Impact of irradiation time on reaction kinetics and thermo-mechanical properties of an UV light sensitive adhesive

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Keywords

HAAKE MARS MARS 40/60 and MARS iQ Air Rheometer, UV light induced curing, UV rheology, adhesives, free radical curing, DMTA, glass transition temperature, DELOLUX UV LED light source

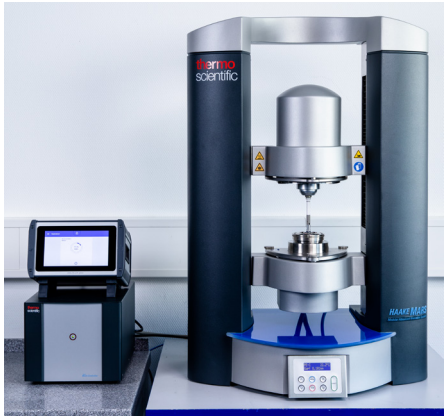


Figure 1: The HAAKE MARS 60 Rheometer equipped with a DELOLUX UV LED light source setup.

Introduction

UV light sensitive adhesives cure into a chemically crosslinked polymer network when exposed to UV light. Depending on the resulting crosslinking density, some polymer chains may not be fully integrated in this network. Therefore, the degree of cure, and hence the share of crosslinked polymer chains of an adhesive, are reflected in its resulting mechanical properties (1).

Polymer chains become increasingly mobile as the free volume expands with increasing temperature. Beyond a certain temperature, polymeric materials show a phase transition from a rigid and inflexible glassy state into a softer and more flexible rubbery state. This so-called glass transition causes mechanical properties to change dramatically, and this transition, therefore, defines the upper temperature limit for an adhesive joint (2).

When equipped with an UV light source and a temperature control device, a rheometer can be used to investigate both the reaction kinetics during the curing process as well as the resulting thermo-mechanical properties of the UV light sensitive material.

In this application note, the influence of different irradiation times on the curing kinetics and resulting thermo-mechanical properties of a UV light sensitive adhesive are presented and discussed. Details on the measurement procedure are also provided.

Materials and methods

For this study, a Thermo Scientific™ HAAKE™ MARS™ 60 Rheometer was used, equipped with a Peltier temperature module (CM-UV-C32) and an electrical temperature-controlled hood (TM-EL-H). Counter cooling of the temperature modules was provided by a Thermo Scientific™ Refrigerated Bath Circulator. The subject of this investigation was a DELO™ PHOTOBOND™ adhesive.

During curing, UV light sensitive adhesives undergo a structural change from a low-viscosity to a solid-like material. The cured adhesives also form a permanent joint between the measuring plates. The rheometer was therefore equipped with disposable parallel plates with a diameter of 15 mm. The integrated optical path of

the CM-UV-C32 allows for homogenous sample illumination through a borosilicate glass plate from the bottom. More information regarding the CM-UV-C32 can be found in (3). An electrical temperature-controlled hood (TM-EL-H) was used to shield the sample from environmental UV light, to protect the operator from leaking UV light during the measurement, and to improve temperature control during the measurement. UV light was supplied by a DELOLUX™ UV LED light source equipped with a 400-nm lamp head. A radiation intensity of 200 mW/cm^2 was adjusted before each measurement using a DELOLUXcontrol radiometer. Figure 1 shows the rheometer setup together with the UV LED light source.

The measurement routine of the Thermo Scientific™ HAAKE™ RheoWin™ Rheometer Control Software is shown in Figure 2. After sample loading and trimming, a measuring gap of 300 µm was set and the temperature was held constant for 200 seconds to ensure a homogenous temperature distribution within the sample, and to relieve any loading-related stresses. A deformation γ of 1% and a frequency f of 5 Hz were chosen for the curing measurement. The UV light source was switched on 40 seconds after the beginning of the test using the automatic trigger function in Thermo Scientific™ HAAKE™ RheoWin™ Software. The irradiation times were adjusted to 12 and 24 seconds, respectively. The curing experiment time was set to 200 seconds. After the isothermal curing step, an additional temperature ramp ranging from 20° C to 120° C was performed, with a heating rate of 3 K/min, deformation of 0.4%, and a frequency of 1 Hz. During the curing measurement, a constant normal force control of 0.1 N ± 0.1 N was applied and the gap change was monitored. During the measurement of the thermo-mechanical properties, a normal force of 5 N was applied to the sample to ensure good contact between the measuring plates and the sample.

