatures from 10°C to 40°C is shown in Figure 2. After opening of the shutter, the UV-induced initiation leads to radical polymerisation and to the build-up of a cross-linked polymer network. Cross-linking transforms the initially liquid formulation into a solid polymer, which is usually vitreous. This transformation is reflected by a strong increase of the shear modulus by up to 9 orders of magnitude. The initial slope of the complex shear modulus increases with increasing temperature, which reflects a faster build-up of the network due to a faster curing reaction. However, the shear modulus of samples cured at higher temperatures tends to level off soon, whereas it further increases for samples cured at lower temperatures. This behaviour is related to (i) the higher conversion achieved in the former samples and (ii) the decreasing difference of the curing temperature to the glass temperature. Therefore, the shear modulus was measured again for all samples after cooling down or heating up, respectively, to 25°C. It is apparent that the order of the samples reversed: the higher the temperature, at which the sample was cured (e.g. the higher the conversion), the higher is the module at room temperature.

The strong influence of temperature on the kinetics of the UV-induced polymerisation reaction and the resulting conversion of the acrylate double bonds is shown in Figure 3. The higher the temperature of the sample, the faster the curing reaction becomes, which clearly correlates

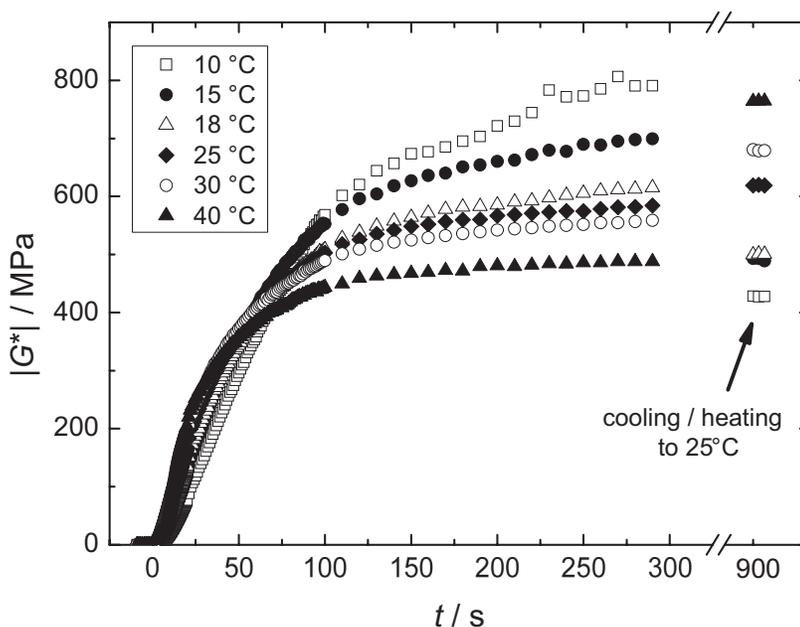


Figure 2. Evolution of the complex shear modulus  $|G^*|$  as function of time at various temperatures.

with the results in Figure 2. The observed value of double bond conversion at the end of the measurement also depends on temperature. Predictably, it strongly increases with increasing temperature. Furthermore, the polymerisation rates  $R_p$  were determined from the conversion curves. Results are given as an inset in Figure 3. According to the Arrhenius law, the maximum polymerization rate at 40°C is about 3.3 times higher than at 10°C. Moreover, the time of the occurrence of the maximum polymerization rate is shifted from 0.8 s at 40°C to 2.7 s at 10°C.

Gelation corresponds to the transition from a viscous liquid to an elastic solid. The gel point is defined as the point, at which the loss factor  $\tan\delta$  becomes independent of frequency. In the present study, it was determined from the crossover of the storage and the loss moduli (i.e.  $\tan\delta = 1$ ). However, the gel point can be also derived from spectroscopic data. It is well-known that it corresponds to the maximum in the curve of the polymerisation rate  $R_{p,\max}$ . The development of a continuous network strongly limits the mobility of the functional groups, which leads to a sharp decrease of the reaction rate. Consequently, the time to achieve  $R_{p,\max}$  has to be in accordance with the gelation time  $t_{\text{gel}}$ . Figure 4 compares the values of  $t_{\text{gel}}$  determined by rheometry with  $t_{R_{p,\max}}$  extracted from spectroscopic data. It is apparent that both series show excellent correlation, which clearly proves the inherent consistency of the data obtained by the two coupled experimental techniques.

