Applications of Simultaneous DSC-Raman

Differential scanning calorimetry (DSC) and Raman spectroscopy are both commonly applied to the same problems, especially in looking at polymers and pharmaceutical materials. They complement each other because Raman spectra can provide qualitative information to supplement the quantitative information from DSC. Raman spectra provide similar information to FT-IR and can be obtained much more readily from a sample in a DSC. An immediate question is what advantage a simultaneous system has over the combination of a DSC and a Raman spectrometer with a hot stage. One reason is the flexibility of the DSC, which in the case of PerkinElmer’s unique double-furnace DSC 8000 and 8500 means true isothermal performance, fast equilibration, and controlled heating or cooling rate up to 750 °C/minute. More importantly, it ensures there is no doubt about the relationship between the observed spectra and the thermal transitions when the behavior depends on previous thermal history. This will be especially significant when trying to unscramble complex transitions where Raman can show different spectral changes for overlapping events.
Practical Considerations

Both the RamanStation™ 400 and the RamanFlex™ lines of Raman spectrometers from PerkinElmer allow the use of a remote probe for collecting spectra. This makes an optical fiber connection between the spectrometer and the DSC. The lid of the DSC is modified to hold the focusing and collecting optics, with XYZ adjustment to align the laser beam with the sample. These modifications serve to protect the remote probe from high temperatures in the DSC, as well as to protect and maintain the controlled thermal environment required for proper DSC operation. The laser illuminates a spot approximately 200 μm across. The sample will normally be in an open pan, although a quartz window can be used for volatile materials. Figure 1 shows the PerkinElmer® DSC-Raman system.

A typical DSC-Raman experiment would use a heating rate of 10 °C per minute with spectra obtained every 1 or 2 °C. The laser power is generally tens of milliwatts with exposure times of a few seconds, which affects the heat flow in the DSC. Since both intensity and time of the laser pulse can be adjusted in the PerkinElmer Raman spectrometers, some turning is needed to adjust, thus to minimize its effects on the sample. One way to minimize sample heating and the possibility of sample damage is the ability to block the laser except when measuring. The rapid response of the double-furnace DSC removes this heat from the sample so little to no temperature occurs in the bulk material but it appears as a modulation of the heat flow curve that can be removed by smoothing. One should note that the amount of heat from the laser depends on the light-scattering properties of the sample which often change at a thermal transition. Because of this, it is probably best to obtain quantitative thermal data without the laser and use the heat-flow curve from the simultaneous measurement to verify the occurrence of thermal transitions.

Polymer Applications

DSC is used largely to look at glass transitions (Tg), crystallization and melting transitions in thermoplastic polymers. Raman spectra appear to show only small changes through glass transitions but are very sensitive to crystallinity. Hence in the former cases, the advantage of the DSC over a hot stage is readily apparent as the DSC detects a transition that may not be seen in the Raman spectrum. As many physical properties like decomposition rate, gas permeability, etc. change at the Tg, missing it can be catastrophic. Typically, Raman spectra of amorphous and crystalline forms show similar bands but the features in the amorphous state are much broader. This reflects the wider range of local environments for molecules in a disordered phase.

Polyphenylene oxide (Figure 3 – Page 3) shows how Raman can add qualitative information to DSC observations. As received, the material melts at about 70 °C but on a second heating, the melting point is 4 °C lower. The Raman spectra obtained during the first and second heatings are different. We can examine this difference more easily by looking at the spectra obtained by subtraction. This difference is identical to the spectra obtained from the melt, corresponding to amorphous material. This shows that the lower melting point is caused by an increased amorphous component after the first heating. This is mostly caused by differences in the cooling rate or heat history experienced by the original sample and the cooling rate used in the DSC study.
Pharmaceutical Applications

The obvious application in pharmaceutical studies is to look at the polymorphic forms of various components. Polymorphs often have quite different biological activity and are also important in protecting the intellectual property. These forms, which are different crystalline states of the material, generally have quite distinct Raman spectra. While DSC is an excellent tool for detecting the existence of these forms, and the energy of their inter-conversions, it cannot by itself determine which state is present. Raman spectra can, and by combining the two techniques, a very precise understanding of the inter-conversion of one from another can be obtained. An example of this approach is the combined spectra for acetaminophen in Figure 5 (Page 4).
Even more interesting is the opportunity to investigate complex transitions such as those where crystallization and a polymorphic change overlap. In these cases, DSC may provide only a single curve but the bands in Raman spectra may respond differently to the two changes.

**Figure 5.** DSC thermogram for a 10 °C/minute scan of acetaminophen is shown with the four different Raman spectra overlaid on it.

**Conclusions**

The combination of DSC and Raman spectroscopy into a single technique offers unique opportunities to further our understanding of complex behavior in materials. The combined technique gives us access to information that neither technique alone would provide and presents a powerful tool for understanding how different materials respond.

To learn more about DSC-Raman or other hyphenated technology, visit www.perkinelmer.com/hyphenation