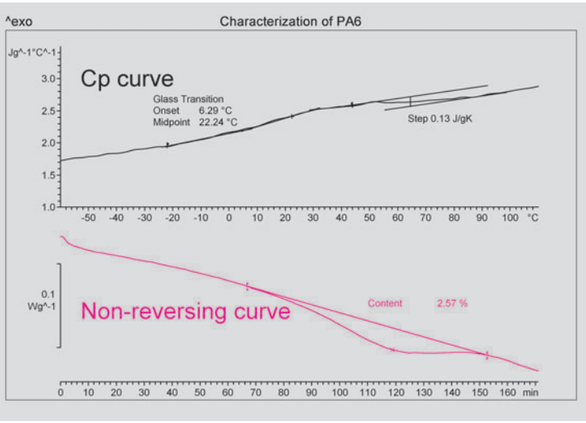
Application examples

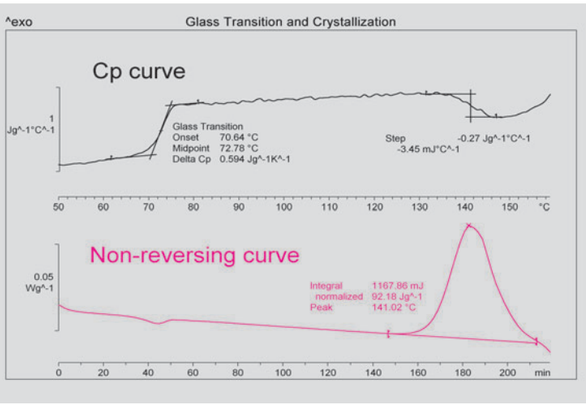
Enhanced characterization of nylon (PA6)



Due to its mechanical properties, polyamide 6 (PA6) has been used for many years for the manufacture of gear wheels, bearings, screws, etc. The glass transition temperature (T_g) of PA6 can vary by as much as 70 K depending on the moisture content. The T_g is therefore a quality control value, which also indicates the material's moisture content. In conventional DSC curves, the peak due to the evaporation of water usually overlaps the T_g. This makes the evaluation of the T_g difficult. With IsoStep™, however, the effects are clearly separated – the T_g is measured in the c_p curve and the evaporation in the non-reversing curve.

The diagram shows the c_p and non-reversing curves of PA6 (isothermal and heating intervals of 60 s and heating rate of 2 K/min).The c_p curve shows a glass transition with a midpoint at about 22 °C. Compared with the typical T_g of dry PA6 (about 60 °C), the glass transition is shifted to lower temperatures through the influence of the moisture content, which acts as a plasticizer. Evaporation of the moisture gives rise to the broad endothermic peak in the non-reversing curve. The evaporation also causes the c_p of the sample to decrease (step of 0.13 J/gK in the c_p curve).

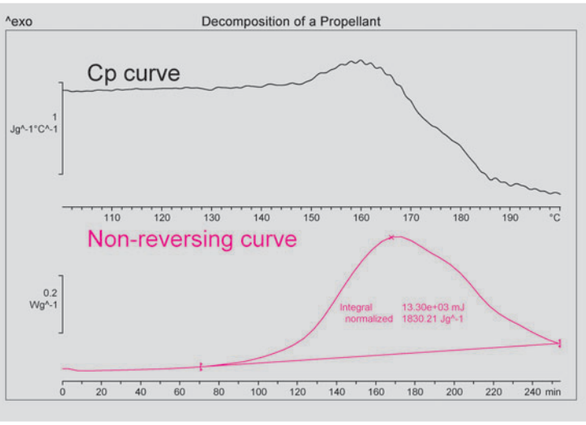
Glass transition and crystallization of amorphous sugar (sucrose)



In food technology, the glass transition temperature and the crystallization process of sucrose are important factors. They affect the stability of candies, the texture and shelf life of dried foods, and deep-freezing processes. One of the most interesting features of IsoStep™ is that it can separate different thermal processes such as the glass transition and crystallization.

Sucrose is usually amorphous when shock-cooled from the melt. The glass transition temperature is about 72.8 °C with a c_p change of 0.59 J/gK. This glass transition temperature is typical for anhydrous sugar. Moisture acts as a plasticizer and shifts the glass transition to lower temperatures. The enthalpy of crystallization is obtained by integrating the cold crystallization peak in the non-reversing curve. The c_p curve shows that the c_p decreases by about 0.27 J/gK during crystallization.

Investigation of the decomposition of a propellant



Exothermic chemical reactions present a number of potential hazards, such as the formation of toxic or inflammable gases or vapors, thermal decomposition and deflagration or even detonation of the reacting material. A thorough understanding of the materials used is essential to ensure the safety of a chemical plant or processes. The energy produced in an exothermic reaction is of particular interest to chemical engineers for process design and optimization. The autocatalytic behavior of a compound is also important from the safety point of view. IsoStep™ is an excellent technique to study such processes.

