# RHEOLOGICAL AND TECHNOLOGICAL ASPECTS OF UV CURING THICK POLYMER LAYERS WITH FIBER REINFORCEMENT

Michael Müller-Pabel[1], Johann Faust[1], Florian Schmidt[1], Eckart Kunze[1], Maik Gude[1]

[1]Dresden University of Technology, Institute of Lightweight Engineering and Polymer Technology, Holbeinstr. 3, 01307 Dresden, Germany

## ABSTRACT

UV curing allows energy-efficient and fast resin solidification for many different applications. By combining suitable photoinitiators and light-emitting diode (LED) light sources, cure depths of more than 1 mm have become available, which makes UV curing also a promising candidate for the development of innovative manufacturing technologies including fiber-reinforced polymers (FRP). This contribution suggests experimental methods that help to understand the interaction between process parameters, curing behavior and resulting material properties of a novel UV resin. UV-rheology is used to replicate close to reality process conditions during curing as well as to analyze the underlying phenomena including the mechanical and the volumetric material behavior. When investigating thick polymer layers, opposing effects such as heat accumulation within the resin volume and limited penetration depth of the UV light need to be taken into account. Both effects will have influence on the reaction rate and at the same time affect the optical properties of the resin. By evaluating UV-rheological experiments in conjunction with additional experimental data obtained in UV-DSC, a holistic understanding of the governing phenomena during UV curing of thick reinforced and unreinforced polymers becomes possible.

## INTRODUCTION

Industrial applications of photopolymerization reactions can be found in versatile fields like additive manufacturing[1], dental medicine and coating[2]. All these have in common that they require curing of layers with a thickness of less than 200 µm. In the course of efficiency increases in light-emitting diode (LED) technology[3] and the development of new photoinitiators[4], the use of ultraviolet (UV) light has proven to be a promising mechanism that enables extremely short reaction times (< 1 s) as well as use of cheap and unheated tools which allows significantly improved energy efficiency[5]. The usability of UV-resins in processing of fiber-reinforced polymers (FRP) was demonstrated for pultrusion[6], resin injection[7], additive manufacturing[8] and prepreg processing[9]. It was shown that energy-efficient curing of layers of more than 10 mm is possible[10]. However, the basic process-property-relationships governing those technologies is still missing, which is why no guidelines for definition of process windows are available. To fully exploit the potential of UV curing in FRP processing, the interaction mechanisms between radiation transport, curing reaction and temperature development need to be understood. UV-rheology can help to answer these questions. In previous studies UV-rheology was used to analyze the cure behavior of UV-resins destined for stereolithography (SLA)[1,11] and Digital Light Processing (DLP)[12]. Due to the focus on thin layers of less than 200 µm, some aspects were neglected that are of crucial importance for curing thick layers (> 1 mm) and FRPs. This includes exothermal heat and the spatial distribution of optical properties. In order to adapt established rheological methods to the analysis of UV-resins,

additional information about the thickness-dependent reaction kinetics and curing speed is required. To meet these requirements, within this contribution rheological and calorimetric measurements are combined to characterize the UV curing properties of a vinyl ester resin. To demonstrate feasibility of UV curing FRP, a winding process was set up and used for manufacturing of composite sleeves. During these trials different process parameters including winding speed and light intensity were varied in order to validate the previously derived process window.

## MATERIALS AND METHODS

The resin system analysed in this study is the vinyl ester resin Raylok C1101 (supplied by Allnex GmbH). The recommended wavelength for UV-light curing is 365 nm. A DELOLOX 80 in combination with a DELO-UNIPRO Light control unit is used for this purpose.

