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NEW ROUTES FOR THERMAL ANALYSIS AND CALORIMETRY AS APPLIED TO POLYMERIC SYSTEMS

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Abstract

Over the last few decades there has been a strong decrease in the number of Thermal Analysis and Calorimetry (TA&C) ‘practitioners’ – scientists who know the ins and outs of TA&C and its (im)possibilities and are capable of initiating new developments. By contrast, an increasing number of TA&C ‘users’ are scarcely able to acquire in-depth knowledge of TA&C. It is therefore of great importance that national TA&C societies create the infrastructure for dedicated education. In addition, the feasibility of setting up one or more expertise centers per country, where ‘practitioners’ can do research, carry out contract research and give advice to users, needs to be investigated.

Equally important, the TA&C community needs to address a number of challenges in the coming decade with the aim of controlling the ‘knowledge cycle’ in the field of polymers: to translate non-optimal properties into improved processing conditions or even a more suitable macromolecular architecture, in order to reduce the lead times for the development and optimization of materials.

Although Thermal Analysis and Calorimetry can generally be considered to be ‘mature’, in specific subareas a large number of new developments take place. A few examples of these developments and of state-of-the-art TA&C are given: quantitative heat capacity measurements by means of DSC; (very) high pressure DSC; real-time morphological analysis and temperature-modulated X-ray analysis. In addition, a new form of TA&C is discussed: High Performance DSC (HPer DSC), which is also a high rate DSC and a high throughput DSC.

Keywords: crystallization, heat capacity, High Performance DSC, high pressure DSC, high rate DSC, high throughput DSC, in situ mesurements, knowledge cycle, morphology, real time

Introduction

Thermal Analysis & Calorimetry (TA&C) is a collection of analytical tools that has been found to be of great importance in supporting the development and characterization of (raw) materials and products based on them. In particular the thermal behaviour of polymers is nowadays widely investigated using DSC [1, 2].

The state of affairs in this specialized field has recently been analyzed [3–6]. Although TA&C can generally be considered to be ‘mature’, in specific subareas a large

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number of new developments are taking place [6, 7]. These include temperature modulated DSC (TMDSC) [8, 9] and temperature modulated calorimetry in general [2, 6, 10–13] as well as the analysis of materials through a combination of TA&C and morphological techniques, such as scanning probe microscopy (SPM) and X-ray analysis. Such combinations are of interest because the morphology of a material can increasingly be characterized in real-time and in-situ. Since DSC is a technique that supplies relatively little specific information on morphology, it is very useful to combine it with specific techniques that can supply complementary and more direct information.

The analysis shows that there is an urgent need for these new possibilities in day-to-day industrial practice and that the TA&C community is now facing the challenge of shifting the frontiers even further. In this report we will show that this is possible and that new fields of application will be opened up in the process.

The question is whether research institutes at universities and industrial companies have the right infrastructure to achieve real breakthroughs in TA&C. In the author’s opinion this is insufficiently the case. At universities there has scarcely been any interest in analytical activities since the late 1980s. In the last two decades, attention shifted to the development of new (raw) materials, one reason being that this kind of work is more likely to be sponsored by industry. As a result, industrial research institutes have been forced to be actively involved in the development of analytical techniques for many years, because such techniques were crucial to portfolio renewal. In recent years, however, industrial companies, in particular polymer producers, have been focusing on maximizing production and minimizing costs. In an increasingly fierce competitive battle, globally operating industrial giants are concentrating on fewer activities and are trying to consolidate their market shares via growth. At the same time, these companies are becoming more and more short-term oriented under the influence of their shareholders. As a consequence, they strongly focused on technological breakthroughs in reactor and production technology, optimization of logistics and selective maintenance in combination with the implementation of ‘best practices’. In some companies, this has resulted in a strongly reduced focus on innovation in product properties via product development. This makes life difficult for expertise centers that support product innovation and improvement. All too easily such companies assume that they will be able to fall back on universities or even outsource activities to universities in emergency situations. This assumption is not realistic, because the expertise available at universities in the field of analytical support has been reduced to almost zero, and anyway universities are not equipped to deliver a continuous high-quality output on a large scale – and rightly so. Sharing development work between industries could be a solution for maintaining the required critical mass, but this appears to be very difficult to achieve because of the confidential nature of some of the data and because in many cases characterization facilities need to be located close to the development activities. Expertise groups run the risk of becoming sub-critical or even disappearing altogether. Expertise centers that remain in place often have little or no budget to maintain their expertise at a high level. The business units of many companies frequently question the need for high-level analytical expertise; they argue that ‘good is good enough’. This is basically correct, the solution should fit the problem, and ‘overkill’ is not desirable, but there are situations in which a company’s analytical department has to be able to pull out all the stops. As far as developments are concerned currently, on the one hand, this kind of efforts are less often required and, on the other hand, the number of research groups that are capable of making such efforts is decreasing.

