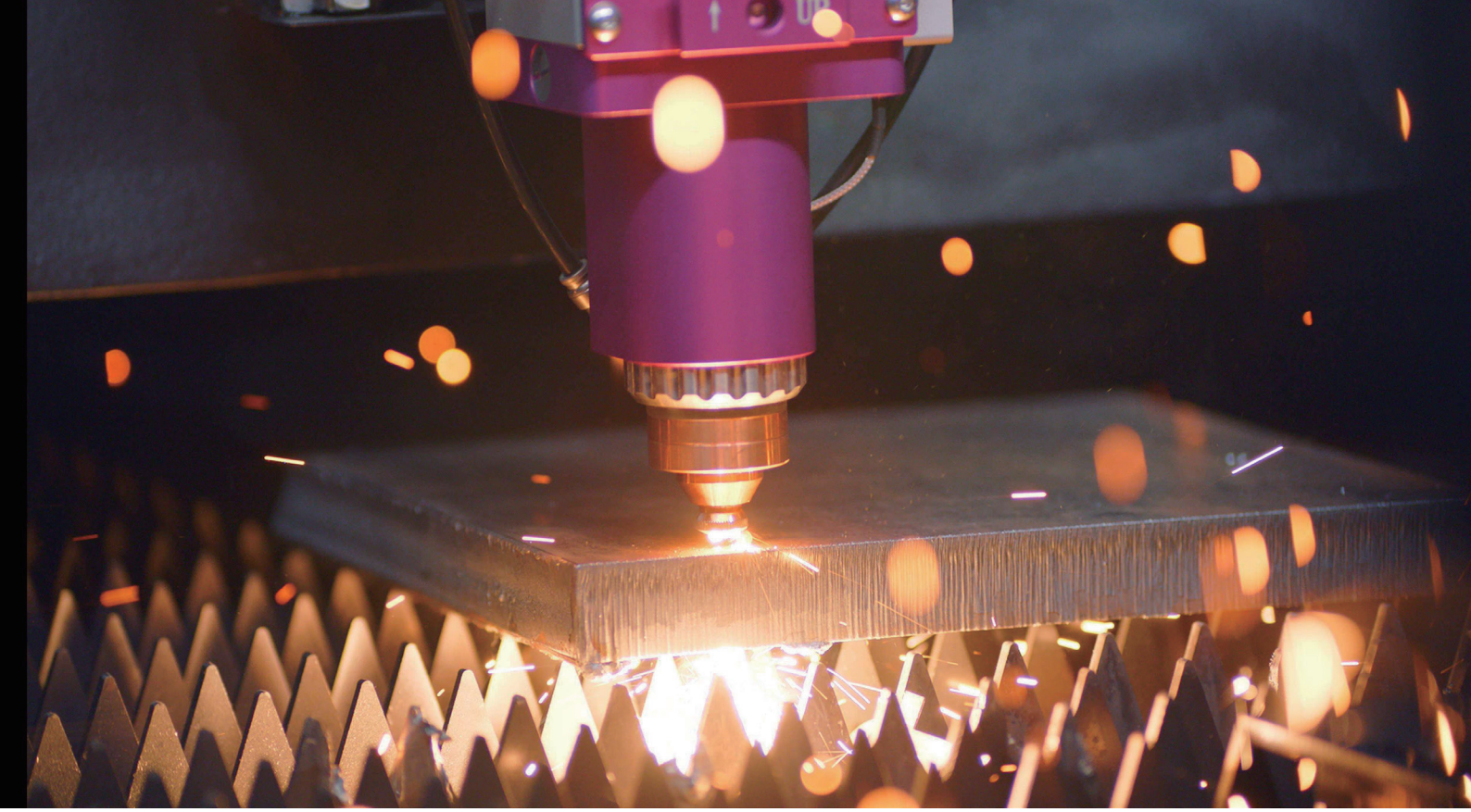
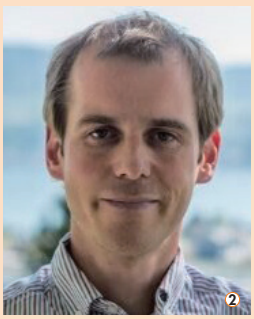