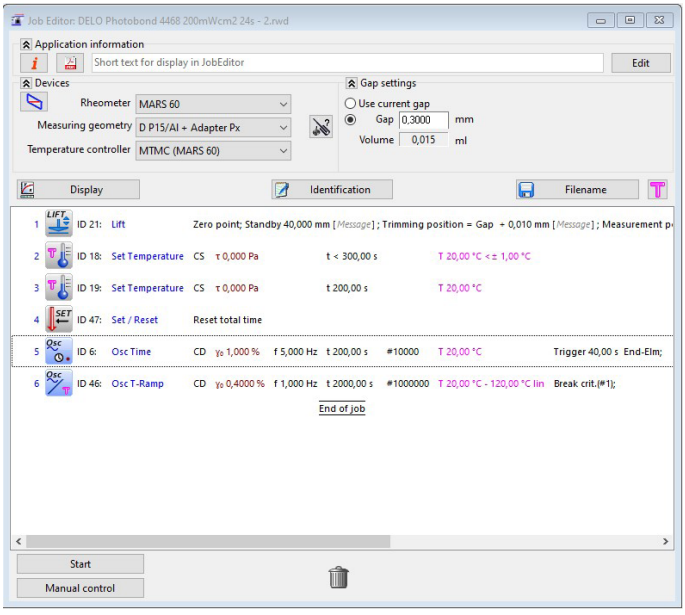


Figure 2: Measurement routine in HAAKE RheoWin Software.

Result & discussion

Influence of irradiation times on curing behavior

Figure 3 shows the rheological parameters storage modulus (G') and loss modulus (G"), and the gap height (h) recorded during curing of the DELO PHOTOBOND adhesive. After a 40 second measuring time, the sample was exposed to UV light with an intensity of 200 mW/cm^2 for a period of 12 and 24 seconds, respectively.

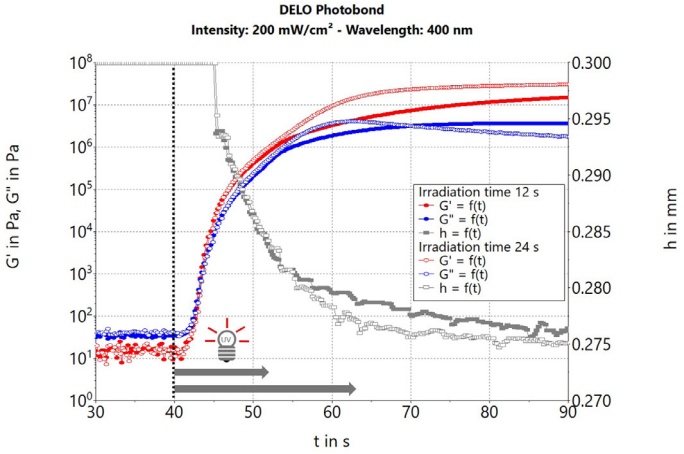


Figure 3: Storage modulus, loss modulus, and gap height data as a function of time for a UV light sensitive adhesive irradiated with 400 nm UV light for 12 and 24 seconds, respectively.

Curing started for both measurements at the same time, after the photochemical reaction was initiated by the UV light source at 40 seconds. As expected, not only the onset of the reaction but also the initial state change (from a liquid to gel/solid-like state) caused by network formation remained the same. The resulting crossover point of G' and G", therefore, occurs after the same time.