An utterly pessimistic view? No, a realistic picture of the present situation. This situation will not improve of its own accord, and I fear that things have to get even worse before they start to get better. A major condition for improvement is a fresh demand for breakthroughs in the properties of polymeric systems and for polymers with new functionalities.

Does it influence TA&C? Of course, it does. Over the years this development has resulted in a strong decrease in the number of Thermal Analysis and Calorimetry ‘practitioners’ – scientists who know the ins and outs of TA&C and its (im)possibilities and are capable of initiating new developments in the TA&C field. This is a rare and dying breed. By contrast, there has been an increase in the number of TA&C ‘users’, that is, people who know how to use TA&C equipment but are scarcely able to acquire in-depth knowledge of TA&C. One reason for their lack of in-depth knowledge of TA&C may be that their employers require them to be flexible, which means that they have to be familiar with various techniques and spend relatively little time in the same job. To them, instruments are of necessity ‘black boxes’, and they have to rely on instrument suppliers and the procedures and methods provided by them. Incidentally, the increase in the number of ‘users’ is not a negative development, on the contrary.

In view of these trends it is of great importance that over the next few years the ‘users’ are given ample opportunity to acquire in-depth knowledge of TA&C in an efficient way. National Societies for TA&C should create the infrastructure for proper education. It must also be investigated whether in a minimum scenario it is possible to set up one or more expertise centers per country where ‘practitioners’ can carry out state-of-the-art research, develop methods and techniques, carry out contract research and give advice to ‘users’.

In this report we will give some examples of state-of-the-art TA&C. We will show that quantitative heat capacity measurements can be carried out with the aid of DSC (and that the results are of the same quality as those obtained via adiabatic calorimetry). We will also report research that is being carried out into (very) high pressure DSC, emphasize the importance of real-time morphological research, show the possibilities of temperature modulated X-ray analysis and present a new form of TA&C: High Performance DSC (HPer DSC).

But first we will present a number of challenges for the coming decade that have emerged from polymer development practice. We will translate these challenges into development objectives for TA&C.

Challenges

Context: the ‘knowledge cycle’

Before giving concrete examples of new routes to be followed in TA&C it is worthwhile to specify the context in which these routes are being developed: the accumulation of know-how and expertise in the field of polymers via the ‘chain of knowledge’. This means gaining an insight via the natural route to the development of polymeric materials: starting from chemistry (polymerization with a suitable catalyst and suitable reaction conditions) via processing to materials and products with certain desired physical properties, chemical resistance, durability and recyclability. Straightforward as this may seem, it is very difficult to optimize this chain. The development of a new, commercial polymer via this route easily takes 5 to 10 years, and production will often be profitable only after 10 to 20 years. In this regard, the situation in the polymer industry is similar to that in the pharmaceutical industry. This explains why there is a strong tendency to shorten the development route by blending existing materials and, in view of the recycling problems associated with blends, to use multi-purpose materials, such as all-polypropylene parts for the automotive industry. In the latter case special product characteristics are obtained mainly through special processing methods. This mostly involves influencing the rheology and crystallization during molding in a targeted way, resulting in the desired morphology.

However, this calls for a thorough understanding of the ‘chain of knowledge’, and it will in fact be necessary to control the ‘knowledge cycle’. By this I mean that it is not only important to relate polymerization conditions to product properties with a minimum of trial and error, but that it is also crucial to master the reverse route, in other words to translate non-optimal properties into a more appropriate processing method or even a more suitable macromolecular architecture. The advantage of con-

