

Thermal analysis of amorphous materials (polymers, metallic glasses)

Differential Scanning Calorimetry (DSC) is a thermal analysis technique that looks at how the materials heat capacity is changed by temperature. A sample of known mass is heated or cooled and the changes in its heat capacity are tracked as changes in the heat flow. This allows the detection of transitions such as melts, glass transition, phase changes and curing. Because of this flexibility, since most materials exhibit some sort of transition, DSC is used in many industries, including pharmaceuticals, polymers, food agriculture manufacturing and electronics.

The biggest advantage of DSC is the ease and speed with which it can be used to see transitions in materials. If somebody works with polymeric materials of any type, the glass transition is important to understanding investigated material. In liquid crystals, metals and pure organics, one can see phase changes or polymorphs and study the degree of purity in materials. The DSC measurements give knowledge of a material's heat capacity and heat content change (enthalpy) can be used to estimate how efficiently studied process is operating. For these reasons, DSC is the most common thermal analysis technique.

DSC is a technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned. The term DSC was coined to describe this instrument which measures energy directly and allows precise measurements of heat capacity.

An alternative technique, which shares much in common with DSC, is differential thermal analysis (DTA). In this technique it is the heat flow to the sample and reference that remains the same rather than the temperature. When the sample and reference are heated identically, phase changes and other thermal processes cause a difference in temperature between the sample and reference. Both DSC and DTA provide similar information. DSC measures the energy required to keep both the reference and the sample at the same temperature whereas DTA measures the difference in temperature between the sample and the reference when they are both put under the same heat.

Applications

Differential scanning calorimetry can be used to measure a number of characteristic properties of a sample. Using this technique it is possible to observe fusion and crystallization events as well as glass transition temperatures (T_g). DSC can also be used to study oxidation, as well as other chemical reactions.

Glass transitions may occur as the temperature of an amorphous solid is increased. These transitions appear as a step in the baseline of the recorded DSC signal. This is due to the sample undergoing a change in heat capacity; no formal phase change occurs. As the temperature increases, an amorphous solid will become less viscous. At some point the molecules may obtain enough freedom of motion to spontaneously arrange themselves into a crystalline form. This is known as the crystallization temperature (T_x). This transition from amorphous solid to crystalline solid is an exothermic process, and results in a peak in the DSC signal. As the temperature increases the sample eventually reaches its melting temperature (T_m). The melting process results in an endothermic peak in the DSC curve. The ability to determine transition temperatures and enthalpies makes DSC a valuable tool in producing phase diagrams for various chemical systems.

Examples

The technique is widely used across a range of applications, both as a routine quality test and as a research tool. The equipment is easy to calibrate, using low melting indium at 156.6 °C for example, and is a rapid and reliable method of thermal analysis.

Metallic glasses

In order to avoid crystallization, the metallic glasses were cooled down very quickly, and the liquid/liquid phase separation has been found to play an important role at deep undercooling, reducing the thermal stability and in many cases deteriorating the mechanical properties of these materials. When bulk glassy-type alloys are heated at an ordinary heating rate, they always exhibit glass transition, followed by a significant supercooled liquid region with a temperature interval of 40–130 K and then crystallization. This is in contrast to the direct transformation to the crystalline phase for the amorphous-type alloys produced by rapid solidification.

Since the magnificent importance of the glass transition, many methods have been adopted to conduct the determination. For instance, the differential scanning calorimetry, thermo-mechanical analysis, dynamic mechanical analysis, density measurement and viscosity measurement. Among them, DSC measurement is most widely used, since the endothermic and exothermic processes are very obvious on the DSC curve. The initial temperature of the glass transition which is most commonly used in the research is determined by seeking the inflection point within the first endothermic elevation.

Thermal stability of BMGs can also be determined by using the kinetic parameter called the activation energy of the crystallization process, which is closely connected to the crystallization onset temperature. The higher this energy is, the harder the alloys get crystallized, that is why higher T_x is expected.

In the supercooled liquid region, one can recognize the Newtonian viscosity, as evidenced by a nearly constant viscosity in a wide strain rate range . The supercooled liquid region ΔT_x , which equals to the difference between T_x and T_g , means the stage between the glass transition temperature T_g and the crystallization temperature T_x . This region exists before crystallization, during which the amorphous phase relaxes and changes into a metastable liquid with high viscosity. The viscosity will also vary during the heating process. It can even change from 10^{12} Pa*s at the glass transition temperature, to 10^5 Pa*s at the crystallization temperature.

The activation energy of crystallization could be obtained by the Kissinger equation :

$$\ln \left(\frac{dT}{dt} \right) = - \frac{E_a}{RT_p} + \text{Const}$$

where E_a stands for the activation energy of crystallization, dT/dt stands for the heating rate, T_p is the peak crystallization temperature, R is the real gas constant with the value of $8.3145\text{J/mol}\cdot\text{K}$, and the constant depends on the material. In order to calculate the activation energy, the T_p at several heating rates are needed.

Schedule

1. Determination by the differential thermal analysis characteristic temperatures, such as: T_g – glass transition temperature, T_x – onset temperature of crystallization, T_m – melting temperature.
2. Continuous heating of alloys with a range of heating rates in order to calculate activation energy. Activation energy is needed in the Kissinger equation.