The energy of decomposition of a propellant can be evaluated from the non-reversing heat flow in an IsoStep™ experiment (isothermal intervals of 240 s, heating intervals of 60 s, heating rate of 2 K/min). Besides the reaction energy, data is also obtained on the decrease of c_p due to the decomposition of the sample.

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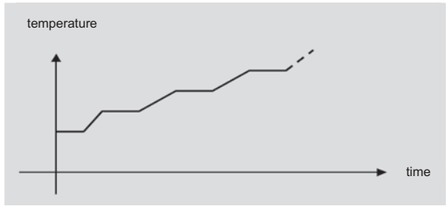
IsoStep™

This new software option allows thermal effects that occur simultaneously to be separated from one another. A typical IsoStep™ temperature program consists of a number of dynamic segments that begin and end with an isothermal segment.



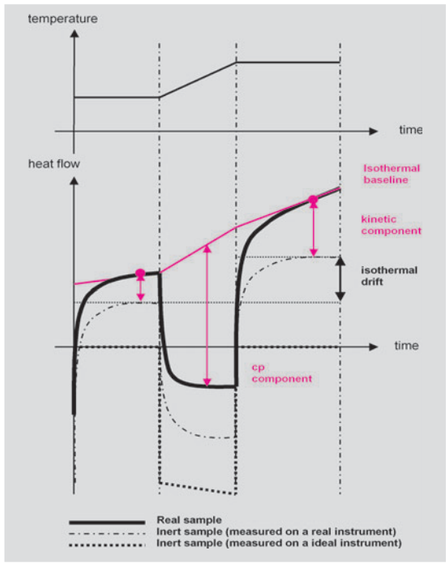
The evaluation method is based on an idea of Dr. S. C. Mraw and Dr. H. Dörr. The isothermal segments allow the isothermal drift of the dynamic segments to be corrected. This results in better c_p accuracy. The isothermal step may also contain kinetic information, for example of a chemical reaction.

IsoStep™ allows

- accurate c_p determinations to be made using a sapphire standard and
- kinetic effects to be separated from changes in heat capacity.

A number of interesting applications are foreseen for this technique:

Industry	Effects that can be analyzed with IsoStep™
Automobile and aerospace	Curing reactions, influence of moisture, glass transition, vitrification
Chemical	Exothermic reactions (safety investigations), glass transition, kinetics, crystallization behavior, polymorphism, drying, heat capacity
Electronics	Curing reactions, glass transition, vitrification
Paints	Curing reactions, influence of moisture, glass transition, drying, vitrification, evaporation
Rubber (elastomers)	Glass transition, phase behavior, melting, vulcanization
Plastics (thermoplastics, thermosets, fibers, films, textiles, adhesives, packaging cables)	Curing reactions, influence of moisture, enthalpy relaxation, glass transition, cold crystallization, phase separation, melting, melting and crystallization, vitrification, heat capacity
Foodstuffs	Influence of moisture, gelation, glass transition, stickiness, polymorphism, drying
Pharmaceuticals	Influence of moisture, glass transition, melting (isothermal step melting point), crystallization behavior, polymorphism, drying, heat capacity, decomposition behavior



Theory

DSC signals usually have to be corrected for baseline drift. In IsoStep™ this is done with the baseline correction procedure shown in the diagram.

One data point of the non-reversing curve is calculated for each isothermal segment (red dots).

The c_p of the sample at a temperature T can be calculated using measurements with a sapphire standard according to the following equations (sapphire is abbreviated to sap.):

$$c_{p\,\mathrm{sap.}}(T) = c_{p\,\mathrm{sap.\ lit.}}(T) = (\phi_{\mathrm{sap.}}(T) - \phi_{\mathrm{blank}}(T)) / (m_{\mathrm{sap.}} \cdot \beta) \cdot \mathrm{corr}(T)$$

where corr (T), the correction factor, is given by the equation

$$\Rightarrow \mathrm{corr}(T) = c_{p\,\mathrm{sap.\ lit.}}(T) / (\phi_{\mathrm{sap.}}(T) - \phi_{\mathrm{blank}}(T)) \cdot m_{\mathrm{sap.}} \cdot \beta$$

$$c_{p\ \mathrm{sample}} = (\phi_{\mathrm{sample}}(T) - \phi_{\mathrm{blank}}(T)) / (m_{\mathrm{sample}} \cdot \beta) \cdot \mathrm{corr}(T)$$

$$= (\phi_{\mathrm{sample}}(T) - \phi_{\mathrm{blank}}(T)) \cdot c_{p\,\mathrm{sap.\ lit.}}(T) / (\phi_{\mathrm{sap.}}(T) - \phi_{\mathrm{blank}}(T)) \cdot m_{\mathrm{sap.}} / m_{\mathrm{sample}}$$

