Collected Applications
Thermal Analysis

ELASTOMERS
Volume 1
This application booklet presents selected application examples. The experiments were conducted with the utmost care using the instruments specified in the description of each application. The results were evaluated according to the current state of our knowledge.

This does not, however, absolve you from personally testing the suitability of the examples for your own methods, instruments and purposes. Since the transfer and use of an application is beyond our control, we cannot of course accept any responsibility.

When chemicals, solvents and gases are used, general safety rules and the instructions given by the manufacturer or supplier must be observed.

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Preface

This applications booklet provides an introduction to the thermal analysis of elastomers with a large number of practical examples. The main techniques used for sample measurement are thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). In particular cases, thermomechanical analysis (TMA) and combined techniques (TGA gas analysis) have also been employed.

In practice, thermal analysis is widely used for qualitative analyses. In fact however, the interpretation of the results and the final conclusions that can be drawn are greatly improved when quantitative measurements and evaluations are performed. We have therefore focused our attention on quantitative thermal analysis and outlined the basic principles for performing reliable measurements. The influence of experimental conditions on the measurement results is also covered.

Besides elementary considerations, a number of complex analyses and relationships are discussed.

The Elastomer Collected Applications booklet is published in two separate volumes.

Volume 1 contains Chapters 1 to 3 and includes an introduction to methods of thermal analysis, a description of the structure, properties and applications of elastomers as well as a discussion of the basic thermal effects observed with elastomers. This volume also contains an experimental section in which the various methods used to evaluate these effects are described.

Volume 2 contains Chapters 4 and 5 and presents a large number of application examples. It includes a detailed interpretation of the results as well as a summary of the results.

I hope that the applications described in these two volumes will find wide interest and stimulate new ideas both for experts and for newcomers to this rather complex and interesting field.

I would like to thank Dr. Claus Wrana (Bayer AG, Leverkusen) in particular for making the samples available and for many discussions. I also thank Willi Weber (Huber and Suhner AG, Pfäffikon) for supplying the measurement data for Sections 4.3.1 and 4.7.1 and Christian Krebs (Uetendorf) for assistance in procuring samples.

Furthermore I would like to thank all my colleagues at METTLER TOLEDO, Schwerzenbach, Switzerland for their help and motivation: above all Dr. Markus Schubnell (for measurements on filled SBR and MS measurements), Cyril Darribère (for FTIR measurements), Dr. Rudolf Riesen (for TMA measurements and helpful discussions), Georg Widmann and Dr. Dudley May for proofreading the original German manuscript. I also owe my thanks to Dr. Dudley May for translating the German text into English and for many helpful suggestions.

Schwerzenbach, June 2002

Dr. Jürgen E. K. Schawe
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3. Basic thermal effects of elastomers

This section discusses the basic effects observed in the thermal analysis of elastomers and their starting materials. A number of different evaluation possibilities are presented.

3.1. Measurement effects with DSC

3.1.1. Evaluation of glass transitions

Measurement of the glass transition temperature with DSC

<table>
<thead>
<tr>
<th>Purpose</th>
<th>To evaluate the glass transition using SBR as an example.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>Uncross-linked SBR</td>
</tr>
<tr>
<td>Conditions</td>
<td>Measuring cell: DSC822(^e) with liquid nitrogen cooling option</td>
</tr>
<tr>
<td></td>
<td>Pan: Aluminum 40 (\mu)l</td>
</tr>
<tr>
<td></td>
<td>Sample preparation: Flat disk of approx. 10 mg cut from the starting material. The sample was first cooled from room temperature to (-100) °C at 5 K/min.</td>
</tr>
<tr>
<td></td>
<td>DSC measurement: Heating from (-100) °C to 50 °C at 10 K/min</td>
</tr>
<tr>
<td></td>
<td>Atmosphere: Nitrogen, 50 ml/min</td>
</tr>
</tbody>
</table>

Glass Transition of SBR

- Onset \(-22.75\) °C
- Midpoint \(-19.82\) °C
- Midpoint ASTM, IEC \(-19.82\) °C
- Delta \(\Delta cp\) ASTM, IEC 0.433 Jg\(^{-1}\)K\(^{-1}\)
Interpretation

Amorphous and semicrystalline materials exhibit a glass transition after cooling to a sufficiently low temperature. Above the glass transition, the material is a more or less viscous liquid. Cross-linking through vulcanization does not change this situation either. Vulcanization does however restrict the flow to such an extent that the material retains its shape. The molecules can perform liquid-specific cooperative rearrangements in this temperature range. Below the glass transition temperature, cooperative molecular rearrangements are “frozen”. The material is in a glassy state. The change in molecular mobility causes a step in the heat capacity curve at the glass transition.

