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THERMAL ANALYSIS FOR PLASTICS AND RUBBER ENGINEERING

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A survey of the possibilities of Thermal Analysis (TA) in the plastics and rubber industry is presented. As well as giving examples from research (liquid crystalline main and side chain polymers) and construction (laminates of carbon fibre reinforced epoxy resin prepregs), the field of quality assurance and material characterization is specially discussed. The correlation between TA-characteristics such as the degree of crystallinity and mechanical properties (e.g. hardness or green strength) is demonstrated. The application of thermogravimetry for a precise compositional analysis of compounded rubbers is shown. In practice, Thermal Analysis is most important for failure analysis and the characterization of processing parameters during the production of moulded parts as TA-methods are usually much faster than traditional standard methods. Moreover, the increasing importance of combining TA-methods with other techniques of instrumental analysis is demonstrated. An example of this combination is the TG-DSC-MS coupling which is invaluable in the area of environmental protection especially in the production, application and recycling of moulded parts from polymeric materials.

Introduction

Thermoanalytical instrumentation also coupled with other instruments for physico-chemical analysis such as mass spectrometry, infrared spectroscopy, etc. is an efficient tool which can be used to investigate the properties of polymeric materials as a function of temperature, time and mechanical load, even under a given sample atmosphere. The application of these techniques is not limited to the field of research, development and quality control, but they also used increasingly both in the ranges construction, processing, failure analysis and in environmental pollution control. In this work examples from all these ranges are discussed. All methods of Thermal Analysis are more or less equally important, which is also proved from experience in the field of polymers [1].

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Examples from research, development and construction

In the last few years self-reinforcing thermoplastics, the so-called liquid crystalline polymers (LCP), appeared as a new polymer class in the range of the polymer production. These materials are competitors of the fiber-reinforced thermoplastics and thermosets. The self-reinforcing effect is caused by the arrangement of the rod-shaped molecules parallel to the flow direction of the melt during the filling of the mould. This causes a high tensile strength parallel, and a lower one perpendicular to this direction. This anisotropy and the formation of binding seams during processing, which cause a tremendous reduction in tensile strength, are the main problems in the way of a broader application of LCP.

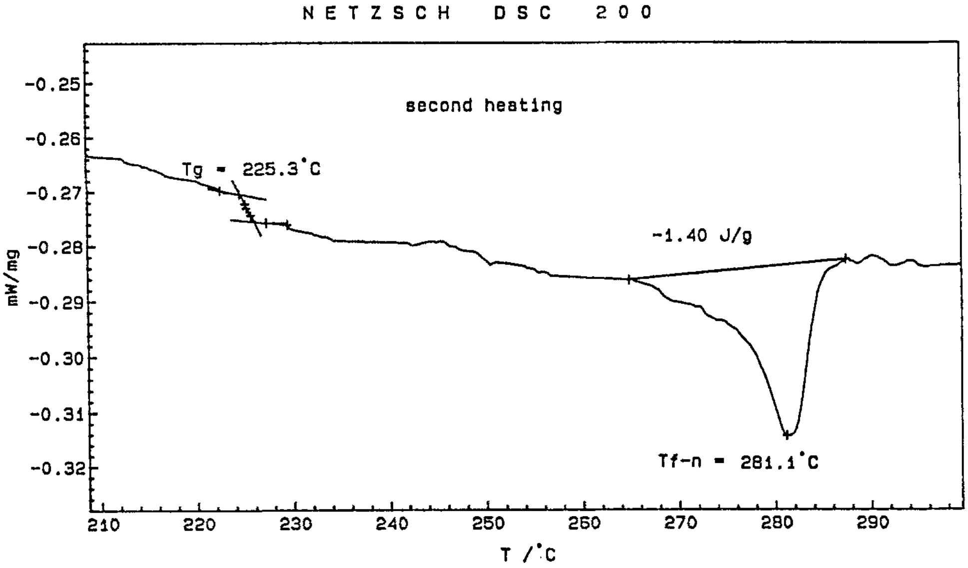


Fig. 1 DSC-curve of a liquid crystalline thermoplast with transition from a rigid crystalline order to the nematic liquid crystalline order

At the moment only thermotropic main chain-LCP [2, 3] are commercially available as injection moulding and extrusion grades. Because of the rigid chain structures most of the polymers with mesogenic groups in the main chain are high-melting. Therefore so-called spacers must be built in the chain for processing from the melt. Injection moulding grades mostly show a nematic structure. In this way an extremely low processing viscosity is reached which is necessary for filling thin-walled, complicated moulds. This is due to the fact that only very small heats of fusion appear during the transition from the rigid condition to the mesophase (Fig. 1) which also leads to very small heats of crystallization when the part freezes. These small heats of crystallization allow processing with short cycle times and one can therefore produce economically although the price of the raw material is very high.

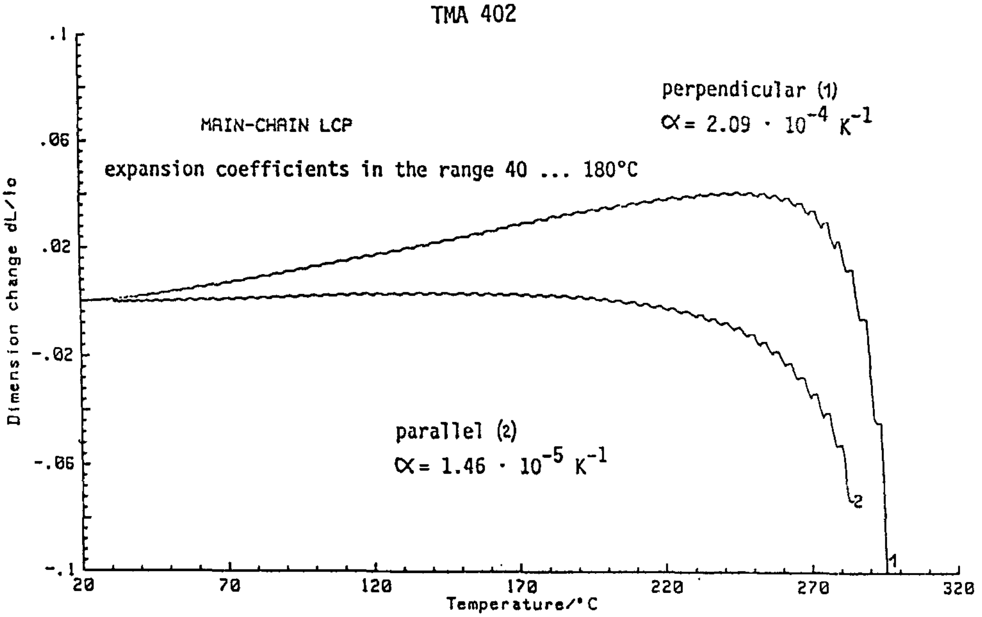


Fig. 2 Thermal expansion coefficient of a main-chain LCP parallel and perpendicular to the direction of flowing of the melt

If the finished part is tempered at temperatures between T_g and T_f concerning partly crystalline LCP, some LCP show a post-crystallization which leads to an additional increase in stiffness.