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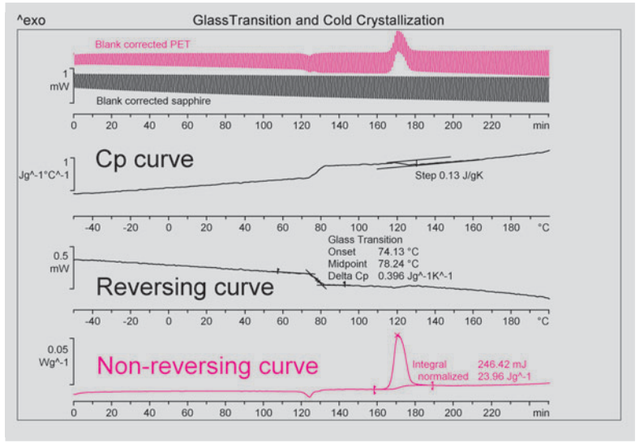
Tutorial example – PET



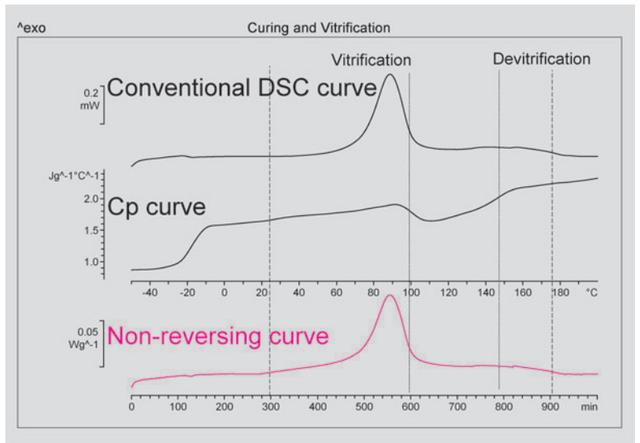
A typical IsoStep™ experiment consists of measuring the blank corrected sample and sapphire curves (two uppermost curves). The lower envelope of each curve corresponds to the heat flow during the dynamic segments, and the upper envelope to the heat flow during the isothermal segments. The IsoStep™ evaluation uses this data to calculate the c_p curve and the reversing and non-reversing curves:

1. The c_p curve – this shows changes in the specific heat capacity, for example due to a glass transition or a cold crystallization process. The curve is calculated from the data in the dynamic segments.
2. The reversing curve – this is calculated from the c_p curve and therefore contains the same information as the c_p curve.
3. The non-reversing curve – this shows effects such as enthalpy relaxation during a glass transition, evaporation, crystallization or a chemical reaction. The curve is calculated from the data in isothermal segments.

The c_p and reversing curves of the PET sample show a glass transition at about 78 °C. This is accompanied by enthalpy relaxation shown as an endothermic peak in the non-reversing curve. The sample then crystallizes at about 120 °C (exothermic peak in non-reversing curve) with a decrease in heat capacity of about 0.13 J/gK.