The actual shape of the curve at the glass transition varies depending on the thermal and mechanical history of the sample. If the material is stored below the glass transition temperature, undergoes mechanical stress or is cooled slowly to the glassy state, a peak can often be observed next to the glass transition step on heating. The peak is due to enthalpy relaxation.

Evaluation

The most important quantities in the evaluation of the glass transition are the temperature of the glass transition, $T_g$, and the change in the heat capacity at the glass transition, $\Delta c_p$.

These quantities are determined by drawing tangents on the heat flow curve at temperatures above and below the glass transition. The tangents should be selected carefully because they have a significant effect on the quality and reproducibility of the evaluation.

The glass transition temperature is a characteristic temperature for the step in the measurement curve. It can be determined according to various standard methods, e.g. as the temperature at half the step height or as the point of intersection of the bisector of the angle between the tangents with the measurement curve.

In the above diagram, the glass transition temperature of uncross-linked SBR was determined using the ASTM standard method. The value of $-19.8$ °C obtained is identical to the $T_g$ determined from the point of intersection of the angle bisector (midpoint).
Evaluation possibilities for the glass transition

Purpose
To describe the various methods for evaluating the glass transition using SBR as an example.

Sample
Uncross-linked SBR

Conditions
Measuring cell: DSC822e with liquid nitrogen cooling option
Pan: Aluminum 40 µl, with pierced lid
Sample preparation: Elastomer sample of 11.970 mg; The sample was cooled from 10 °C to −50 °C at 0.2 K/min or 20 K/min.
DSC measurement: Heating from −100 °C to 50 °C at 10 K/min
Atmosphere: Nitrogen, 50 ml/min

<table>
<thead>
<tr>
<th>Method</th>
<th>Glass Transition</th>
<th>Onset</th>
<th>Midpoint</th>
<th>Delta Cp</th>
<th>Midpoint DIN</th>
<th>Midpoint ASTM,IEC</th>
<th>Midpoint Richardson</th>
<th>Delta cp DIN</th>
<th>Delta cp ASTM,IEC</th>
<th>Delta cp Richardson</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exo</td>
<td></td>
<td>−19.83 °C</td>
<td>−18.34 °C</td>
<td>0.463 Jg−1K−1</td>
<td>−18.40 °C</td>
<td>−18.05 °C</td>
<td>−22.31 °C</td>
<td>0.472 Jg−1K−1</td>
<td>0.449 Jg−1K−1</td>
<td>0.461 Jg−1K−1</td>
</tr>
</tbody>
</table>

The figure shows the DSC curves of samples that had been cooled beforehand at 0.2 K/min (black curve) or at 20 K/min (red curve).

Interpretation
The shape of the glass transition curves depends on the thermal history of the sample. If the heating rate is greater than the rate at which the sample was cooled, then the glass transition is accompanied by an enthalpy relaxation peak. This effect can be seen in the black curve. The red curve was measured after the sample had been cooled rapidly, i.e. the heating rate of the measurement was less than cooling rate. In this case, an enthalpy relaxation peak is not observed. Storage of the sample at temperatures in the range of the glass transition or below can also give rise to an enthalpy relaxation peak.
The characteristic quantities of the glass transition are the glass transition temperature, $T_g$, and the step height at the glass transition, $\Delta c_p$. Various standard methods are used to determine these quantities. Several of these methods are incorporated in the STAR® software. Besides the STAR® method itself, these include the DIN 51007 (DIN), the ASTM E 1356 and IEC 1006 (ASTM, IEC) evaluation methods as well as the determination of the fictive temperature at the glass transition according to Richardson (also described in DIN 51007).

As can be seen from the figure, the values obtained for the glass transition temperature and the step height depend on the method of determination used. If the glass transition does not have an enthalpy relaxation peak, the glass transition temperatures determined by the STAR®, ASTM and DIN methods are practically the same. The value determined by the Richardson method is slightly lower (about 0.6 K). A comparison of the step heights at the glass transition shows that the $\Delta c_p$ values can be divided into two groups (STAR®, and DIN methods: 0.466 J/gK; ASTM and Richardson methods: 0.432 J/gK).

If an enthalpy relaxation peak occurs, then the differences between the individual $T_g$ and $\Delta c_p$ values obtained from the different evaluation methods increase. The various methods are described below to show how these differences arise and to provide a basis for selecting the most suitable evaluation method for a particular application.