UV-DSC measurements were conducted with a Mettler Toledo DSC 3+ and the corresponding UV-equipment. Open Aluminium crucibles with a volume of 40 µl, an isothermal temperature of 25 °C and a nitrogen purge gas rate of 20 ml/min were selected. UV-rheology tests were performed with an Anton Paar MCR 502 being equipped with a bottom glass plate (P-ETD 300) as well as a hub (H-ETD 300), both of them heated electrically. Disposable plates with a diameter of 25 mm were used. The measurements were performed in oscillation mode with a frequency of 10 Hz and an amplitude of 0.05 %. Normal force control was activated in order to detect shrinkage induced volume change after gelation. Prior to all DSC and rheology measurements, the light intensity at the sample position was determined with a DELOLUXcontrol light intensity meter.

Winding experiments were performed with the winding machine (Bolenz & Schäfer) at the ILK and monitored by thermography using a VarioCAM HD (supplied InfraTec GmbH).

## RESULTS

### UV-DSC measurements

To gain insight into the radiation-dependent curing behaviour of the selected resin system, preliminary UV-DSC measurements with varying sample mass and irradiation parameters were conducted at room temperature ($T_R = 25.00$ °C). It was found that due to the high reactivity, it is necessary to prevent excessive heat release, as a temperature increase of more than 1 K contradicts basic principles of calorimetry, Table 1. It was concluded that the use of small a sample mass $m$ (~2 mg), a low intensity $I$ (20 mW/cm²) and a short irradiation time $t_I$ (0.1 s), resulting in an energy dose $E$ per pulse of 2 mJ/cm², is suited to control the curing reaction.

**TABLE 1:** sample peak temperatures $T_{Smax}$ measured in UV-DSC at a ref. temperature $T_R = 25.00$ °C

| **Sample mass $m$ /mg** | **Intensity $I$ / mW/cm²** | **Irradiation time $t_I$ /s** | **Energy dose per pulse / mJ/cm²** | **Sample peak temperature $T_{Smax}$ /°C** |
|---|---|---|---|---|
| 6.05 | 950 | 1.0 | 950 | 39.98 |
| 4.06 | 950 | 1.0 | 950 | 35.52 |
| 2.23 | 950 | 1.0 | 950 | 31.97 |
| 1.29 | 950 | 1.0 | 950 | 28.51 |
| 4.96 | 475 | 1.0 | 475 | 39.47 |
| 5.06 | 95 | 1.0 | 95 | 36.06 |
| 5.14 | 950 | 0.1 | 95 | 29.47 |
| 2.92 | 20 | 0.1 | 2 | 25.32 |

Subsequently, measurements with multiple consecutive pulses of 2 mJ/cm² were performed. The time span between the pulses was chosen according to the peak height and the time required for the heat flow to return to the baseline. As can be seen in Fig. 1, both the measured heat flow and the corresponding reaction rate depend on the pulse number. From pulse 1 to pulse 5 the reactivity increases and subsequently declines indicating that almost no further crosslinking takes place after 10 pulses. Summing up the measured enthalpy values results in a total heat release of 173 J/g, which corresponds to a degree of cure of 35 %. This low value can be explained by the vitrification effect as the measurements took place at 25 °C, which is far below the ultimate glass transition temperature of 152 °C indicated in the datasheet.