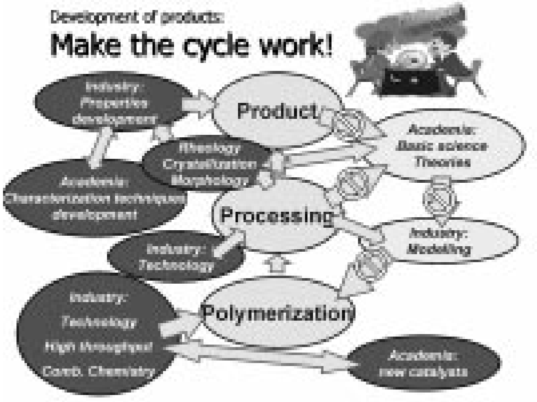

Fig. 1 Cartoon illustrating the roles of Academia and Industry and existing challenges with respect to the ‘knowledge cycle’ for the development of a polymer product from polymerization via processing and optimization via the reverse route. Links that do not work (well) are presented by ⃠

trolling the 'knowledge cycle' – that is, of being able to reverse the normal development process – is a shorter lead time in the development and optimization of materials.

Figure 1 shows a cartoon of the 'knowledge cycle'. The symbols used are self-explanatory. The picture is of course greatly simplified, but the message is that the left half of the figure shows that the route from catalyst to properties works reasonably well but that the reverse route, see the right half of the figure – relating properties to processing conditions and, at a still deeper level, to molecular structure – barely exists. It is not difficult to sum up the missing information and possibilities. The points that, in my opinion, need to be given attention in the coming years have been formulated below as challenges in relation to the different roles associated with research groups at industrial companies and universities:

Different challenges for different groups

Challenges for academia: know-why

- Identify industry needs
- Develop basic knowledge and usable models
- Develop new characterization techniques and methods

Challenges for instrument companies

- Develop dedicated instrumentation
- Develop new characterization techniques and methods
- Develop user-friendly software and 'state-of-the-art' expert systems

Challenges for industry: know-how

- Challenge the academic community
- Have researchers who understand their university counterparts
- Bring the models developed 'down to earth'
- Translate ideas and findings into applications

Challenges for thermal analysis & calorimetry societies

- Educate members via dedicated programmes
- Stimulate national expertise centers for TA&C
- Inform and communicate

Challenges both for academia and industry

Besides the issues listed above for the various groups, there are a number of special challenges that will be of great importance for all those who work in the field of polymers in the coming decade. A number of these challenges are listed below. They will be elaborated on in the Results and Discussion section.

- Do quantitative research
    Perform heat capacity measurements

- Aim at conditions as occuring in practice
  - Such as those prevailing during processing
    - High pressure
    - High cooling rate
    - Shear etc.
  - Pay much more attention to dynamic cooling/ heating conditions
  - Handle complicated temperature – time ramps as in 'real life'
- Perform in-situ/real-time measurements
  - During processing
    - Synchrotron X-ray
    - Ultrasound, dielectric spectroscopy etc.
  - Matching processing
    - HPer DSC
  - During polymerization
    - AFM, solid-state NMR, spectroscopy etc.
- Be aware of metastability and low order
  - Leading to reorganization as a function of time and during heating
    - Such as cold crystallization
    - Or recrystallization
    - And annealing
  - As a result of which the connection between the morphology immediately after processing and subsequent measurements at higher temperatures is most probably lost
    - Use real-time X-ray, solid-state NMR etc. (chart morphology)
    - Apply HPer DSC (chart morphology and restore connection).

Results and discussion

Quantitative research

Heat capacity measurement and crystallinity

It is remarkable that in a discipline like TA&C, which in many respects may be regarded as 'mature', there are only a few scientists who publish work of a truly quantitative nature. What I mean by 'quantitative work' in this context – I am specifically referring to DSC – is research based on heat capacity measurements, or at least measurements in which instrumental curvature is corrected for by subtracting empty pan measurements and in which instrumental drift is avoided as a standard procedure. It is possible to carry out heat capacity measurements with the commercial equipment currently available, although avoiding drift is not trivial because the day-to-day stability of the present commercial DSCs is still not good enough. In addition, the software available for carrying out such measurements in a standard way is usually too cumbersome. Apparently, the demand for appropiate hardware and software is low, which explains why instrument suppliers do not assign priority to the development needed. Of course, this says something about the researchers. In my opinion the low demand for sophisticated hardware and software is due to the fact that the researchers involved in TA&C are generally ‘users’ (in the sense indicated earlier), who are probably unaware of the advantages of quantitative measurements or for whom quantitative measurements would be too time-consuming with the current limited and complicated software. It is revealing that even many of the DSC measurements reported in specialist TA&C journals are hardly more quantitative than those reported in the fifties. In this connection it should also be noted that in those cases in which a comparison with quantitative literature data (as present in the ATHAS data bank [14]) is possible, this is not done. As a result, there is a gap between groups that routinely carry out state-of-the-art DSC measurements (researchers who in the current context can be referred to as ‘practitioners’) and groups that use DSC in a qualitative sense (the vast majority: the ‘users’). It should be a challenge to National TA&C Societies and to the International Confederation for Thermal Analysis and Calorimetry, ICTAC [15], to bring these two groups into contact with each other and thus provide the basis for an optimal exchange and utilization of knowledge and expertise. This can be done in a number of ways, but certainly via dedicated training courses (that is, courses differentiated according to need) and possibly via National Expertise Centers for TA&C, see my earlier remark.