**Evaluation of the glass transition temperature:**

**STAR® method (+):**
The bisector, $a_1$, of the angle between the tangents above and below the glass transition is drawn. The point of intersection of this line with the measured curve is the glass transition temperature (midpoint).
**DIN method (Δ):**
The glass transition temperature (midpoint DIN) is the temperature at which the measured curve is equidistant between the upper and lower tangents (c1 = c2). c1 is the distance between the measured curve and the tangent below the glass transition. c2 is the distance between the measured curve and the tangent above the glass transition.

**ASTM method (◊):**
The tangent is drawn at the point of inflection in the region of the glass transition in the measured curve. The glass transition temperature is the midpoint between onset and endset of the inflectional tangent (b1 = b2).

**Richardson method (□):**
Areas are determined between the extrapolated tangents and the measured curve. The individual areas are drawn in the diagram and labeled A1, A2 and A3. The highest temperature of the area A1 is identical to the lowest temperature of the area A2. When A1 + A3 = A2, this temperature is defined as the glass transition temperature.

![Diagram showing determination of the fictive temperature](image-url)
Evaluation of the step height at the glass transition:

\[ \Delta c_p = \frac{\Phi_u - \Phi_o}{m\beta} \]

\( \Phi_u \) and \( \Phi_o \) are the heat flows at the points of intersection of the extrapolated tangents with the inflectional tangent above and below the glass transition temperature, \( m \) is the sample mass and \( \beta \) the heating rate.

**DIN method:**

The step height is determined at the glass transition as in the \text{STAr}^e method, but instead of the inflectional tangent, the tangent of the measured curve at the DIN glass transition temperature is used. The tangent is shown in the diagram as a dashed red line.

**ASTM method:**

The distance between the extrapolated tangents at the ASTM glass transition temperature is calculated.

**Richardson method:**

The distance between the extrapolated tangents at the Richardson glass transition temperature is calculated.
Comments  The Richardson glass transition temperature describes the actual state of the material before the measurement. It cannot be determined if chemical reactions or physical processes (such as crystallization, evaporation) take place in the glass transition region or if glass transitions overlap. The value of the glass transition temperature obtained with the other methods is also influenced by the shape of the curve, i.e. by the measurement conditions. For comparative measurements, it is therefore important to use the same measurement conditions and evaluation method for the $T_g$ determination. In the ASTM and Richardson methods, the step height, $\Delta c_p$, at the glass transition temperature is determined. Differences in these values can arise because the two glass transition temperatures differ. The values can be directly related to properties of the materials such as degree of crystallinity or filler content. This is not possible with the other methods for determining $\Delta c_p$ (STAR and DIN) because the step heights determined then depend on the width of the glass transition (slope of the tangents). These values are therefore greater than those from the Richardson and ASTM methods. The ASTM method was therefore used to determine $\Delta c_p$ in the experiments described in this booklet (unless otherwise noted).

Conclusions  When determining quantities at the glass transition, it is important to quote the measurement and evaluation methods used.
Influence of sample pretreatment on the glass transition

The glass transition is a physical phenomenon related to cooperative rearrangements. If a supercooled liquid is cooled to a sufficiently low temperature, molecular movement freezes at the glass transition. The glass then formed has the mechanical properties of a solid but the structure of the liquid. This characteristic temperature is also known as the fictive temperature of the glass. The fictive temperature depends on cooling and storage conditions. The slower the cooling rate, the later molecular movement freezes. This is the reason why the fictive temperature is lower at lower cooling rates. The fictive temperature can also be defined as a glass transition temperature. The method used to determine this glass transition temperature in the STAR® software is the Richardson method.

Besides this definition of the glass transition temperature, other evaluation methods are also often used in practice. These methods involve the use of the curve shape such as the point of inflection or the temperature at which half the step height is reached (Section 3.1.1. Evaluation possibilities for the glass transition).

**Purpose**
To demonstrate the influence of the cooling conditions on the glass transition temperature using an amorphous elastomer as an example. The fictive temperature (Richardson method) and ASTM evaluation methods are compared.