The thermal expansion coefficient may also show large anisotropies depending on the processing parameters (Fig. 2). This is a very important characteristic for composite construction. The thermal expansion coefficient, parallel to the flow direction, is adjustable between about 0 and 20 × 10^{-6} 1/K. The consequence of this very small thermal expansion is also, of course, a very small shrinkage in this direction, which helps the production of high precision parts [4].

While the group of the main chain LCP already has a small application range, especially in the electrical and electronics industry, the application possibilities of the side chain LCP are still to be explored. In the literature

[5], for example, the possibility is discussed of using such side chain LCPs with cylindrical structure as optical information storage.

DSC is a powerful instrument to characterize the relationship between mesophase-transformations and molecular setup of the LCP. This could be demonstrated for side chain polymethacrylate-LCP.

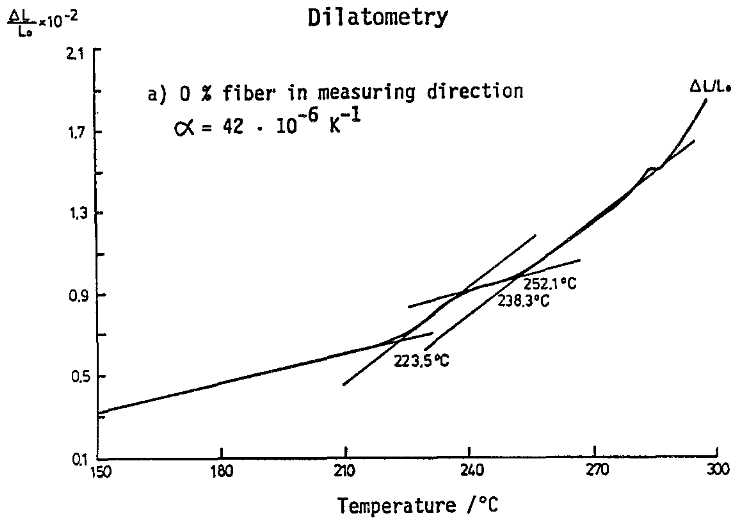


Fig. 3a Dilatometer curves of a CFR-laminate with 0% fiber part parallel to the measuring direction (a)

However, today LCP do not yet play as important a role as fiber reinforced materials. The carbon fiber laminates are of great importance, especially in aircraft construction. Among TA-methods in this field, TMA plays a very important role for the evaluation of expansion coefficients of uni- or multidirectional laminates in relationship to the measuring direction [6]. Figure 3a shows a dilatometer curve of a laminate with an effective percentage of 0% of fibers in measuring direction. In this case, a nearly linear expansion coefficient of 42 × $10^{-6}K^{-1}$ up to T_g at 223.5° is obtained which is mostly caused by the EP-resin matrix. DSC- and DMA-measurements reveal that the deflection of the TMA-curve at 238.5° is due to postcuring of the EP-resin. However, regarding multidirectional laminates with a percentage of about 60% of fibers in the measuring direction (Figs 3b and 3c), the expansion coefficients of about 4.7 × 10^{-6} K^{-1} are much lower than those of a laminate with 0% fiber in the measuring direction. The small differences between the two measuring directions in Fig. 3 are reproducible and can be explained by the different inhibition of the expansion by the carbon fiber due

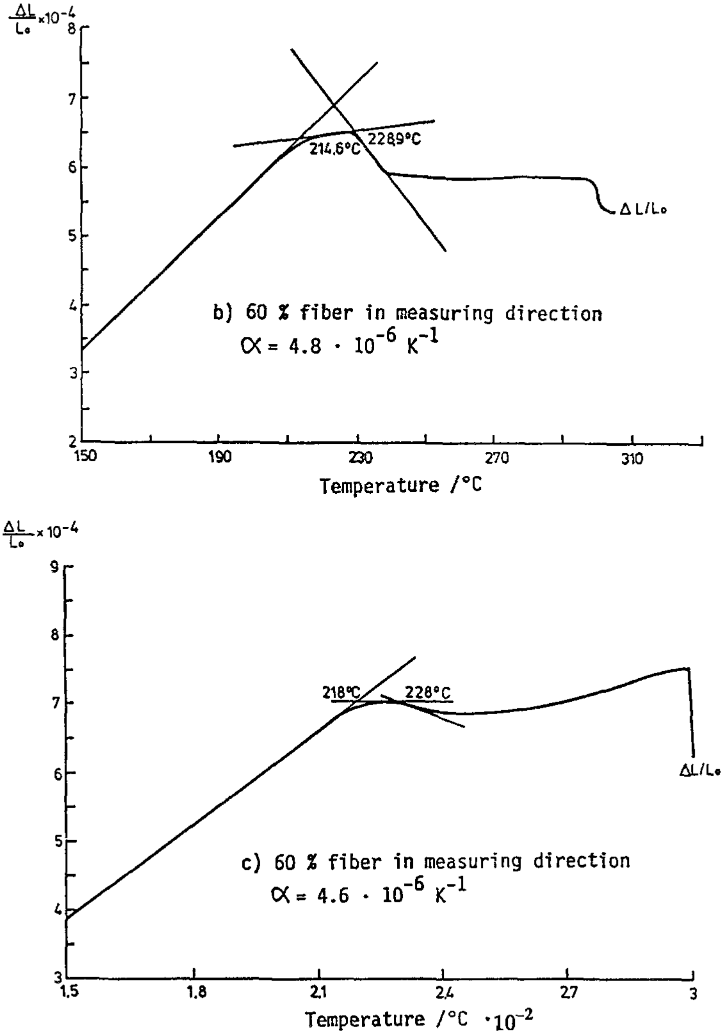


Fig. 3b,c Dilatometer curves of CFR-laminates with about 60% fiber part in two different measuring directions

to the manufacturing process of the laminates. The negative expansion above 230° again corresponds to the postcuring. Such postcuring of EP-resins is frequently discussed in the literature (see 7). After complete curing at about 240° no expansion of the sample can be observed. The sudden deflection of the expansion curve at about 300° can be explained by delaminations which could be proved by investigation by microscopy.