Due to a remaining number of free radicals, the curing still proceeds for an additional period when the lamp is switched off after 12 seconds. However, the slopes of both G' and G" decrease significantly when compared to the data obtained with 24 seconds of irradiation time. Furthermore, the distance between G' and G" can be used as an indicator of the degree of crosslinking. Longer irradiation time leads to a bigger distance between the G' and G" curves and, consequently, to more elastic material behavior.

By evaluating the simultaneously recorded normal force data, the axial shrinkage of the sample during curing can be characterized as well. In this case, gap height changed approx. 20 µm during the first 10 to 15 seconds of irradiation. Therefore, the difference in shrinkage is almost negligible when comparing irradiation times of 12 and 24 seconds.

Influence of irradiation times on thermo-mechanical properties

The thermo-mechanical properties of a material can be investigated by applying a sinusoidal force or deflection to a solid sample while simultaneously varying the experiment temperature. This so-called dynamic mechanical thermal analysis (DMTA) is a widely used characterization technique to obtain information about the glass transition of polymers.

As the glass transition does not occur at a single temperature, but over a temperature range, several evaluation methods can be used to obtain a single reference value (T_g) as an indicator for the glass transition. Figure 4 shows a thermogram of a crosslinked adhesive obtained with torsional DMTA.

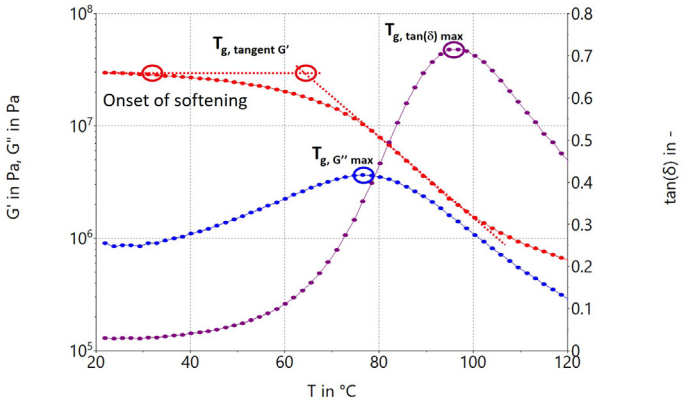


Figure 4: Example for a typical thermogram obtained with DMTA.

Method 1: As the sample leaves its glassy plateau region due to an increase in temperature, its overall stiffness decreases. Hence, the material starts to soften and the storage modulus G' becomes smaller. This onset of softening can be used to evaluate the glass transition, especially if the application of the adhesive prohibits any material softening or loss of stiffness. The glass transition temperature $T_{g,tangent\ G'}$ can be calculated as the intercept of the two tangents from the glassy plateau region and the G' inflection point. Note: depending on the temperature range tested and the data quality obtained, this method of evaluation can be difficult to perform in a reproducible manner. Therefore, it is much more common to apply one of the two following methods instead.

Method 2: As the temperature is increasing and the polymer network starts moving, the material can dissipate more load-introduced energy due to enhanced molecular motion. This generates additional friction and leads to an increase in loss modulus G". Once a certain temperature is exceeded, the free volume reaches a point at which the molecular friction is once again decreasing and G" decreases as well. The resulting maximum can then be evaluated as a measure for the glass transition temperature $T_{g,\ G''\ max}$.

Method 3: It is also possible to evaluate the signal of the loss factor tan(δ), which is the ratio of G" to G' and characterizes the damping ability of the sample. The loss factor combines information about the elastic and viscous properties of the material. Temperature induced changes of these properties can be identified by a maximum in tan(δ). Therefore, this maximum can also be used as an evaluation parameter $T_{g,\ tan(\delta)\ max}$ for the glass transition temperature.

More information regarding the evaluation of DMTA measurements can be found in (4).

Figure 5 shows the thermo-mechanical measurement data obtained after irradiating a DELO PHOTOBOND sample with an intensity of 200 mW/cm² for 12 and 24 seconds, respectively.