Figure 2 (top) shows an example of a calculation of the crystallinity as a function of temperature on the basis of quantitative DSC measurements. To compare two homogenous ethylene-1-octene compolyers, polymerized using single site catalysts (one based on vanadium and the other on metallocene), heat capacity measurements in cooling and heating were carried out over a wide temperature range [16]. The results were subsequently compared with reference values for linear polyethylene [17]. Such reference values are available for a large number of other polymers in the ATHAS data bank [14]. The obvious advantage of this is the possibility of an independent check of measurements. Furthermore the reference values allow the enthalpy values obtained by integration of the heat capacity measurements to be compared with literature values. Finally, the crystallinity and the base-line and excess heat capacities can be calculated [1]. This also obviates a problem many researchers are facing: how to draw a ‘base-line’ in order to ‘do something’ with the area under the DSC curve. The method does not allow researchers to make any choices of this nature because there simply are no choices to be made. Incidentally, for a quantitative evaluation of the crystallinity as a function of temperature it is not necessary to carry out heat capacity measurements [1, 18]: for everyday use a software package has been developed [19] which gives excellent results for quantitative measurements (without instrumental curvature, for example after correction with the aid of an empty pan measurement). The software in question can be used in combination with measurements carried out with DSCs and calorimeters of different makes. Although the crystallinities in Fig. 2 (top) were evaluated using a two-phase model (in which molecules are assumed to be either in an amorphous or in a crystalline phase), calculations on the basis of a three-phase model are also possible [1, 20].

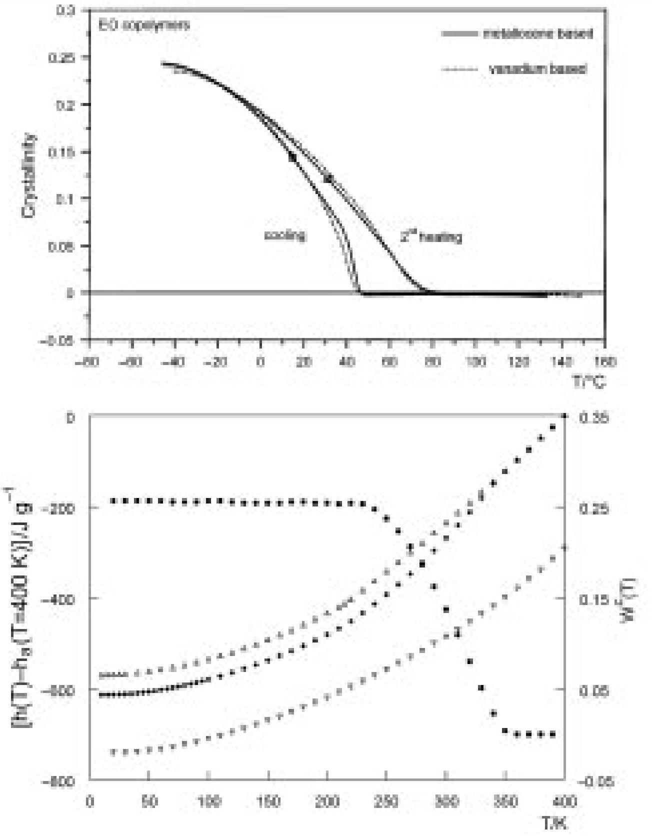

Fig. 2 Top: enthalpy-based mass crystallinity of homogeneous metallocene (the EO M sample) and vanadium based ethylene-1-octene copolymers as obtained from DSC heat capacity data at 20°C min^{-1} in cooling and subsequent heating. Bottom: specific enthalpy of the EO M sample (♦), together with the specific enthalpy of the crystalline phase (∇) and of the amorphous phase (Δ), and the enthalpy-based mass crystallinity (scaling given on the right vertical axis) of the EO M sample (•), all heating curves as obtained by adiabatic calorimetry