DSC and TMA are both well suited for the investigation of the compatibility (solubility) of polymers in blends. Figure 4 shows elastomers with

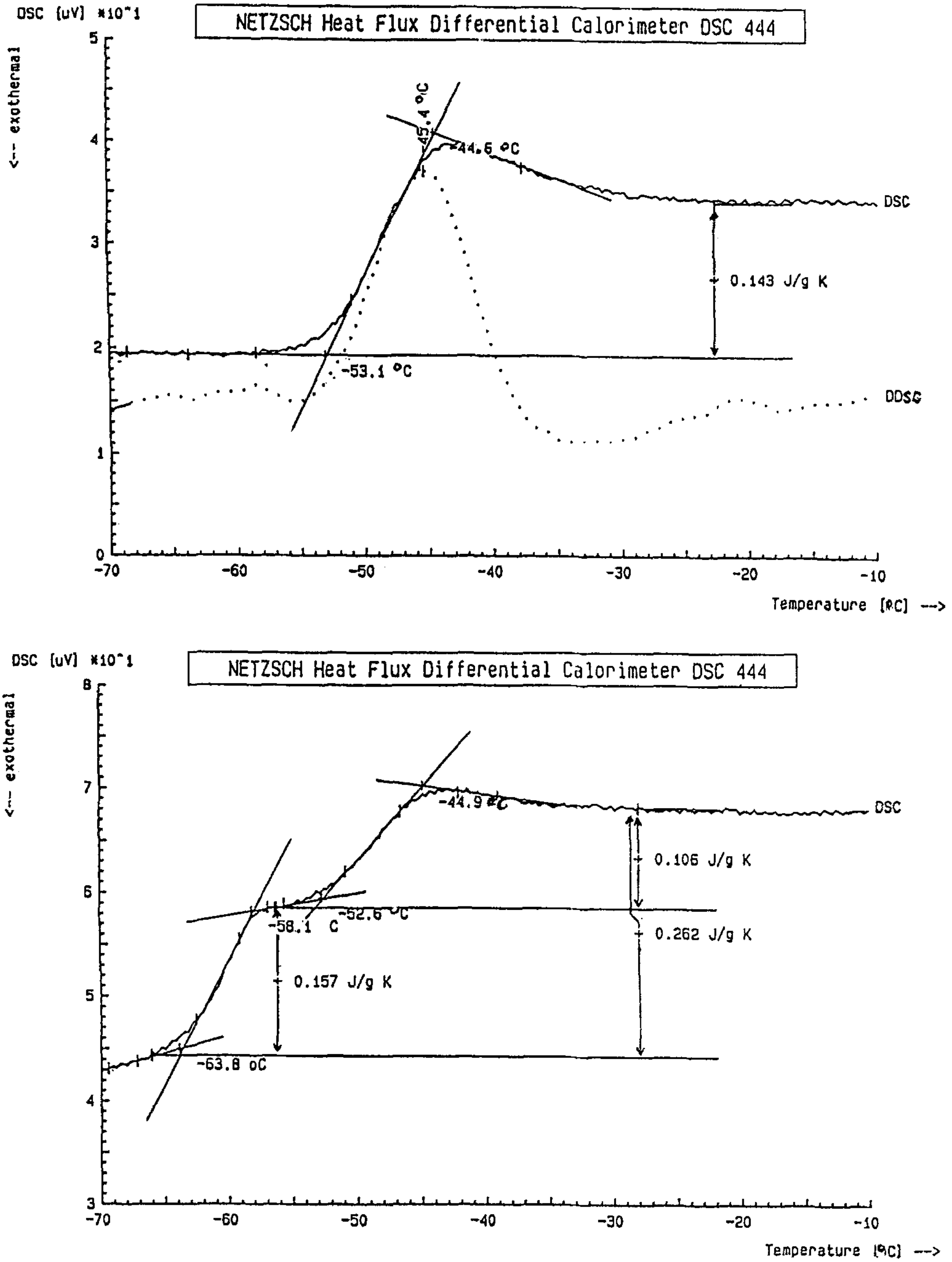


Fig. 4 DSC-curves of glass transition of SBR (on the top) and 50:50 blend of NR/SBR (on the bottom)

poor compatibility (natural rubber NR, Styrene-butadiene rubber SBR). The glass transition ranges known for the two elastomers from separate tests are detected almost unchanged in the blend.

Examples from polymer characterization and quality assurance

Thermoplastics

Not all standardized test methods can be replaced by Thermal Analysis. With the thermoanalytical methods it is possible to achieve a much shorter measuring period for many determinations. For example, determination of the ash content or the melting point, or a purity analysis are much faster compared to the traditional standardized methods. For polyamides, DSC is already standardized for the determination of the melting and the crystallization temperature [8, 9]. Since these values are material data, the thermomechanical history of the sample must be eliminated by a first heating followed by a controlled cooling. This is why mainly the cooling curves and the consecutive heating curves are evaluated [10]. It should be pointed out that the first heating is quite useful for the characterization of processing parameters of injection moulding and for failure analysis (see Chapter 4).

For semicrystalline thermoplastics many properties depend on the degree of crystallinity as, for example, hardness or toughness of the finished

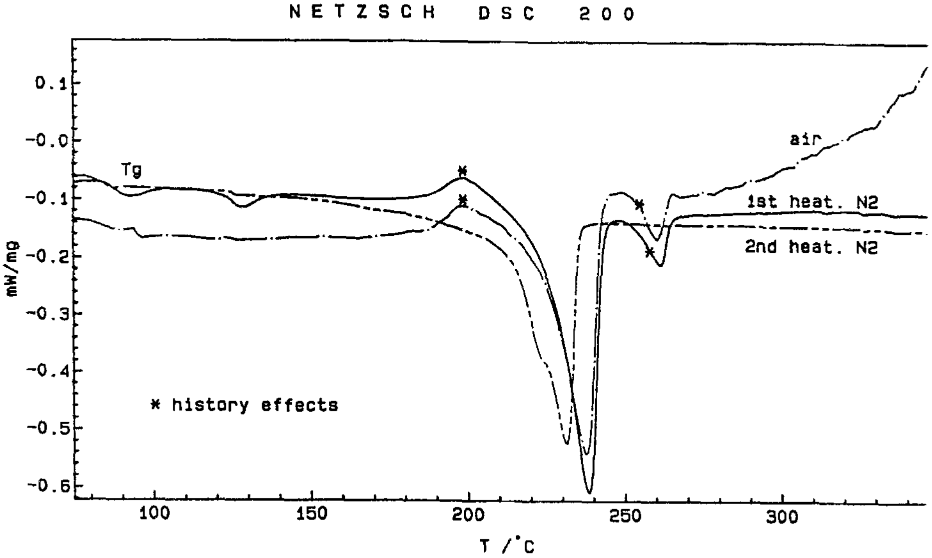


Fig. 5 DSC-curves (first and second heating after controlled cooling) of polyarylamide in dependence on the measuring atmosphere and the history

parts. At this point it should be emphasized that these properties may also strongly depend on the processing parameters like the temperatures of the melt and of the mould, forming different degrees of crystallinity due to the crystallization rate of the melt. In practice the degree of crystallinity is often determined using integral standard samples as a reference because the values given in literature for 100% crystalline material vary considerably. The possibility of investigating the nucleation of semicrystalline thermoplastics with the help of DSC is also important. Nucleated types have higher crystallization temperatures and mostly higher crystallization speeds than non-nucleated types. The producers of raw material often adjust the crystallization behaviour of their products with the help of the DSC or characterize them by DSC.