**Sample**
Unvulcanized L-SBR (solvent-polymerized SBR)

**Conditions**

- **Measuring cell:** DSC822® with liquid nitrogen cooling option
- **Pan:** Aluminum 40 µl, with pierced lid
- **Sample preparation:** Elastomer sample of 11.970 mg. The sample was cooled from 10 °C to below the glass transition (−50 °C) at cooling rates of between 40 K/min and 0.1 K/min.
- **DSC measurement:** Heating rate: 10 K/min
- **Atmosphere:** Nitrogen, 40 ml/min
Evaluation

The glass transition temperatures were determined from the curves according to the ASTM and fictive temperature (Richardson) methods. In the evaluation, care was taken to ensure that the tangents above and below the glass transition were in each case parallel to one another. It can be seen that the glass transition temperatures obtained depend on the cooling rate of the sample prior to the measurement. In the following diagram, the glass transition temperatures obtained were plotted as a function of the logarithm of the cooling rate.
Interpretation

As can be seen in the measurement curve, it is possible that the step in the glass transition and the enthalpy relaxation peak overlap. The nature of this peak depends on the sample history and the measurement conditions. In the experiment described, no peak occurs if the cooling rate is greater than the heating rate (10 K/min). The relaxation peak becomes larger the greater the heating rate is compared with the cooling rate.

As discussed above, one expects the fictive temperature at the glass transition to be lower at lower cooling rates. From theoretical considerations of the glass transition, a linear relationship between the logarithm of the cooling rate and the glass transition temperature is expected. This relationship is confirmed if the glass transition temperature is evaluated according to the Richardson method. With the other methods for determining the glass transition temperature, the result is influenced by the actual shape of the curve. In those cases in which no enthalpy relaxation peak occurs, the glass transition temperatures determined according to the ASTM and Richardson methods show a similar dependence on the heating rate. The glass temperature according to the ASTM method is however about 1 K higher. As the relaxation peak increases, the ASTM glass transition temperature shifts to larger values. All the methods used for the determination of the glass transition temperature that depend on the shape of the curve (e.g. half step height method, point of inflection, etc.) show a similar dependence of the glass transition temperature on the heating rate as the ASTM method.

Conclusions

Whenever glass transition temperatures are quoted, the method of determination used should be stated. When glass transition measurements are compared, sample pretreatment should be identical.
3.1.2. Crystallization and melting

The crystallinity of elastomers can be investigated by DSC. Above the glass transition temperature, the crystallites melt giving rise to an endothermic measurement peak. The peak width, temperature position and area provide information about the structure of the material.

The peak area allows the degree of crystallinity to be evaluated. The greater the proportion of crystallites, the larger the peak. The peak temperature range provides information that relates to the size and degree of perfection of the crystallites. Larger and better crystallites melt at higher temperatures. If melting temperatures and peak areas are used to obtain information on the size of crystallites, polymers of the same type have to be compared because the melting behavior differs with the type of polymer. This difference can also be used to identify polymers.

**DSC investigations on crystallinity**

<table>
<thead>
<tr>
<th><strong>Purpose</strong></th>
<th>To show the influence of crystallinity on DSC curves using different types of chloroprene as an example.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sample</strong></td>
<td>Unvulcanized CR types: CR 110, CR 112 and CR 210 (Bayer AG)</td>
</tr>
</tbody>
</table>
| **Conditions** | Measuring cell: DSC822\textsuperscript{e} with IntraCooler cooling option  
Pan: Aluminum 40 µl, with pierced lid  
Sample preparation: Cubes of approx. 15 mg were cut from the starting material  
DSC measurement: Heating from –60 °C to 100 °C at 10 K/min  
Atmosphere: Nitrogen, 50 ml/min |

| **\( ^{\text{exo}} \text{CR of Different Crystallinity} \)** | |
|----------------|------------------|------------------|------------------|
| CR 110 | CR 110 | CR 112 | CR 210 |
| Integral | \(-2.81 \text{ mJ}\) | \(-1.37 \text{ mJ}\) | \(-107.29 \text{ mJ}\) | \(-2.81 \text{ mJ}\) |
| normalized | \(-0.17 \text{ Jg}^{-1}\) | \(-0.002 \text{ Jg}^{-1}\) | \(-0.2 \text{ Jg}^{-1}\) | \(-0.17 \text{ Jg}^{-1}\) |
| Peak | \(41.23 \degree \text{C}\) | \(42.55 \degree \text{C}\) | \(41.23 \degree \text{C}\) | \(41.76 \degree \text{C}\) |
Evaluation  All the CR samples show a melting peak with a peak maximum at about 42 °C. No information can be gained on the relative perfection and size of the crystallites from the small differences in the peak temperature range. However the large difference in peak areas shows that the proportion of crystallites is very different. The evaluation of the peak area gave the following results:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak area in J/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>CR 110</td>
<td>0.07</td>
</tr>
<tr>
<td>CR 112</td>
<td>0.17</td>
</tr>
<tr>
<td>CR 210</td>
<td>6.00</td>
</tr>
</tbody>
</table>

For CR 210, both the clearly defined glass transition and the relatively small peak area of 6 J/g indicate that the degree of crystallinity is low. A comparison of the peak areas, however, shows that the degree of crystallinity of CR 210 is about 86 times greater than that of CR 110, and that of CR 112 about 2.5 times greater than that of CR 110.