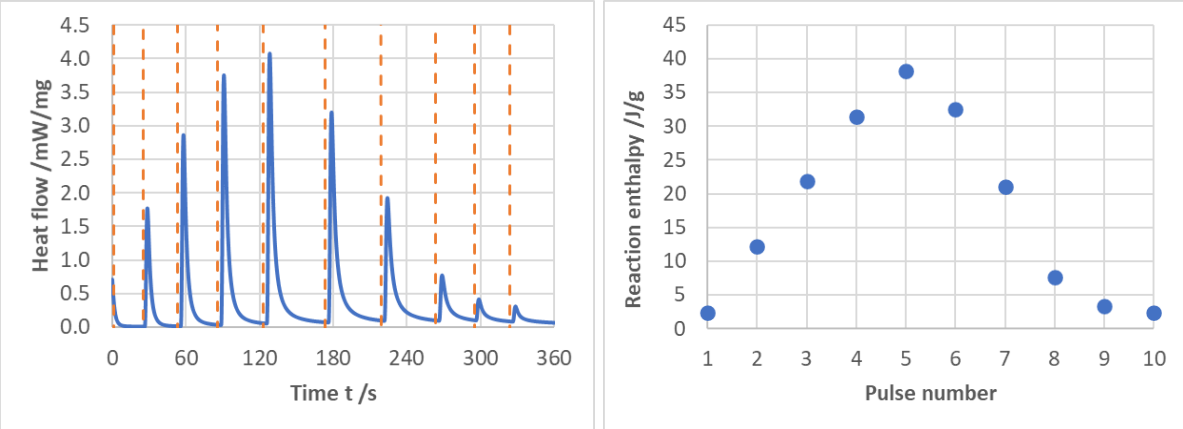


**FIGURE 1:** Results of UV-DSC measurements with light pulses of $I = 20$ mW/cm² and $t_I = 0.1$ s

## UV-rheology measurements

Given the good controllability of the UV curing reaction by pulsating irradiation demonstrated with the UV-DSC measurements, this method is also favoured for the UV-rheology tests. In this case, a uniform dwell time of 10 s was inserted between the pulses of $t_I = 0.1$ s and $I = 20$ mW/cm². In order to investigate the influence of different sample volumes, the initial gap $d_0$ was varied between 0.25 mm and 2.05 mm. The number of pulses applied was varied in dependence on the gap distance. The results of the shear storage modulus $G'$ and the volumetric shrinkage $\beta$ calculated based on the time-dependent gap $d(t)$:

$$\beta = \left[1 + \frac{1}{3}\left(\frac{d(t) - d_0}{d_0}\right)\right]^3 - 1 \qquad (1)$$

are shown in Fig. 2. A clear dependence of the mechanical and the volumetric properties on layer thickness can be deduced from the diagrams. While at low $d_0$ values (between 0.25 mm and 0.40 mm) the increase of the storage modulus and the onset of shrinkage starts after 4 pulses (40 s), the required energy dose increases exponentially at higher $d_0$ values. At $d_0 = 2.05$ mm a total of 32 pulses (320 s) is required to reach gelation. This behaviour corresponds to the behaviour predicted by the Beer-Lambert law[1].

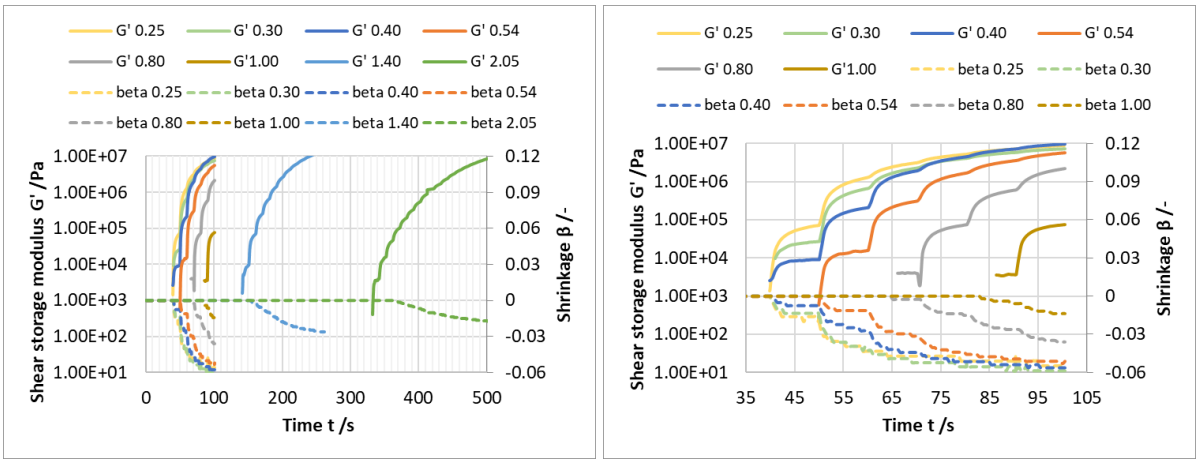


**FIGURE 2:** Left: thickness-dependent shear storage modulus and shrinkage measured during UV-rheological measurements with pulsing irradiation ($I = 20$ mW/cm² and $t_I = 0.1$ s) and intermediate dwell times of 10 s, right: zoom into the early test phase