Table 1 Composition of the NBR mixture for oil-resistant sealings

Components	phr	%
NBR with an acrylonitril-content of 28%	100	49.1
carbon black N 650	60	29.5
synthetic plasticizer	30	14.7
processing means	3	1.5
protection means against aging	2	1.0
zinc oxide	5	2.5
sulphur	2.4	1.2
accelerator system	1.3	0.6
total	203.7	100.0
(phr: parts per hundred resin)	(%: % per weight)	

The influence of the sample atmosphere (air and N_2) as well as the first and second heating after a defined cooling of the melt is shown for polyarylamide (Fig. 5). While the effect at 92° during first heating can be assigned to the glass transition with enthalpy relaxation, the effect at 128° could not be made clear as it did not appear for other measurements in air. The exothermal peak at 200° belongs to the thermomechanical history of the sample and is mainly due to recrystallization. The endothermal peak at 260° is probably a second crystalline phase as during second heating two effects also appear in the melting range.

Rubbers

The most well-known application of thermogravimetry in the polymer field is the quantitative determination of the components of a rubber mix-

Table 2 Pyrolysis behaviour of rubber polymers [13] (heating rate: 30 deg/min, N_2)

Polymer	Peak range, °C	Peak maximum, °C	Pyrolytic carbon black, %
NR	325 – 450	380	–
SBR	350 – 490	455	up to 1.5
NBR	350 – 490	450	up to 7.0
EPDM	420 – 495	475	–
IIR	390 – 450	405	–
CB	330 – 490	380/460	–
CR	300 – 350/ 420 – 470	330/ca. 440	up to 20
PVC	260 – 300/ 400 – 500	280/ca. 460	in mixtures up to 30
Si	500 – 700	630	SiO_2-formation[1]
EVA	320 – 400/ 400 – 500	370/480	–
PE	420 – 500	480	–

[1] Caution: Should traces of oxygen be present, SiO_2-formation and therefore SiO_2-coating of the balance takes place.

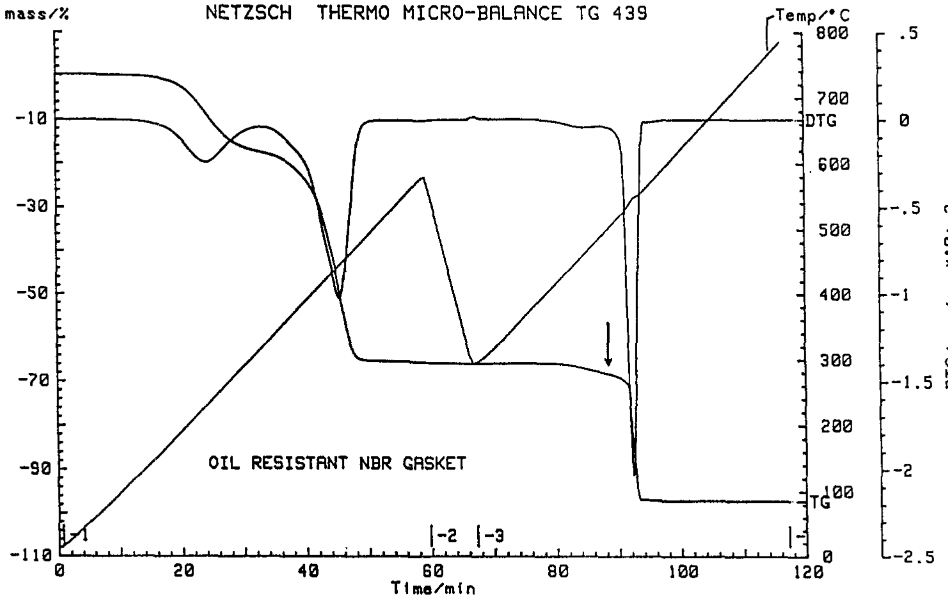


Fig. 6 TG-curve of an NBR-mixture for oil-resistant sealings

ture. In the following example important experimental parameters are indicated for the TG analysis of a nitrile rubber mixture the rubber polymer (NBR) is an acrylonitril-butadiene copolymer used for the production of oil resistant sealants. The composition is given in Table 1.

In order to avoid misinterpretation in the evaluation of TG-measurements of vulcanisates it is necessary to know the decomposition behaviour of the polymer. Table 2 shows an overview of the pyrolytic decomposition of the most important rubber polymers [14] with the amounts of the pyrolytic carbon black produced during TG-measurement. As one can see, it depends on the type and grade of the polymer. Thus the TG curve for the vulcanised mixture (Table 1) may be interpreted (Fig. 6). In nitrogen-atmosphere a first step can be seen from about 100° onwards which can be related to the evolution of moisture and the loss of the plasticizer and residue of the accelerator system. This step is finished at approximately 300°. The decomposition of the polymer starts at 335°, shows a maximum rate of decomposition at about 430° and is nearly complete at 490°. At 600° it is then cooled down to 300° and changed over to air. Only now the pyrolytic carbon black produced by the polymer and the carbon black N 650 burn down. The residue is the ash content of the mixture.

Table 3 Quantitative TG-analysis of the NBR mixture from Table 2

	Content in %		
	Measured values		Actual values
Components	with	without	
	correction		
NBR with an Acrylonitril content of 28%	49.3	47.8	49.1
carbon black N 650	28.0	29.2	29.6
synthetic plasticizer	14.5	17.6$^{1)}$	14.7
ash	5.1	5.4	

$^{1)}$ Including processing and protection means against aging as well as components of the accelerator system.

Table 3 shows the measured values with and without correction for the pyrolytic formed carbon black of the polymer itself and its ash content in comparison to the actual values.

As one can see, the main deviation exists between the TG results and the actual values for the amount of carbon black. Literature research [14–16] reveals that the quantitative and qualitative determination of carbon black in an unknown vulcanisate by TG is up to now an unsolved problem, because no general answer exists as to how to set up the measuring parameters like heating, flow rate of the gases, temperature for turnover from inert to oxidizing gas, and so on. But it should be emphasized that this is only a problem if one measures samples of an unknown composition; it is no problem if one uses TG for the quality control of ones own production. In this

