Characterization of microencapsulated PCMs using DSC and TGA

Differential scanning calorimetry measures heat flow, allowing a sample's melting and freezing temperatures as well as latent heats of fusion and freezing to be calculated. Thermogravimetric analysis, which measures a sample's weight change as a function of temperature, can provide insight about a material's thermal stability, estimated product lifetime and other important characteristics.

By Heather M. Watson, Ph.D.

How is the amount of contained PCM determined?

Microencapsulated phase change material (mPCM) contains a spherical core of PCM within a shell coating. The amount of PCM is expressed as a relative amount to that of the shell, a *Core %*. The latent heat (LH) of contained PCM is reduced proportionally to the thickness of shell coating. It is common in industry to use this relationship to express the amount of PCM as $Core\ \%\ PCM = \frac{LH\ of\ mPCM}{LH\ of\ neat\ PCM} * 100$, where the neat PCM refers to the unencapsulated PCM. These latent heat measurements are made with a differential scanning calorimeter (DSC).

How do you detect free or unencapsulated PCM?

Measuring the amount of free PCM is important for quality control and microencapsulation process optimization. This can be accomplished by extracting the sample with solvent that the PCM is freely soluble in. Take care not to vortex or use any type of harsh mixing to avoid mechanical rupture of shell. Extracted PCM can then be further analyzed with a compatible method such as HPLC MS, GC FID or TLC. Standards can be prepared for accurate quantitation.

How do you measure the amount of energy stored in the mPCM?

Differential scanning calorimetry (DSC) measures heat flow. A typical DSC curve plots heat flow versus temperature. The sample's melting and freezing points, the onset of these transition temperatures, as well as the latent heats of fusion and freezing are easily obtained from these graphs.

151 Cheshire Lane N., Suite 400, Plymouth, MN 55441 USA
P: +952-941-0306 | F: +952-944-6893 | www.puretemp.com

What is thermogravimetric analysis?

Thermogravimetry (TG) or thermogravimetric analysis (TGA) measures a sample's weight change as a function of temperature in a controlled environment. Both weight changes and rates of change give information about the physical and chemical nature of the sample. TGA can provide insight about a material's thermal stability, waters of hydration, estimated product lifetime, composition of multicomponent materials and oxidation. For mPCMs, TGA is used in the optimization of microencapsulation processes as well as for quality control between lots/batches. Information regarding shell integrity, unencapsulated PCM and residual process residues can all be attained via TGA.

Why do TGAs from two labs look different even from the same sample?

Most events measured by TGA are kinetic. This means that the changes observed depend on absolute temperature and the time the sample experiences that temperature. Any factor that affects the reaction rate will change the transition temperatures and the shapes of the TGA curves. A few parameters must be carefully controlled so that interlaboratory data can be compared.

- The sample pan material, size and shape.
- The temperature ramp rate.
- The purge gas and its flow rate.
- The amount and morphology of the sample itself.

What is a common TGA procedure performed on mPCMs?

Thermal stability / degradation of mPCMs. Alumina or platinum sample crucibles are used and carefully cleaned between experiments. In this procedure, PureTemp sample masses are kept between 10 to 12 mg and a constant temperature ramp and inert environment is maintained. Temperature ranges from ambient to 600°C at 5°C/min with nitrogen flow rate of 100 mL/min.

Why is a purge gas used in TGA?

An inert purge gas such as nitrogen or helium is used to remove off gases from the sample chamber and to keep the delicate microbalance clean. A constant flow rate prevents baseline fluctuations.

Why such a small sample mass range of PureTemp for TGA studies?

Keeping a small range of sample masses results in data that can more accurately be compared. Larger samples thermally protect the center of the sample from

151 Cheshire Lane N., Suite 400, Plymouth, MN 55441 USA
P: +952-941-0306 | F: +952-944-6893 | www.puretemp.com

experiencing high temperatures for a period of time. This kinetic effect can be misinterpreted when comparing two mPCM batches with greatly differing starting masses.

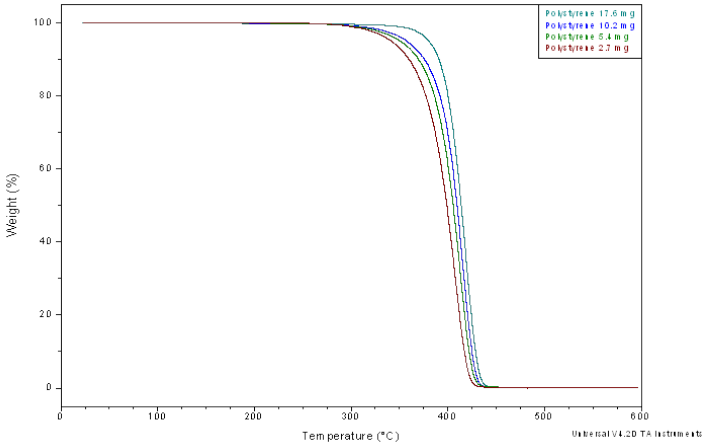

Figure 1. The effect of TGA sample mass

Why is 5°C/min used as your TGA ramp rate?

Apparent temperature shifts occur when various heating rates of the same material are examined. This is also due to the kinetic nature of the TGA events. Heating rates must be kept the same to compare sets of data. Increased ramp rates result in apparent degradation temperature shifts and vice versa. As with most instrumental parameters there is a tradeoff. Faster run times lead to less resolution between events; slower ramp rates take longer but lead to better sensitivity. Each experiment is different and can be customized for the specific sample type, sample history and information desired. By keeping the ramp rates the same, the data from neat PCM, shell coating and the mPCMs can be more accurately compared.