Application example

Curing behavior of epoxy resin

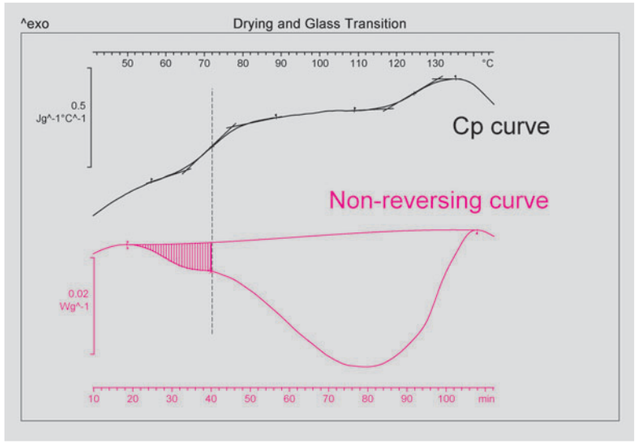


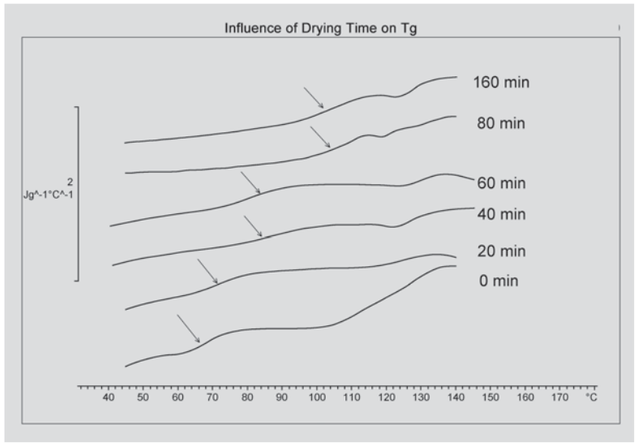
Thermosetting resins are widely used in the automobile, electronics, aerospace, and household products industries. DSC is often used to characterize the properties of thermosetting resins such as the glass transition, heat of reaction and degree of curing. Conventional DSC, however, cannot directly separate the effects of vitrification and devitrification from those of the curing reaction itself. Vitrification and devitrification have a dramatic effect on the kinetics of the reaction and hence on the curing process. IsoStep™ is an excellent method to obtain accurate information on vitrification and devitrification processes.

IsoStep™ (isothermal and heating intervals 60 s, heating rate 0.5 K/min) was used to measure the curing behavior of a two-component epoxy resin system. The diagram shows the c_p and non-reversing curves evaluated from the IsoStep™ measurement curves. For comparison, a conventional DSC curve (measured at 0.5 K/min) is also presented. It shows a glass transition at about –20 °C and curing reaction at about 90 °C. The IsoStep™ c_p curve shows a decrease in heat capacity due to vitrification at about 100 °C. The slow heating rate gives the sample sufficient time to form a relatively dense polymer network. As a result, the glass transition increases and becomes larger than the actual sample temperature, leading to vitrification of the sample. At this point, the reaction rate slows considerably, although the sample has not fully cured. On further heating, the glass transition of the partially cured material is finally reached at about 150 °C.

Application examples

Drying and glass transition of a pharmaceutical substance



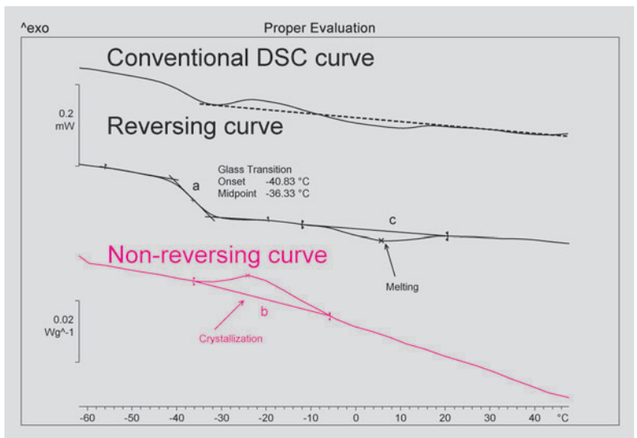


Different thermal events often occur simultaneously in a DSC measurement, e.g. crystallization, evaporation, glass transition. The separation of overlapping processes is important in order obtain data to optimize the storage and processing of food or pharmaceutical products.

The diagram shows the c_p and non-reversing curves of a pharmaceutical product dried at 80 °C for 20 minutes. The samples were measured in standard 40-µl aluminum crucibles (pierced lids – self-generating atmosphere) with isothermal and heating intervals of 30 s and a heating rate of 2 K/min. The c_p curve shows two glass transitions at about 70 °C and 125 °C. The broad evaporation peak observed in the non-reversing curve extends over the range of both glass transitions. The peak is so large that the glass transitions are not resolved in a conventional DSC curve. The first glass transition depends on the water content and is responsible for the powder being sticky. The actual water content at a particular temperature can be calculated from the ratio of the partial area (shaded) to the total area of the non-reversing curve.

The second diagram shows c_p curves measured after drying for different times at 80 °C. The glass transition is shifted to higher temperatures with longer drying times. These experiments allow the relationship between the glass transition temperature and water content of the material to be established. The results can be used to optimize processing conditions.

Interpretation of an elastomer analysis



The interpretation of DSC results from polymeric materials is not always easy without detailed knowledge of the sample because the transitions are sometimes very weak or overlapped by other events. In particular, the evaluation of the glass transition is often made difficult due to the presence of additives. IsoStep™ can often help to distinguish between different processes.

The diagram shows the conventional DSC curve of an SBR- based elastomer measured at a heating rate of 2 K/min as well as the IsoStep™ reversing and non-reversing curves (isothermal and heating intervals of 60 s, heating rate of 4 K/min). The DSC curve exhibits several thermal events, but the interpretation is not so obvious. The reversing and non-reversing curves, however, clarify the situation. The reversing curve indicates that a glass transition occurs at around -35 °C (**a**). The exothermic peak (**b**) in the non-reversing curve is attributed to the crystallization of additives. On further heating, a melting process occurs at about 5 °C, which is seen as an endothermic peak in the reversing curve.