Application note | V299

Impact of the UV light intensity on the shrinkage and curing behavior of an UV light sensitive adhesive

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Keywords

HAAKE MARS 40/60 and MARS iQ Air rheometer, UV light induced curing, UV rheology, adhesives, free radical curing, DELOLUX UV LED light source

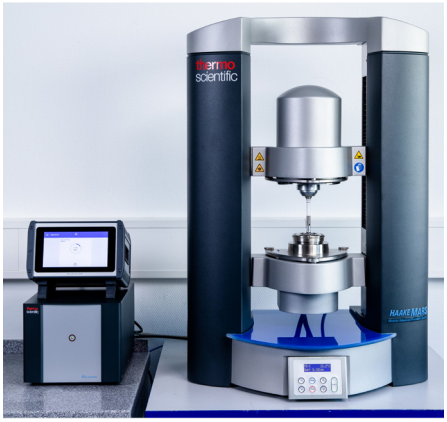

Figure 1: The HAAKE MARS 60 Rheometer equipped with a DELOLUX UV LED light source setup.

Introduction

UV light sensitive adhesives offer several advantages when it comes to establishing an adhesive joint compared to conventional adhesives like 2-component or solvent based among other things. They can be described as a single component material with an on-demand curing capability within seconds once it is exposed to UV radiation. Besides this, the curing can be conducted at room temperature.

When equipped with a UV light source, a rheometer can be used to investigate the reaction kinetics during the curing process as well as the shrinkage resulting from the UV light exposure. The curing mechanism of many UV light sensitive adhesives is based on the generation of free radicals out of a photoreactive component, a so-called photoinitiator. These radicals interact with the monomeric and oligomeric components to form a chemically crosslinked polymer network. The curing speed of such mechanisms depends highly on the UV light intensity. When utilizing free radical polymerization, the formation of adhesive joints is usually achieved within seconds. (1)

In this application note, the UV light induced curing of an adhesive exposed to two different light intensities is presented and discussed. Furthermore, details on the measurement procedure are provided.

Materials and methods

For this study, a Thermo Scientific™ HAAKE™ MARS™ 60 Rheometer equipped with a Peltier temperature module CM-UV-C32 was used. Counter cooling of the Peltier element was provided by a HX R heat exchanger. The subject of this investigation was a DELO™ Photobond adhesive.

During curing UV light sensitive adhesives undergo a structural change from a low viscous to a solid-like material. Besides this, cured adhesives form an adhesive joint between the used measurement geometries. Therefore, the rheometer was equipped with disposable plate geometries with a diameter of 15 mm. The integrated optical path of the CM-UV-C32 allows for a homogenous sample illumination through a borosilicate glass plate from below. More information regarding the CM-UV-C32 can be found in reference 2.

To shield the sample from environmental UV light and to protect the operator from leaking UV light during the measurement, a PEEK sample hood was used. UV light was supplied by a DELOLUX™ UV LED light source setup equipped with a 400 nm wavelength lamp head. Radiation intensities of 50 mW/cm^2 and 100 mW/cm^2 were adjusted before each measurement using a DELOLUXcontrol radiometer. Figure 1 shows the rheometer setup together with the UV LED light source.

The measurement routine is shown in Figure 2. After sample loading and trimming, a measuring gap of 150 µm was set and the temperature was held constant for 200 s to ensure a homogenous temperature distribution within the sample and to relieve any loading-related stresses. A deformation γ of 1 % and a frequency of 5 Hz were chosen as parameters for the curing measurement. The UV light source was switched on 40 s after starting the test using the automatic trigger function of the Thermo Scientific™ HAAKE™ RheoWin™ Software. The irradiation time was adjusted to 20s. The overall experiment time was set to 200 s. During the measurement the normal force control was active and set to 0.01 N ± 0.1 N and the gap was monitored.

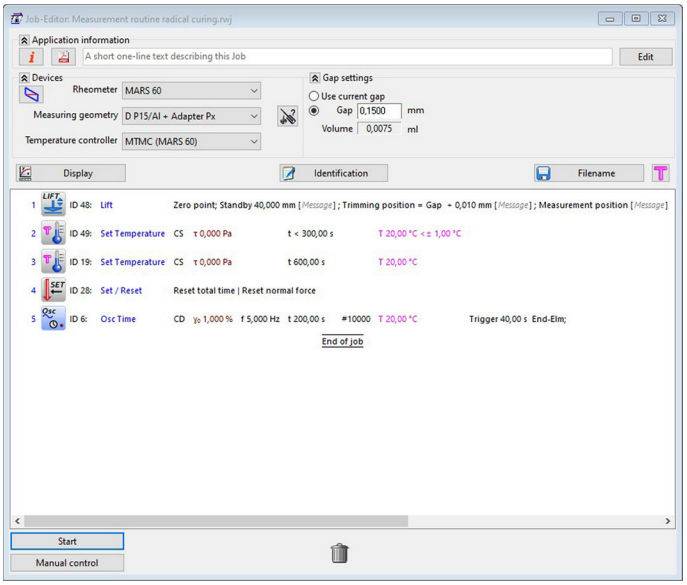

Figure 2: Measurement routine HAAKE RheoWin Software.