Interpretation  All three chloroprene curves show a glass transition at approx. −40 °C and an endothermic peak at about 40 °C that is due to the melting of the polymer crystallites. The ability of the CR types to crystallize differs because the structure of the polymer chains are different. This is why the peak areas are different. CR 210 has a relatively large tendency to crystallize. The relatively small melting peak of CR 110 shows that the tendency of this material to crystallize is appreciably less. Hardly any crystallites at all could be detected in CR 110. A melting peak was only visible after 50-fold scale expansion (see upper left diagram).

The absolute degree of crystallinity cannot be determined without knowledge of the specific enthalpy of fusion of the 100% crystalline material. This is, however, not needed for comparative measurements.

Conclusions  An evaluation of the peak area of melting peaks yields information on the degree of crystallinity of elastomers.
Determination of crystallinity

Semicrystalline polymers exhibit an endothermic peak in the DSC curve that is due to the melting of the crystallites. The degree of crystallinity of the material can be determined from the peak area. This is described using EPDM as an example.

**Purpose**
To determine the degree of crystallinity from DSC curves.

**Sample**
Unvulcanized EPDM (EPG 6170).

**Conditions**
- Measuring cell: DSC822e with liquid nitrogen cooling option
- Pan: Aluminum 40 µl, with pierced lid
- Sample preparation: Cube of approx. 5 mg cut from the starting material. The sample was heated to 100 °C before the measurement and then cooled at 5 K/min to the starting temperature.
- DSC measurement: Heating from −120 °C to 100 °C at 10 K/min
- Atmosphere: Nitrogen, 50 ml/min.

**Interpretation**
The step in the curve at −45 °C shows the glass transition of the partially crystalline material. Only the mobile amorphous part is involved in the glass transition. The endothermic melting peak begins immediately afterward.
**Evaluation**  With such broad melting peaks, it is not always so easy to reproducibly determine the beginning of the peak for the determination of the peak area. In such cases it helps if the DSC curve has been recorded over a sufficiently wide range in the melting region. The baseline of the peak should agree well with the linear extrapolation of the heat flow curve to lower temperature from the region of the melt (see Section 3.1.2. *Glass transition and melting of EPDM*). The degree of crystallinity, \( \alpha \), can then be estimated from the peak area:

\[
\alpha = \frac{\Delta h}{\Delta h_c} \cdot 100\%
\]

where \( \Delta h \) is the specific enthalpy of fusion (in J/g) of the sample determined from the peak area, and \( \Delta h_c \) is the enthalpy of fusion of a 100% crystalline material. In the case of EPDM, the value of polyethylene of 290 J/g can be used for \( \Delta h_c \). The evaluation of the measured curves yielded the following values:

- Peak area: 46.0 J/g
- Crystallinity: 15.9%

**Conclusions**  The specific enthalpy of fusion of a sample determined from the peak area is proportional to its degree of crystallinity. The proportionality factor, \( \Delta h_c \), is equal to the enthalpy of fusion of a 100% crystalline material. If the value is known, the degree of crystallinity can be determined from the melting curve.

**Comments**  In general, for polymers, the enthalpy of fusion of the fully crystalline material, \( \Delta h_c \), cannot be obtained from DSC measurements - due to their molecular structure polymers have amorphous (non-crystalline) regions.

The values of \( \Delta h_c \) can often be obtained from the scientific literature or databases.

One method for the determination of \( \Delta h_c \) is the combination of wide angle X-ray scattering (WAXS) and DSC. In this method, a material is used that, because of its chain structure, can attain a relatively high degree of crystallinity. The material is thermally treated so that a high degree of crystallinity is obtained. This can be done, for example, by slow cooling from the melt (e.g. at 0.1 K/min) or through stepwise isothermal cooling. The degree of crystallinity, \( \alpha \), is then determined by X-ray measurements. DSC measurements yield the specific enthalpy of fusion, \( \Delta h \). This data is then used to calculate \( \Delta h_c \):

\[
\Delta h_c = \frac{\Delta h}{\alpha} \cdot 100\%
\]