The data from Fig. 2 can be further used to construct the working curves shown in Fig. 3, left, and mathematically described by[12]:

$$C = D_p \cdot ln\left(\frac{E}{E_c}\right), \tag{2}$$

where, $C$ is the cure depth, $D_p$ represents the penetration depth and $E_c$ is the critical energy dose required to achieve gelation of a layer with infinitesimal thickness.

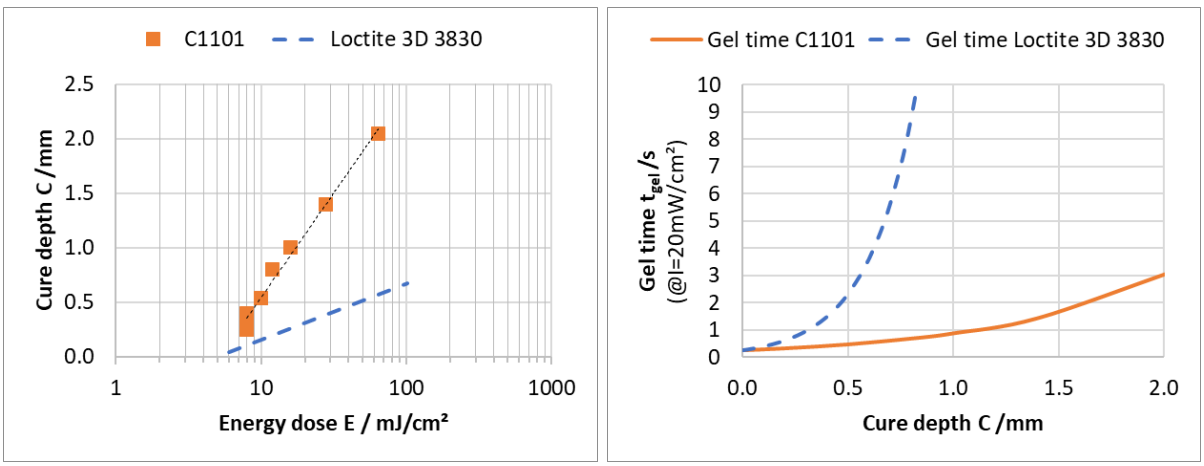


**FIGURE 3:** Left: working curve data and right: calculated thickness-dependent gel time at continuous irradiation with an intensity of 20 mW/cm² (values for Loctite resin are calculated based on data taken from literature[1])

Deriving $D_p$ and $E_c$ from the working curve (Fig. 3, left) gives $D_p = 0.82$ mm and $E_c = 5.21$ mJ/cm². To illustrate the deep cure ability of the investigated resin, the working curve of another commercial resin which is recommended for use in SLA (Loctite 3D 3830) is plotted in the same diagram. As can be seen, the Raylok C1101 allows largely improved deep cure when compared to the Loctite system. By rearranging Eq. 2 it is possible to calculate the thickness-dependent gel time for a given irradiation intensity:

$$t_{gel} = \frac{E_c}{I} \cdot exp\left(\frac{C}{D_p}\right) \quad (3)$$

Inserting the investigated gap values $d_0$ into the cure depth $C$ and assuming a constant light intensity $I = 20$ mW/cm², yields the theoretical gel times shown in Fig. 3, right. As can be seen, both resins show comparable gel times at layer thicknesses below 0.1 mm. At higher thicknesses, however, C1101 clearly outperforms the Loctite system in terms of gel time. These results indicate that the mechanical properties shown (cf. Fig. 2) must be interpreted with regard to thickness gradients, especially if the measurements were performed at gaps above 1 mm. The temperature development of the resin due to the exothermal reaction is another source of error, which is not completely understood until now and needs further investigation (cf. Table 1).