Result and discussion

Influence of UV radiation intensity on curing behavior

Figure 3 shows the rheological parameters storage modulus G', loss modulus G", and the phase angle δ obtained during curing of the DELO™ Photobond adhesive, while exposed to UV light with an intensity of 50 mW/cm^2 for a period of 20 s.

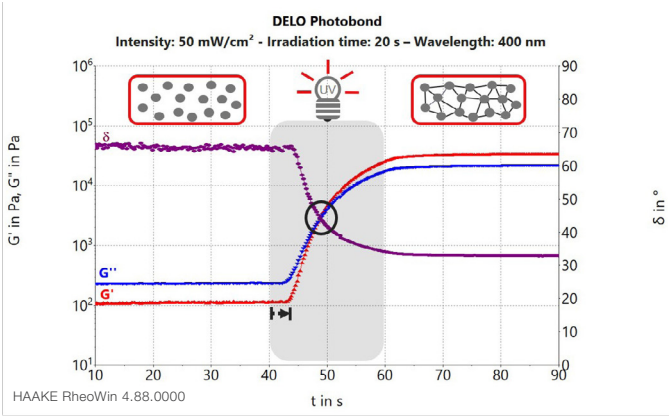

Figure 3: Storage modulus, loss modulus, and phase angle data as a function of time of a UV light sensitive adhesive.

Before starting the reaction by triggering the UV light source after 40 s, the sample showed a liquid-like behavior in its uncured state. This is indicated by a phase angle δ higher than 45 ° as well as the loss modulus G" dominating the storage modulus G'. After switching on the UV light source, the reaction did not start immediately. This latency was caused by the fact that a certain amount of energy is needed to generate enough free radicals to initiate the curing. Once this threshold is overcome, the chain growth followed by the network formation starts, and the generation of the adhesive joint begins. During this photopolymerization, the structural changes can be monitored utilizing G' and G". Since the elastic modulus G' is a measure of the elastic properties of a sample, the crosslinking can directly be linked to an increase in G'.

Once G' is larger than G", the elastic properties are dominating the viscous properties indicating a gel-like or solid-like structure depending on the degree of curing. The resulting crossover point is often referred to as the gel point and can be used as an easy to determine and widely used evaluation parameter. Therefore, it is used as a close approximation in this application note. Unfortunately, the crossover may not represent the "true" gel point as it is frequency dependent. (3) Per definition, the G' and G" curves are crossing each other at an δ of 45°. In this case, the crossover occurred after 8 s of irradiation. A final phase angle of approx. 33 ° is reached, which indicates a solid-dominating character.

It is worth noting, that the curing did not stop when the irradiation ends after an irradiation time of 20 s. Due to the remaining number of generated free radicals, the curing persists until all generated radicals are used up.

To investigate the effect of a higher UV light intensity on the curing of a UV light sensitive adhesive, measurements were also performed at an irradiation level of 100 mW/cm^2. A comparison of the rheological results for the curing reactions with intensities of 50 and 100 mW/cm^2 are shown in Figure 4.

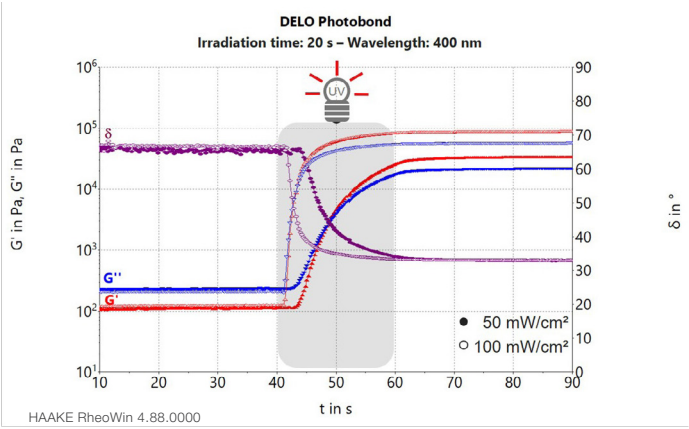

Figure 4: Comparison of different UV light intensities on the curing behavior of UV light sensitive adhesives.