中红外**激光光谱**原位监测固化反应

In Situ Monitoring of Curing Reactions with Mid-Infrared **Laser Spectroscopy**



快速光谱监测是在研发和生产环境中久经考验的工具，可用于深入了解化学反应。本文展示了 IRis-F1 双梳状光谱仪如何用于监测固化反应，它可以提供有关涂料和胶粘剂性能的宝贵见解。

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红外光谱在许多方面是此应用程序的理想测量技术，因为它能够执行非侵入性原位测量，从而提供有关样品的结构和成键的直接信息。但是，许多高性能胶粘剂具有快速固化速度，而现成的光谱技术的速度是相关分析的限制因素。

IRis-F1基于量子级联激光器（QCL）频率梳技术，该技术可进行毫秒级到微秒级的测量。

Fast spectroscopic monitoring is a proven tool in R&D and production environments, where it is used to gain insight to chemical reactions. This application note showcases how the IRis-F1 dual-comb spectrometer can be used to monitor curing reactions, where it can provide invaluable insight on the performance of coatings and adhesives.

Infrared spectroscopy is an ideal measurement technique

实验

实验装置如**图1**所示。使用单反射金刚石Golden Gate ATR衰减全反射附件（Specac）进行测量。样品是紫外线引发固化的粘合剂，由德国DELO Industrial Adhesives提供。未固化时具有1,613cm^{-1}的红外波段，固化后具有1,638cm^{-1}的红外波段。对于每次测量，在清洁ATR晶体后首先获取背景曲线，然后在固化前，固化中和固化后进行一系列快速测量。

使用的QCL提供的输出光谱为1,585~1,645cm^{-1}。光谱仪的分辨率设置为4cm^{-1}，采集时间为1ms，重复频率为40Hz。在这些设置下，可以在缓冲区充满和重复率降低到1Hz的数量级之前连续采集约30秒。光源采用Hamamatsu LC8汞灯通过光纤提供（**图1，右**）。在光谱仪上开始测量之后，打开灯以启动固化反应，并将所得光谱记录为时间序列。

结果与讨论

图2显示了以25ms为时间增量获取的原始光谱。即使在很短的积分时间内也可以获得良好的信噪比。很明显，约1,610cm^{-1}处的谱带迅速衰减，而一条位于1,640cm^{-1}处的新谱带开始成长。当使用带有ATR棱镜的基于激光的仪器时，可以预期在原始光谱中观察到的条纹。它们是由样品（即胶水对空气）的折射率变化引起的，从而改变了ATR光谱中的穿透深度。传统光源通常不会观察到条纹，因为相干长度足够短，以致于在此长度范围内不受条纹影响。由于它们具有明确定义的周期性，因此可以使用简单的傅立叶转换（FT）滤波器将其删除（**图2，右**）。

可以通过从每个后续的正时光谱中减去未固化胶水的光谱（定义为负时光谱）来生成差异光谱。**图3（左）**显示了差异光谱，突出了固化反应产生的变化。负带表示某个特征消失了，而正带表示一个新特征已经出现。在这里，很明显，不是一个，而是两个新的谱带，即1,638及1,624cm^{-1}新谱带出现了。应该注意的是，**图3（左）**中的光谱没有进行滤波处理。

for this application in many ways as it is capable of performing non-invasive in-situ measurements that provide direct information about the structure and bonding of the sample. However, many high-performance adhesives possess fast curing rates and the speed of off-the-shelf spectroscopic techniques is the limiting factor in their analysis.

The IRis-F1 is based on quantum cascade laser (QCL) frequency comb technology, which allows for measurements on milli to microsecond timescales to be carried out.

Experimental

The experimental setup is depicted in **Figure 1**. Measurements were conducted with a single-reflection diamond Golden Gate ATR accessory (Specac). The sample is a UV-triggered adhesive, which was kindly provided by DELO Industrial Adhesives (Germany). It possesses an infrared band at 1,613 cm^{-1} when uncured and a band at 1,638 cm^{-1} after curing. For each measurement a background file was initially acquired after cleaning the ATR crystal, followed by a rapid series of measurements spanning before, during, and after curing.

The QCL used provides a spectral output of 1,585 – 1,645 cm^{-1} The spectrometer was set to a resolution of 4 cm^{-1} and the acquisition time was 1 ms, with a repetition rate of 40 Hz. At these settings, continuous acquisitions can be acquired for ca. 30 seconds before the buffer fills and repetition rate is reduced to the order of 1 Hz. Illumination was provided using a Hamamatsu LC8 mercury lamp, via an optical fibre (**Figure 1, right**). After the measurement is started on the spectrometer, the lamp is turned on to initiate the curing reaction and the resulting spectra are recorded as a time-series.