## Winding trials

In order to demonstrate the usability of the investigated resin system, a UV-light equipped winding process with glass fibre reinforcement was set up (Fig. 4, left) to manufacture FRP sleeves with an inner diameter of 100 mm and a thickness of 20 mm. To translate the high UV curing speed into high production speed, the use of a two-step process is necessary. During the first step, the glass fibre roving with a thickness of 0.2 mm is impregnated with the UV-resin and subsequently placed on the mandrel. The desired degree of cure after this step is close to gelation but still in a liquid state. During the second step, the succeeding layer will be placed partially on top of the preceding layer, which leads to gelation of the latter while ensuring sufficient tack between both layers. To ensure this stepwise curing, the required energy dose during one exposure to the UV light is set to a value slightly below 5 mJ/cm² (cf. Fig. 3, left). Winding speeds of 5 m/min, 10 m/min, 15 m/min, 30 m/min, 45 m/min and 60 m/min were employed. Given the diameter of the light cone of 20 mm these result in irradiation times of 0.24 s, 0.12 s, 0.08 s, 0.04 s, 0.027 s and 0.02 s. The light intensity was adjusted accordingly.

The winding process was monitored with the help of a thermographic camera in order to detect the heat release at the surface of the impregnated fibres (Fig. 4, right). After completion of the lay-up, the sleeves were post-cured by irradiation with higher intensity.

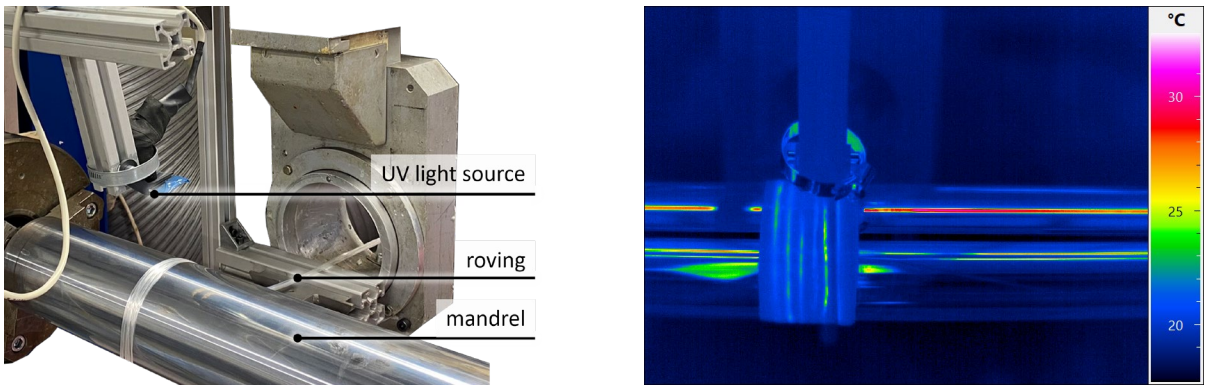


**FIGURE 4:** Left: main components of the UV-winding process, right: thermogram during lay-up

## CONCLUSION

UV curing represents a promising and versatile option for energy-efficient and fast manufacturing of FRP with continuous fibres. While feasibility was shown for some processes, the underlying phenomena including heat transport and light penetration are only poorly

understood. This is mainly due to the fact that previous investigations are limited to thin layers. This contribution highlights some of the challenges associated with deep cure and suggests experimental approaches to give insight into the process-dependent material behaviour. Special attention was paid to the interpretation of UV-rheology measurements and the contribution of thickness effects. By applying the gathered knowledge to a UV-winding process, it was shown that the selected resin system can be employed for fast manufacturing of high-performance lightweight structures. Future work should focus on in-depth analysis of the reaction kinetics, which was shown to be temperature- and irradiation-dependent, as well as on determination of the temperature- and cure-dependent absorption coefficients of the constituents.

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