When doubling the intensity, several effects on the curing behavior were observed. On the one hand, a higher intensity led to a faster sample curing. The crossover as a transition from dominant viscous to dominant elastic behavior shifts to shorter times. On the other hand, higher values for G' and G", and with that a higher degree of curing, were also obtained when the UV light intensity is increased. This may have an impact on the mechanical properties of the final adhesive bonding performance. Interestingly, the phase angle seems not to be affected at all by the change of light intensity. With δ being close to 35 ° in both cases, a certain degree of viscous-like properties causing rubbery-like sample behavior were observed. These rubbery-like properties may lead to an additional damping ability of the final adhesive joint.

Furthermore, the latency time was shorter when the sample is exposed to a higher UV light intensity. This indicates a faster start of the polymerization. All findings are summarized in Table 1. The results show that, structural changes can be significantly sped-up by increasing the intensity of the UV radiation. This is no surprise, as a fixed amount of photoinitiator is present, and a higher UV intensity leads to a larger number of free radicals generated in a shorter period.

Table 1. Comparison of various evaluation parameters obtained from the rheological data.

	Onset of curing G'_{onset}	Crossover modulus G_{cross}	Crossover time t_{cross}	Final phase angle δ_{final}
50 mW/cm2	43 s	2 500 Pa	48 s	33 °
100 mW/cm2	41 s	10 000 Pa	42 s	33 °

Influence of UV radiation on shrinkage

During the polymerization process, adhesives undergo an increase in density. Depending on the degree of curing, the volume is decreasing consequently. This results, among other things, in a reduction of surface adhesion as well as the occurrence of internal stresses. (4) Therefore, the characterization of the shrinkage is of high interest to predict the final properties of the adhesive joint.

To perform accurate rheological measurements, modern rheometers are equipped with both precise gap and normal force control. Information about the shrinkage of an adhesive during curing can be obtained by keeping the normal force constant and adjusting the gap height. Thus, the movement of the upper part of the measuring geometry can be recorded and correlated to the samples' change in volume. Alternatively, by keeping the gap constant, the stress resulting from the shrinkage can be monitored.

Figure 5 shows the change in gap height during curing of a DELO™ Photobond adhesive when exposed to UV light intensities of 50 mW/cm² and 100 mW/cm², respectively.

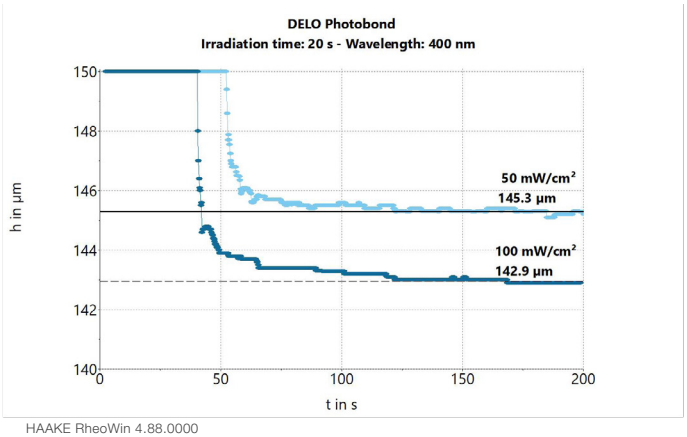

Figure 5: Change in height induced by different UV light intensities.

As already shown in Figure 4, the more energy is inserted into the sample, the more pronounced the curing reaction will be. Besides this, a higher degree of curing also leads to an increased sample shrinkage. In this case, a change in sample height of about 3 % at an intensity of 50 mW/cm² was recorded. Increasing the intensity to 100 mW/cm² led to an increased shrinkage of 5 % for the same sample. Therefore, a dependency of shrinkage on the chosen UV light intensity can be assumed. Furthermore, the onset of the gap change is shifted towards shorter times as the curing is initiated sooner.

Conclusion

In this application note, a HAAKE MARS 60 Rheometer was successfully used to characterize a DELO Photobond adhesive. Several evaluation parameters for the characterization of rheological curing curves like the crossover point of G' and G" or the latency time were proposed and discussed. The results show a clear correlation between the applied intensity and the resulting curing kinetics as well as the shrinkage of the UV light curing adhesives. Thus, a rheometer is clearly a very useful tool for an in-depth characterization of UV light curing adhesives.

The author would like to thank DELO for providing the DELO Photobond sample as well as the DELOLUX UV LED light source setup.

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