Results and discussion

Figure 2 shows the raw spectra acquired in time-increments of 25 ms. A good signal to noise ratio is obtained even at short integration times. It is clear that the band at ca. 1,610 cm^{-1} decays rapidly, while a new band grows at ca. 1,640 cm^{-1}. The fringes observed in the raw spectra are expected when using

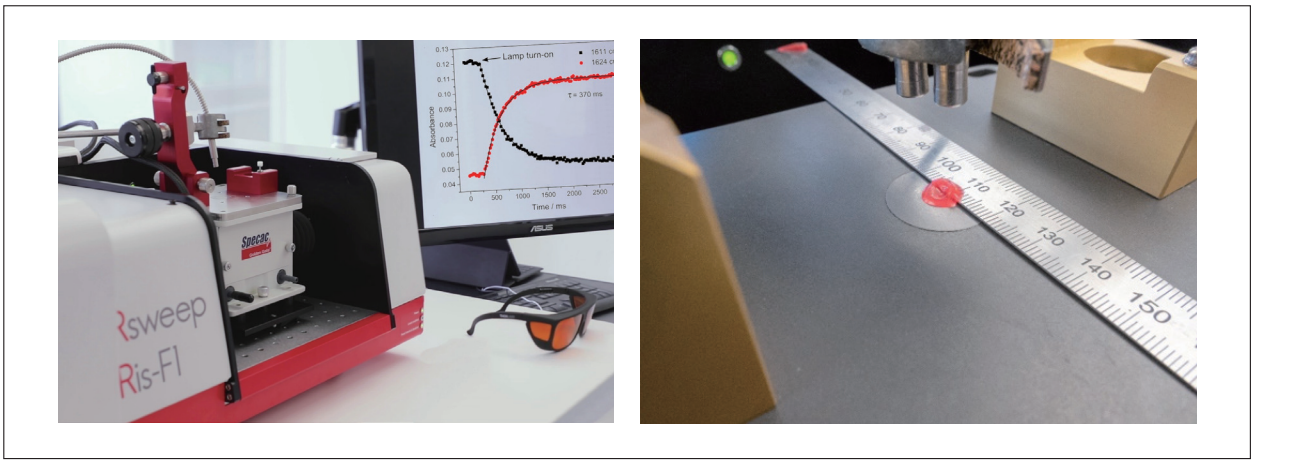

图1：（左）带有Golden Gate ATR附件的IRis-F1光谱仪；（右）安装在钻石反射元件上方的UV光源。
Figure 1: (left) The IRis-F1 spectrometer with the Golden Gate ATR accessory; (right) the UV light source mounted above the diamond reflection element.

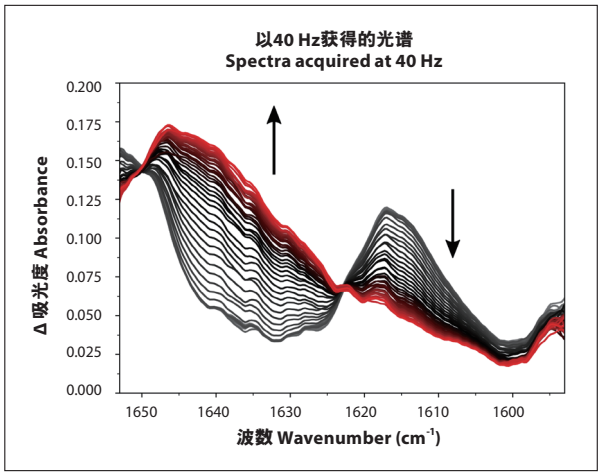

图2：以25ms的时间分辨率测量的固化过程的光谱；使用FT滤镜去除相同的光谱，以去除ATR棱镜上的干涉条纹。
Figure 2: Spectra of the curing process measured with a time-resolution of 25 ms; the same spectra with an FT filter to remove interference fringes from the ATR prism.