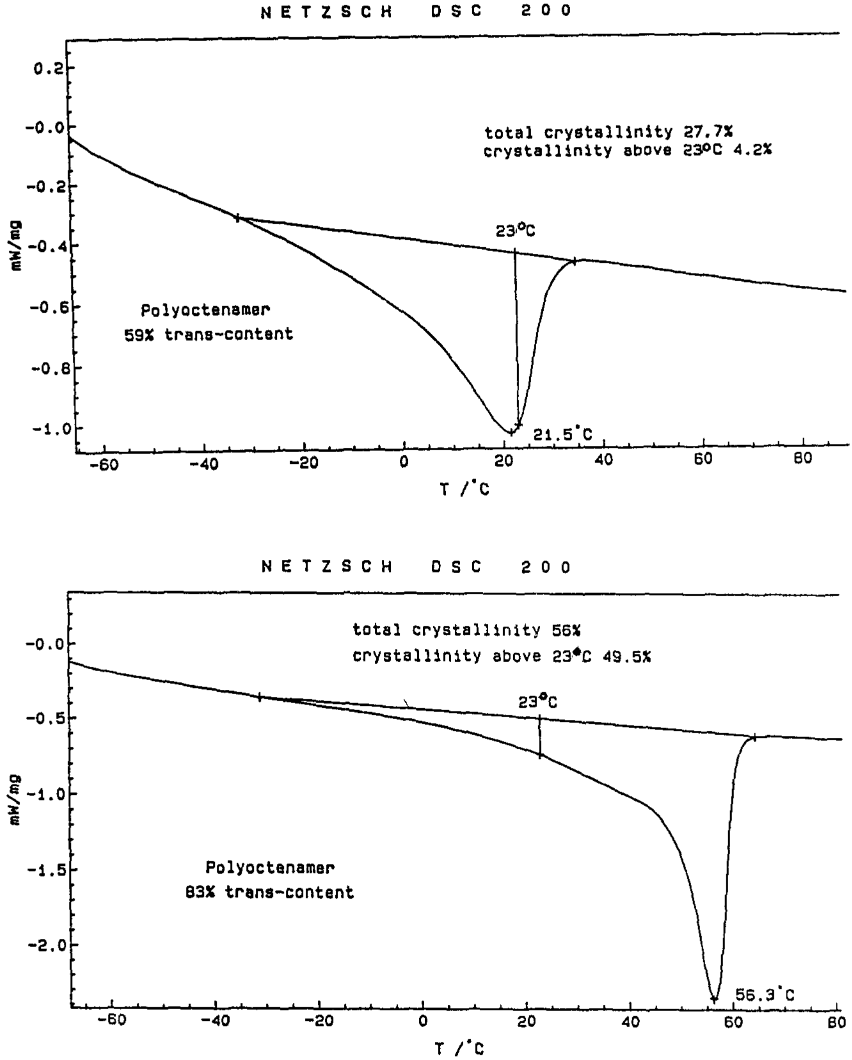


Fig. 7 DSC-curves of polyoctenamer with a trans-content of 58 up to 60 respectively 83 up to 84% (first and second heating)

case the influence of the above mentioned parameters certainly exists and has to be studied in order to develop an optimized method for a given task, but here the reproducibility of the results plays an important role. Furthermore, it must be taken into consideration that the evolution of plasticizers and the starting decomposition of polymers may be superimposed if high boiling plasticizers are used. In the example shown in Fig. 6 a low boiling plasticizer has been used.

As a summary, it can be said that a lot of experience is necessary to determine the quantitative composition of an unknown sample with the help of TG and, in some cases, it is even impossible when applying only a single method. But the main advantage of TG over standard methods is the short time consumption.

In the rubber industry, finished or semi-finished parts are often formed in a first manufacturing step and are then vulcanized later on in a next step. In this case a high green strength of the non-vulcanized product is needed. This may be realised by the crystallization of mixture components during cooling from processing temperature to room temperature. Polyoctenamer is such a component on the polymer side. Therefore, the degree of crystal-

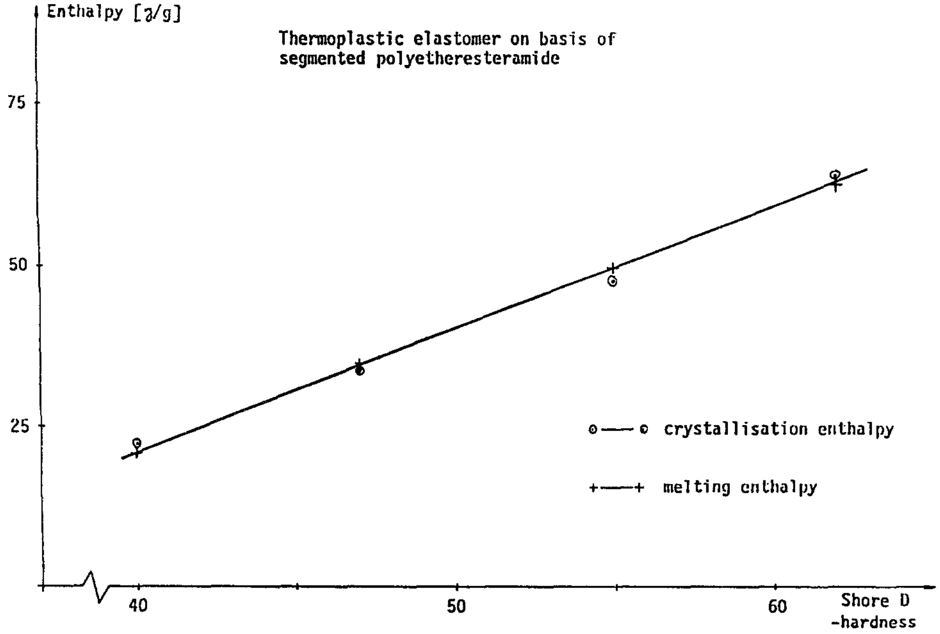


Fig. 8 Relationship between shore D-hardness and melting respectively crystallization enthalpy for segmented polyetheresteramides

linity of polyoctenamer grades is an important criterion in their application and must be tolerated as close as possible in order to guarantee a suitable quality of the parts. In practice, a simple method is necessary. The crystallization behaviour of polyoctenamer is determined by the trans-content of its cis-trans-stereoisomerism. Both structures can form crystals but cis-isomeric structures cannot crystallize together with trans-isomeric structures. The degree of crystallinity can be rapidly and easily determined by DSC-measurement at the known melting enthalpy of the 100% crystalline polyoctenamer of 220 J/g. But this provides reasonable results in practice only if there is a relation between the trans-content of polyoctenamer and its degree of crystallinity. The former can be determined by IR-spectroscopy in a relatively time consuming way. Figures 7a and 7b show typical DSC-curves of polyoctenamer with trans-contents of 58 up to 60% respectively 83 up to 84%. As one can evaluate, a linear relationship exists between melting point, total crystallinity or crystallinity at 23^0 and the trena-content, which is much better for the crystallinities than for the melting points. DSC was therefore chosen for the quality control of polyoctenamers since it can be carried out considerably faster and easier than the IR-spectroscopic measurement [17, 18]. Because the same thermal history is necessary for all samples, TA-values may only be taken from the second heating curves. Additionally it can

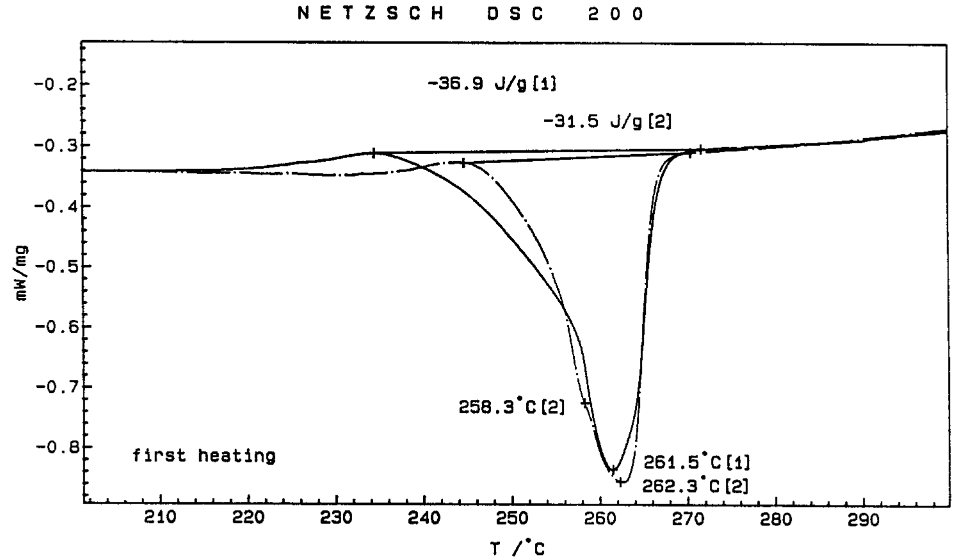


Fig. 9a Characterization of injection moulding parameters of PA 66 by DSC. On the top: (1) rejected part, (2) accepted part in the middle: crystallization of both samples during controlled cooling,on the bottom: second heating