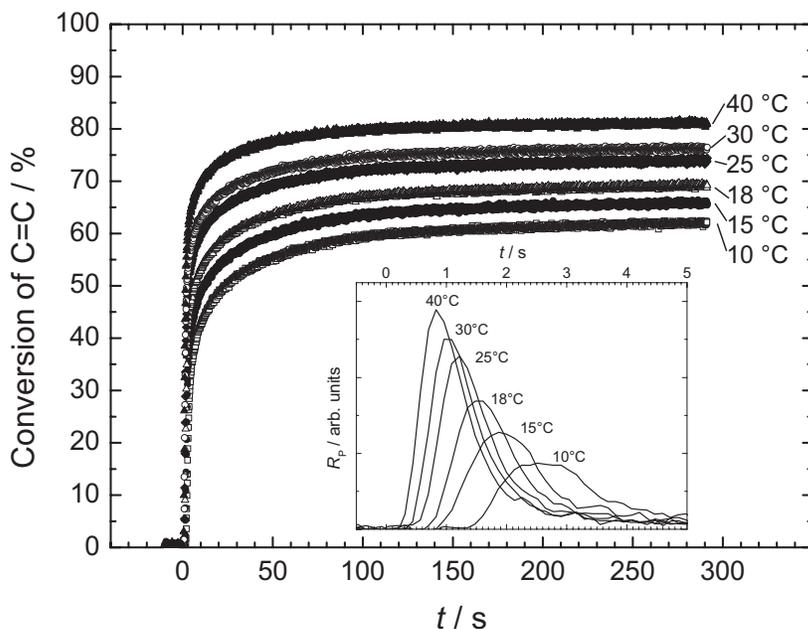
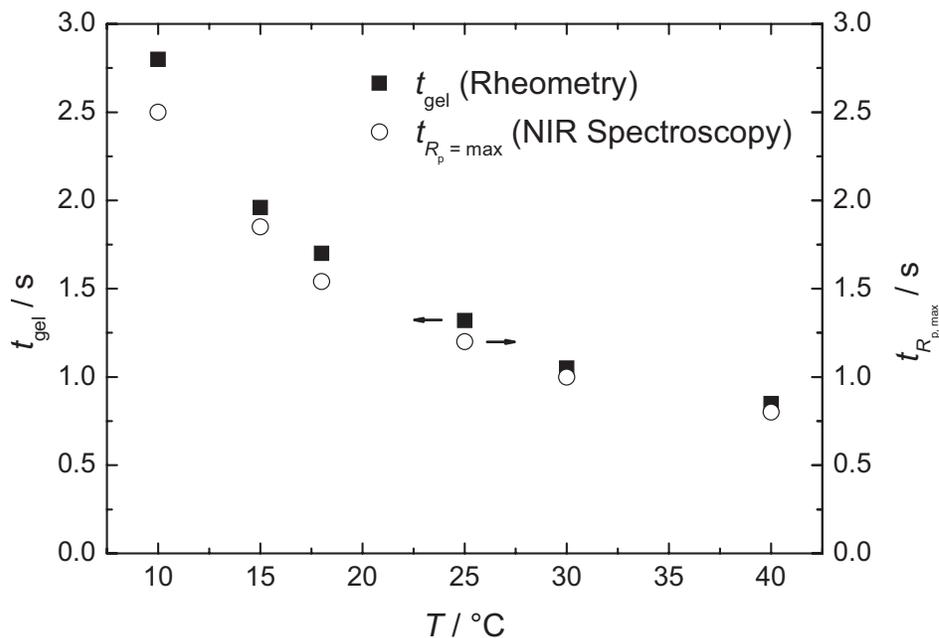


Figure 3. Temperature dependence of the conversion and the polymerization rate  $R_p$  (inset) of the acrylate double bonds.



**Figure 4.** Gelation times ( $t_{\text{gel}}$ ) and times to achieve maximum polymerisation rate ( $t_{R_p, \text{max}}$ ) at various temperatures.

## References

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