The figure shows an increase in crystallinity as a result of crystallization in cooling and a decrease as a result of melting in heating. The conclusion is that although the two ethylene-1-octene copolymers were polymerized with different catalyst systems their crystallization and melting behaviour is the same. This implies that the polymerization kinetics and the resulting ethylene sequence length distributions cannot be very different. The clear hysteresis (difference between crystallization and melting) is the result of the (molecular) nucleation [21, 22] needed for crystallization. There are not many techniques, with the help of which the crystallization and melting of polymers can be measured so quickly and quantitatively. In the case of copolymers with high comonomer contents (and therefore short ethylene sequences), such as the ones discussed here, there is an extra problem. For these copolymers, WAXD, for example, shows scarcely any reflections because the relatively short ethylene sequences can build only small and imperfect crystallites, while SAXS gives quite useful results if the invariant is evaluated as a function of temperature [16, 23–26]. Use must be made of a high intensity source, in this case synchrotron radiation, and that is a disadvantage for application in day-to-day practice. Figure 2 (bottom) shows that the results obtained with the aid of adiabatic calorimetry give a similar picture [27, 28]. This technique, which is no longer applied except in a few places, makes it possible to conduct absolute heat capacity measurements. The measurements with the aid of DSC and with the aid of adiabatic calorimetry cannot be compared in absolute terms because the thermal histories cannot be the same. Particularly the temperature range is different (–70 to 150°C for DSC and –268 to 127°C for adiabatic calorimetry) and the cooling and heating rates are different (20°C min^{-1} in the case of DSC and much lower in the case of an adiabatic calorimeter). For the TA&C community, it is important to confirm that quantitative measurements can be carried out with the aid of DSC, and at reasonably high rates. Naturally that is of advantage in day-to-day industrial practice. Further on we will report on quantitative heat capacity measurements at much higher rates, using HPer DSC.

Conditions as in practice

The need for ‘real-life’ measurements

The conditions chosen in laboratory experiments often greatly differ from those occurring during both processing and during the polymer product’s use in real life. Laboratory measurements are often carried out isothermally or since recently – with TMDSC – under (quasi) isothermic conditions or at best at relatively slow cooling and heating rates – and in an ambient atmosphere. On the one hand, this is a conscious choice – particularly for (quasi-)isothermal measurements in fundamental research – because the results are theoretically better interpretable, but, on the other hand, it is also a forced choice because most techniques cannot be used in scanning. In real life, however, cooling and heating conditions are mostly dynamic, sometimes in complicated temperature-time ramps. During processing high cooling rates (see below), high pressures [2, 29, 30] and high shear rates [31, 32] are common. All these parameters have an important influence on the most important forming processes: vitrification and crystallization.

High-pressure DSC measurements

As mentioned in the previous section, during processing a material may be cooled under high pressure. Particularly during injection molding, pressures of a few hundred Mpa’s are quite normal. Measuring at such pressures is not easy, which explains why there are only a limited number of publications on DSC under high pressure, e.g. [33–37]. Figure 3 [37] shows that the peak melting temperature, and also the peak crystallization temperature (not shown) of a linear polyethylene, LPE, increases by