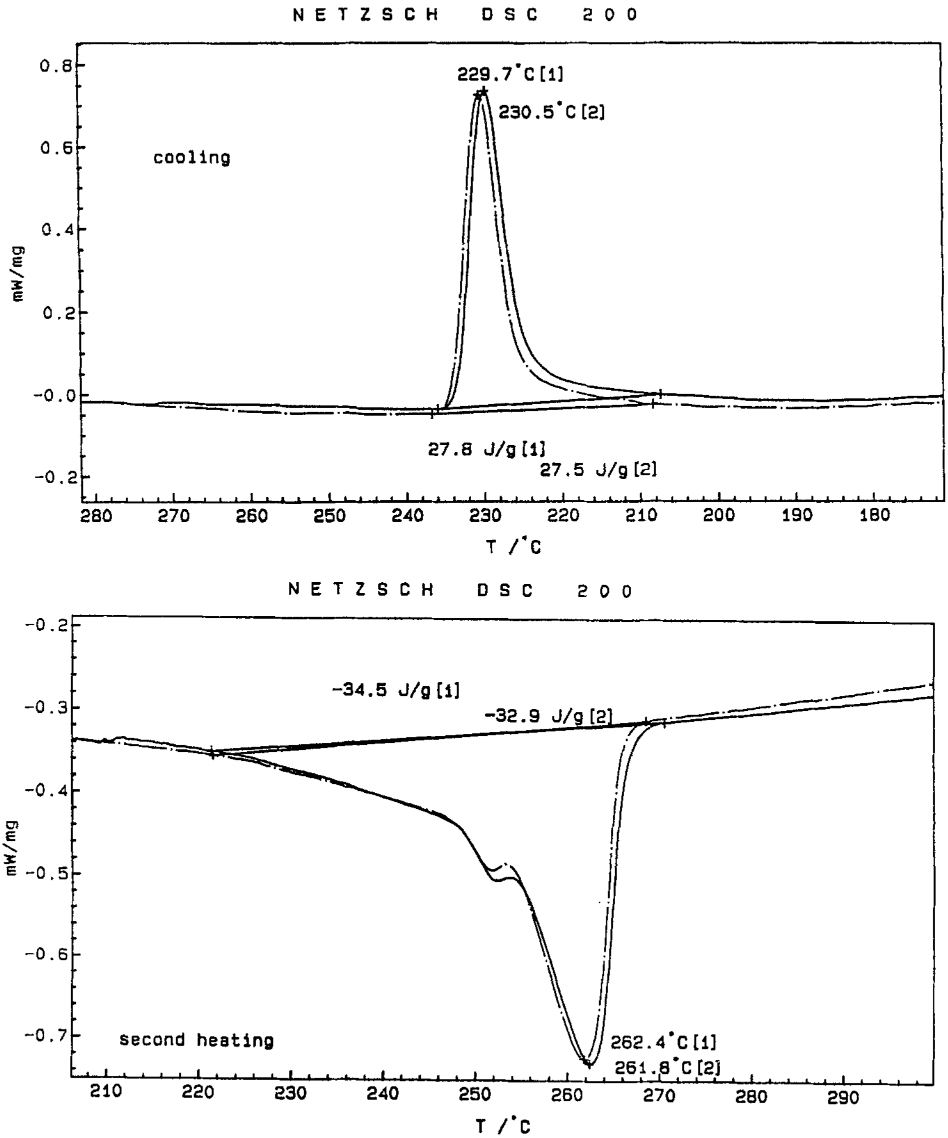


Fig. 9b, c Characterization of injection moulding parameters of PA 66 by DSC. On the top: (1) rejected part, (2) accepted part in the middle: crystallization of both samples during controlled cooling,on the bottom: second heating

be seen that the total crystallinity and the crystallinity at 23° confirm the high-contents. The reason is that melting of grades with high trans-content