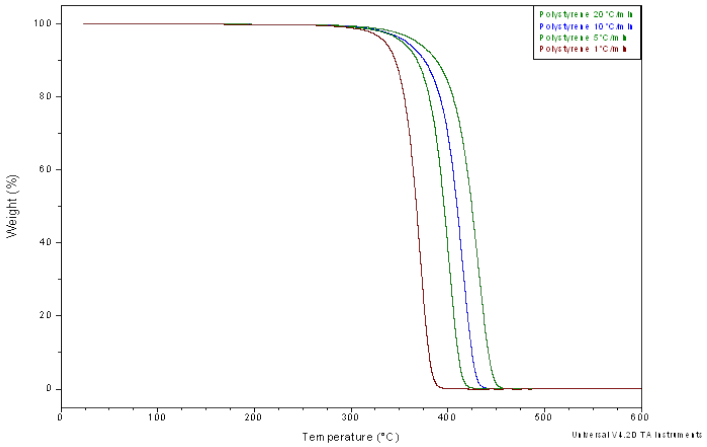

Figure 2. The effect of TGA ramp rate

151 Cheshire Lane N., Suite 400, Plymouth, MN 55441 USA
P: +952-941-0306 | F: +952-944-6893 | www.puretemp.com

How do you ensure correct interpretation of TGA data?

You can't.

- You can minimize misinterpretation by understanding the history of your sample and controlling the experimental procedure, sample mass, pan type, calibration, etc.
- Recognize the difference between real events and artifacts.
- Don't over-interpret the data. When available, use other techniques (DSC and others) for confirmation and to complement TGA. This is especially true when concerned about artifacts or heating rate effects.

How does TGA of mPCMs complement what we find with DSC? Why necessary?

DSC measures mPCMs' thermal properties such as latent heat and melting temperatures. Comparison of the neat PCM to the mPCMs' latent heats gives information about how much PCM is in the core of the microcapsule. It is common in industry to express this as $Core\ \%\ PCM = \frac{LH\ of\ mPCM}{LH\ of\ neat\ PCM} * 100$ where the neat PCM refers to the unencapsulated PCM. This information alone is useful but does not provide insight into the thermal stability of the microspheres.

What other insight can we get from TGA?

- Curves obtained of mPCM A, B, and C (green, red, and blue of Figure 3) demonstrate the determination of **increased ruggedness and stability** of the PCM once it has been protected by an outer coating.
- **Insight into capsule rupture temperature.** When optimizing the microencapsulation process of new PCMs, TGA can give insight into what temperatures might start to decompose the microcapsules. MPCM C appears to be the most durable of these three examples.
- The presence of **water and volatile organic compounds** can be determined by investigating mass losses below 150°C.

151 Cheshire Lane N., Suite 400, Plymouth, MN 55441 USA
P: +952-941-0306 | F: +952-944-6893 | www.puretemp.com

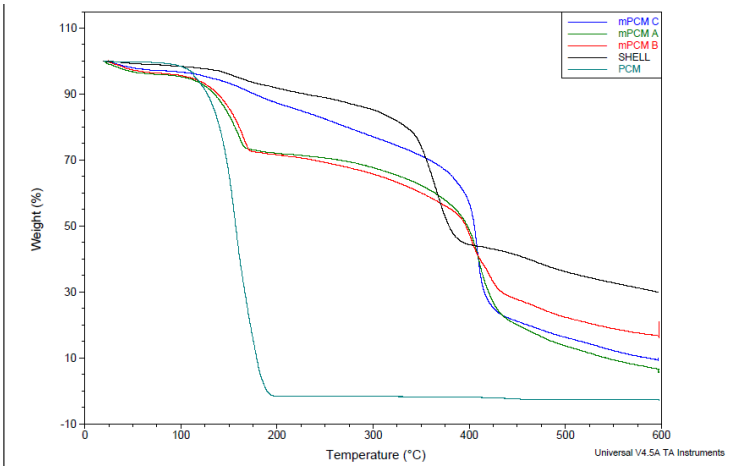

Figure 3. Comparison of three formulations of mPCM to the shell and "neat" PCM.

What are thermal cycling investigations?

MPCMs must maintain structural integrity as well as thermal properties after incremental thermal cycles. RAL Quality Association PCM is a European-based organization that develops standards for the PCM industry.[1] TGA and DSC can be used to monitor thermal cycling effects on the mPCMs at RAL-recommended intervals. Comparison to the original materials is a definitive way to assure that the materials will perform well in final applications.

Reference

1. "Quality and Testing Specifications for Phase Change Materials," RAL Quality Association PCM, November 2013 (http://www.pcm-ral.de/uploads/media/RAL_GZ_896_Phase_Change_Material__Edition_November_2013__03.pdf)

About the author

Dr. Heather M. Watson earned her Ph.D. in chemistry at the University of Alabama in 2011. As manager for analytical services, she developed the lab methods and procedures associated with Entropy Solutions' ISO 9001 quality management system and oversees key analytical laboratory testing of all manufactured lots. She has expertise in a number of advanced analytical techniques including differential scanning calorimetry and mass spectrometry.

151 Cheshire Lane N., Suite 400, Plymouth, MN 55441 USA
P: +952-941-0306 | F: +952-944-6893 | www.puretemp.com