光谱中两个点的动力学轨迹清楚地显示了光源打开的时间点。通过拟合这些点的增长及衰减，可以确定固化过程的动力学特性。在这种情况下，发现时间常数为370ms的一阶反应。但是，反应的确切性质可能取决于样品厚度和辐照功率，而这些参数并未完全控制这些测量值。

从光谱仪的角度来看，当然可以进行更快的测量，但是，当前的设置似乎受到光源开启时间及亮度的限制。不同的光源（例如激光器）将允许明显更快的测量。

结论

在固化过程中对胶水样品进行了具有高信噪比的快速测量，从而洞悉了毫秒级的过程。这有效地将IRis-F1先前展示的能力与微秒时标和秒至分钟时标联系起来。该方法使研究时间跨度超过多个数量级的过程成为可能。

a laser-based instrument with an ATR prism. They are caused by a change in the refractive index of the sample (i.e. glue vs air) changing the penetration depth in ATR spectroscopy. Fringes are typically not observed with traditional light sources, as there the coherence length is short enough to be unaffected by fringes on this length-scale. Thanks to their well-defined periodicity, they can be removed with a simple Fourier transform (FT) filter (**Figure 2**).

Difference spectra can be generated by subtracting a spectrum of the uncured glue (defined as a negative-time spectrum) from each of the subsequent positive-time spectra. **Figure 3 (left)** shows the difference spectra, which highlight the changes produced by the curing reaction. Negative bands indicate that a feature has disappeared, while positive bands indicate that a new feature has grown in. Here, it is evident that not one, but two new bands has emerged, at ca. 1,638 and 1,624 cm^{-1}. It should be noted that no filtering was applied to the spectrum in **Figure 3 (left)**.

The kinetic traces at two points in the spectra clearly show the time-point where the lamp was turned on. By fitting the growth and decay of these points, the kinetic properties of the curing process can be determined (**Figure 3, right**). In this case, a first-order reaction with a time-constant of 370 ms was found. However, the exact nature of the reaction is likely dependent on the sample thickness and irradiation power, which are parameters that were not fully controlled for these measurements.

Faster measurements are certainly possible from the point of view of the spectrometer, however, the present setup appears to be limited by the lamp turn-on time and brightness. A different source (e.g. a laser) would allow for significantly faster measurements.

Conclusion

Rapid measurements with high signal to noise ratios were performed on a sample of glue during curing, giving insight on processes that happen on a millisecond timescale. This effectively bridges the previously-demonstrated capabilities of the IRis-F1 to measure on the microsecond timescale, with the second to minute timescale. It enables processes over many orders of magnitude in time to be studied.

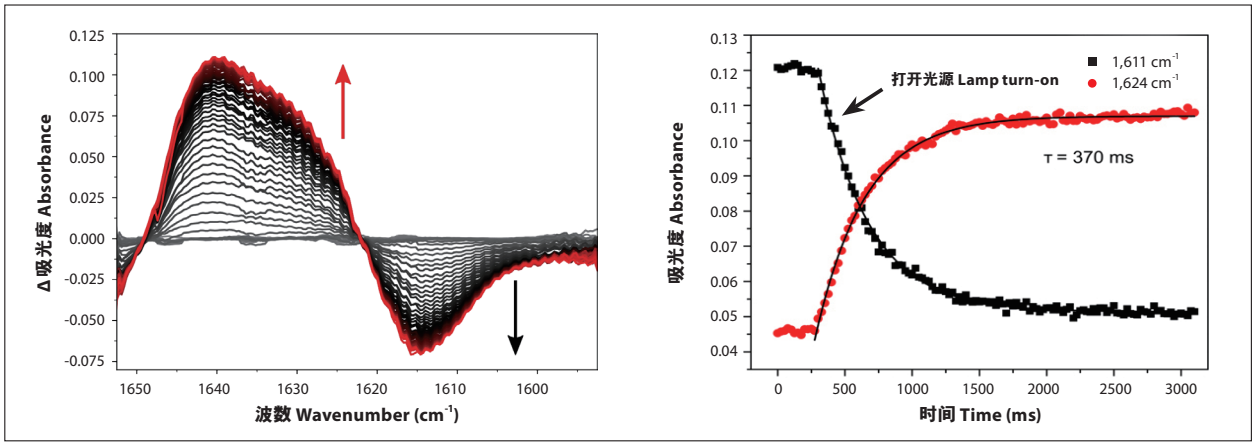

图3：（左）以25ms的时间分辨率测量的固化过程的差异光谱；（右）绝对谱图中两点的动力学轨迹
Figure 3: (left) Difference spectra of the curing process measured with a time-resolution of 25 ms; (right) kinetic traces at two points in the absolute spectrum