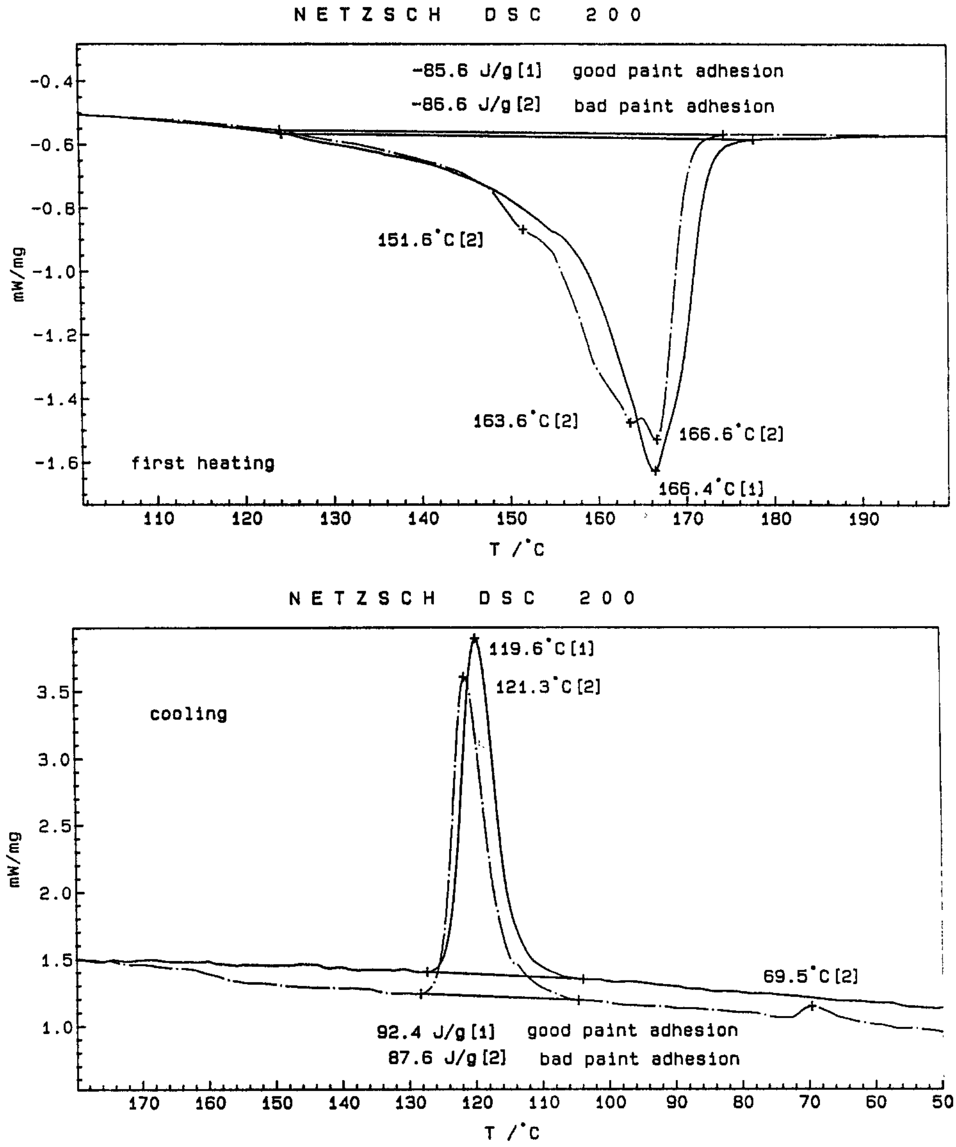


Fig. 10a, b DSC-heating and cooling curves of thermoformed cups of a PP-film with good and bad paint adhesion

clearly starts above 23°. Therefore, such grades are used if one needs an extremely high green strength of the non-vulcanized part.

Figure 8 shows an example of the linear relationship between crystallinity (melting enthalpy) and hardness (Shore D) of products made of thermoplastic elastomers on the basis of segmented polyetheresteramide (PEEA).

Examples from processing control and failure analysis

The first example shows the capabilities of DSC for the characterization of the processing parameters of injection moulding of thermoplastics. Curve (1) originates from a rejected part while curve (2) belongs to an accepted one (Fig. 9a). The different form of the DSC-curves and the magnitude of the melting enthalpy may be due to different mass, mould or nozzle temperatures during injection moulding. The cooling curve (Fig. 9b) and the second heating (Fig. 9c) prove that the same thermoplastic was used in both cases. However, the thermal history of both samples is different (compare also Fig. 5).

The next example deals with the characterization of surface structures of thermoformed parts. Some areas of PP-cups showed good paint adhesion while others showed poor paint adhesion. The reason can be immediately learned from the DSC curves (Figures 10a and 10b). Areas with good paint adhesion show a homogeneous melting and crystallization peak, while areas with bad adhesion show several shoulders on the peaks. This may be due to impurities in the thermoformed film and/or non uniform temperature over the cup's surface during the thermoforming process.

Examples from environmental protection

In the field of environmental protection it is often necessary to use TA-methods coupled with other methods from the area of instrumental analysis such as mass or infrared spectroscopy.

The first example shows the investigation of the fogging problem of PVC-slush skins used for covering dashboards in cars. Because of the fact that dashboards may reach a temperature of up to 130° [19–21] and despite an extensive optimization of the plasticizers used in the last few years, these plasticizers may evolve under such extreme temperature loads and deposit on the windscreen (fogging). Manufacturers of dashboards often do not indicate which plasticizer are used therefore the qualitative identification apart from the qualitative evaluation during the process of fogging is important for the car producers in order to avoid claims. TG coupled with other methods is a very powerful tool for such studies. Figure 11 shows a simultaneous TG-DTA-MS-scan of a PVC-slush skin. The sample was heated in helium atmosphere to the range of decomposition of about 230° at a heating rate of 2 deg/min. The volatiles were transferred directly by a two stage orifice system to the electron impact ion source of a quadrupole mass spectrometer. The ionisation energy was 70 eV. The mass spectrum of the PVC-slush skin shows typical fragments for common phthalic acid esters (m/z = 149) and for C11 phthalic acid diesters (m/z = 154). Additionally PVC-slush skin and a certain C11 phthalic acid diester showed an identical energetic behaviour (DTA) in the range of decomposition. Moreover, the behaviour of evaporation of PVC-slush skins was investigated only for orientation with the vapour pressure balance for 70 hours isothermally at 130°. The sample is evaporated into high vacuum out of an effusion cell (Knudsen cell). The reproducibility of the results was not as good as it should have been because of the short time at disposal. Therefore no results are given here.

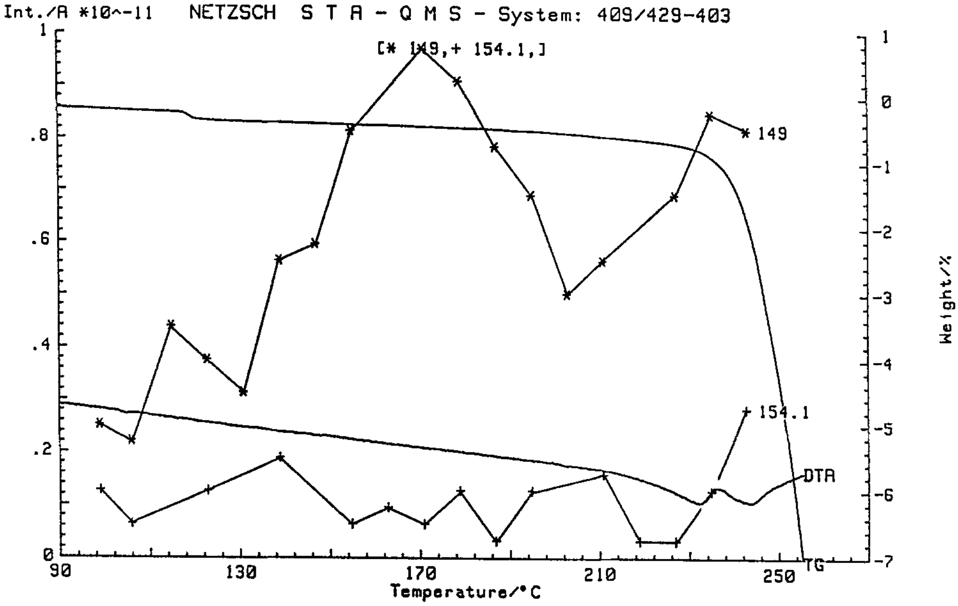
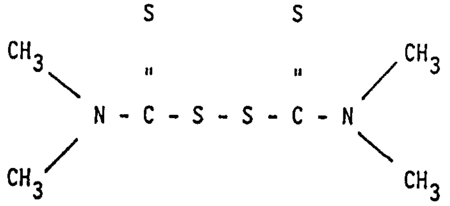


Fig. 11 TG-DTA-MS-curves of a PVC-slush skin

The last example is taken from the rubber industry. Nitrosamine can be formed during vulcanisation from certain accelerators and they are considered carcinogenic. The TRGS 552 (Technische Richtlinien für gefährliche Stoffe) requires an orientation value between 1 μg and 2.5 μg of total nitrosamine content per m^3 of air [22]. Such an accelerator is, for example, tetramethylthiuramdisulfide (TMTD).