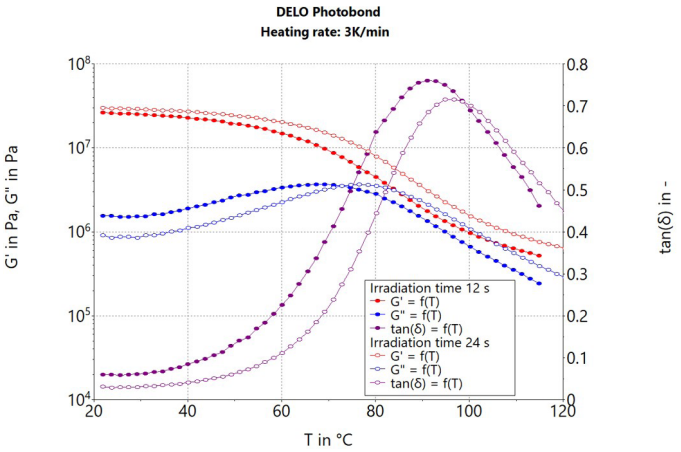


Figure 5: Thermo-mechanical data obtained after irradiating a DELO PHOTOBOND sample with an intensity of 200 mW/cm² for 12 and 24 seconds.

Due to the longer exposure time, crosslinking density increases, leading to a change in mechanical properties. The sample exposed to UV light for 24 seconds shows an overall higher G' and thus a higher elasticity compared to the one irradiated for a shorter period. When evaluating the G' tangent intercept, a clear difference in the onset of the glass transition can be seen. In the case of the DELO PHOTOBOND sample, doubling the irradiation time leads to an increase of $T_{g,\ tangent\ G'}$ of ~10 °C from 56.3 °C for 12 seconds to 66.6 °C for 24 seconds of exposure.

Shorter exposure times (resulting in less integration of polymer chains in the crosslinked network) allow for a faster increase in free volume due to heating. The resulting decrease in internal friction leads to a difference in the curve maximum of G" and a glass transition temperature $T_{g,\ G''\ max}$ of 68.5 °C for 12 seconds and 76.9 °C for 24 seconds of irradiation time, which is a difference of ~8 °C.

Evaluation of the loss factor tan(δ) signal delivers the overall highest glass transition temperature $T_{g,\ tan(\delta)\ max}$. Like the two methods discussed before, the maximum loss factor also depends on the irradiation time. In this case, a variation of ~5 °C from 91.6 °C to 96.2 °C is observed. Additionally, an increase of irradiation time leads to a lower maximum in tan(δ), as the damping properties decrease with higher crosslinking density.

Notably, the difference in glass transition temperature evaluated using these three methods decreases with increasing temperature. This may be an indicator that certain components of the polymer network, responsible for providing specific thermo-mechanical properties at elevated temperatures, may already be forming during the shorter irradiation time. Nevertheless, depending on the application, the resulting effects can be severe, as the overall stiffness decreases significantly.

All evaluation data mentioned above are summarized in Table 1.

Table 1. Comparison of various evaluation parameters obtained from the thermo-mechanical data.

Irradiation time (s)	$T_{g,\ tangent\ G'}$ (°C)	$T_{g,\ G''max}$ (°C)	$T_{g,\ tan(\delta)\ max}$ (°C)
12	56.3	68.5	91.6
14	66.6	76.9	96.2

Independent of the chosen evaluation method, an increase in irradiation time from 12 to 24 seconds leads to an increase of the glass transition temperature. However, when a glass transition temperature is determined by means of dynamic mechanical measurements, it should always be stated which evaluation method was used to ensure comparability.

Conclusion

In this application note, a HAAKE MARS 60 Rheometer was successfully used to characterize a DELO PHOTOBOND adhesive. The results show a clear correlation between the two applied irradiation times, the curing kinetics, and the resulting thermo-mechanical properties of the final product. Longer irradiation times led to a higher overall stiffness and elasticity as well as a higher glass transition temperature.

A rheometer can serve as a highly valuable tool when evaluating the influence of UV light on the reaction kinetics and resulting thermo-mechanical properties of light-sensitive adhesives. This information can help identifying the applicability of an adhesive joint at a particular set of curing parameters.

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