As can be seen from the chemical structure of TMTD, there is a danger because secondary amine radicals (in this case the Dimethylamine radical [mass number 44]) develop at the processing temperatures between 150° and 180° which then form long-lasting nitrosamines. Mass number 76 is also expected for CS_2. This process can be quantified by measurement with the TG-DSC-MS-coupling (Fig. 12). The mass number for the Dimethylamine radical and the CS_2 can be observed above the temperature of 160°, that is at the onset of the decomposition of this accelerator.

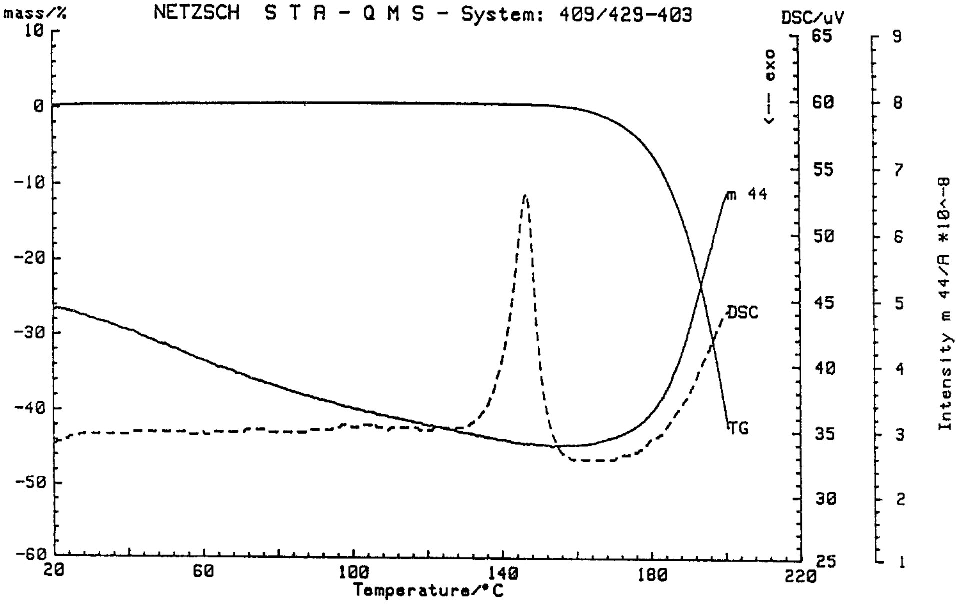


Fig. 12 Simultaneous TG-DSC-MS-investigation of melting and decomposition of tetramethylthiuramdisulfide and the formation of dimethylamine radical

Conclusions

The examples discussed show that the methods of Thermal Analysis are expressive as well as being rapid measuring and testing tools for plastics and rubber engineering. They are also used in research and development, construction, manufacturing, quality control and failure analysis as in environmental protection. TA methods are capable of replacing many time-consuming standard testing techniques. In the future, coupling TA with other methods from the field of instrumental analysis such as mass and infrared spectroscopy or chromatography will certainly play a larger role than today.

References

1 Th. R. Manley, Thermal Analysis, Proc. 9th ICTA Congress, Jerusalem, Elsevier Science Publishers B. V., Amsterdam 1988.
2 D. Braun, 7th H. F. Mark-Symposium, Wien 1988. (see Kautschuk + Gumi-Kunststoffe, 42 (1989) 157.)
3 H. Lingnau, 4th Conf. 'Polymeric High Performance Materials In the Technical Application', Süddeutsches Kunststoff-Zentrum Würzburg, 1989.
4 J. Parey, Conf. Handbook of 1st International Plastics Forum of SPE-Central Europe, Salzburg 1988.
5 N. Rau, Röhm Spektrum, 3 (1987) 88.
6 J. Reininger, Diploma thesis at the Fachhochschule Würzburg, Department of Plastics and Rubber Engineering, FRG 1986.
7 H. Möhler and M. Schwab, Kunstoff, 71 (1981) 245.
8 DIN 16 773 part 2, Polyamid (PA)-masses for injection moulding and extrusion, Homopolymers, Febr., 1989.
9 ISO 3146. Plastics. Determination of melting behaviour of semi-crystalline polymers.
10 D. W. Krevelen and P. J. Hoftyzer, Properties of Polymers. Their Estimation and Correlation with Chemical Structure, Elsevier Scientific Publishing Co., Amsterdam 2nd Edition, 1976.
11 O. G. Lewis, Physical Constants of linear Homopolymers, Springer Verlag, Berlin 1968.
12 A. Frank and K. H. Biederbick, Plastics-Compendium, Vogel-Verlag, Würzburg 1988.
13 J. Brandrup and E. H. Immergut, Polymer Handbook, J. Wiley and Sons, New York 1975.
14 K. Braun, Proceedings of 'Applied Instrumental Analytics for Raw Material and Finished parts made of Polymers', Fachchochschule Würzburg, Department of Plastics and Rubber Engineering, FRG, 1989.
15 N. V. Schwartz and D. W. Brazier, Thermochim. Acta, 26 (1978) 349.
16 N. Probst and G. Berote, Proceedings of 21st International Rubber Conf., (Book of Summaries II), Prague 1989.
17 W. A. Schneider and M. F. Müller, J. Mol. Cat., 46 (1988) 395.
18 P. Müller, Diploma thesis at the Fachhochschuhle Würzburg, Department of Plastics and Rubber Engineering, FRG, 1989.
19 DIN 75 201, Determination of the fogging behaviour of materials for indoor equipment of cars.
20 Th. Bücherl, K. Dörr and H. Möhler, 3rd Polymer Days of Berlin, Berlin 1988.
21 H. Möhler, J. B. Henderson and E. Kaiserberger, 46th ANTEC, New York 1989.
22 Technical rules for hazardous materials. TRGS 552. N-Nitrosamines.

Zusammenfassung — Es wird ein Überblick über die Möglichkeiten der Thermischen Analyse für die Kunststoff- und Kautschukindustrie gegeben. Neben Beispielen aus dem Bereich der Forschung (Haupt- und Seitenketten-Flüssigkristallpolymere) und Konstruktion (Laminate aus kohlefaserverstärkten Epoxyharz-Prepregs) wird besonders der Bereich der Qualitätssicherung und Werkstoff-Charakterisierung behandelt. Hier werden Zusammenhänge zwischen TA-Kenngrössen wie z. B. Kristallinitätsgrad und mechanischen Eigenschaften wie z. B. Härte oder Rohfestigkeit dargestellt sowie die Möglichkeiten der Thermogravimetrie zur quantitativen Gummianalyse gezeigt. Für den Praktiker besonders wichtig sind die Fehleranalyse und die Charakterisierung von Verarbeitungseinflüssen bei der Herstellung von Formteilen, da die Thermische Analyse oft wesentlich schneller Ergebnisse liefert als klassische Methoden. Ausserdem wird die zunehmende Bedeutung der Kopplung thermoanalytischer Methoden mit anderen Methoden der instrumentellen Analytik am Beispiel der TG-DSC-MS Kopplung für Probleme aus dem Bereich des Umweltschutzes im Zusammenhang mit der Herstellung und Anwendung von Formteilen aus polymeren Werkstoffen gezeigt.