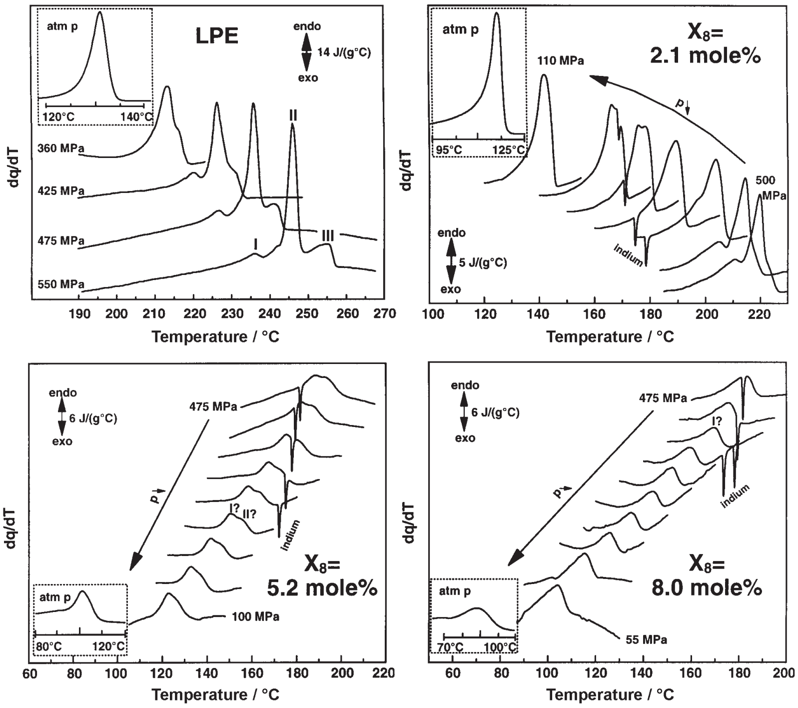

Fig. 3 DSC curves in heating after cooling, both at 10°C min^{-1}, at different pressures of an LPE (JW 1114) and of homogeneous ethylene-1-octene copolymers: JW 1116 (2.1 mole% of 1-octene); JW 1120 (5.2 mole% of 1-octene) and JW 1121 (8.0 mole% of 1-octene). For explanation of I, II and III, see text

approximately 100°C upon a pressure increase to 550 MPa. Homogeneous ethylene-1-octene copolymers with 2.1, 5.2 and 8.0 mole% octene show the same increase. But there is more. From the literature [30, 38, 39] we know that crystallization and melting of LPE is complicated because during cooling at pressures above 200 MPa, LPE molecules can crystallize from the melt in the hexagonal phase in extended form [40], leading to extended chain crystals (ECCs). Upon further cooling a transition from hexagonal to orthorhombic ECCs is likely to occur. At pressures lower than 200 MPa the chains fold during crystallization in the orthorhombic phase, leading to folded chain crystals (FCCs). Extended chain crystallization can take place because the molecules are sufficiently mobile at high temperatures, while the distances between the chains are also larger so that they can be packed in alternative ways, for example in a hexagonal arrangement. On heating, any orthorhombic FCCs that are present melt first, which explains the small peak in Fig. 3, indicated with the symbol I. At II, the large peak, we assume melting of orthorhombic ECCs and/or a solid transition from orthorhombic to hexagonal ECCs. At III the hexagonal ECCs melt. This peak is much smaller because the hexagonal phase is much more similar to the melt in terms of volume and enthalpy than the orthorhombic phase.

In the copolymers [41] peak III disappears with increasing octene content, see the copolymers with 5.2 and 8.0 mole% [37], probably because crystallization and melting take place at increasingly lower temperatures so the mobility required for the hexagonal phase is increasingly lacking. This is in agreement with the fact that peak III moves towards peak II at reduced pressures, and ultimately disappears. Incidentally, at peak II we can no longer speak of ECCs, at most of EESCs: extended ethylene sequence crystals. The reason is that the comonomer distribution gives rise to an ethylene sequence length distribution that constitutes the extreme limit of the possible crystal thicknesses. FCCs, peak I, now represent crystals with stem lengths that are (much) smaller than the ethylene sequence lengths. At the highest comonomer content, 8.0 mole%, only peak I is still present.

Surprisingly, in these copolymers totally new effects are observed that were not observed for LPE and HDPE. WAXD results, for example, point to the occurrence of disordering and possibly even amorphization during pressurizing to the same high pressures at room temperature [42, 43], an effect that resembles inverse melting phenomena [44, 45]. Upon cooling under pressure the WAXD reflections appear to split. This is probably attributable to a segregation according to sequence length and short chain branching into different crystal structures [42, 43]. In short: high pressure is a parameter that is important not only in industrial practice; it also gives rise to a large number of new effects that pose challenges to scientists and application developers. Here, too, it is important to complement DSC information with morphological studies, for example with the aid of X-ray analysis, performed under the same conditions, to obtain a detailed picture.

In-situ/real-time measurements

One of the greatest challenges for the coming years will be in-situ and real-time measurement of processes. This holds not only for processing, although currently the focus is on morphology development during, for example, injection molding [32]. Techniques such as X-ray, ultra sound and dielectric spectroscopy will hopefully create new possibilities in this field. However, during polymerization, too, it is very useful to study the interaction between polymerization ↔ crystallization ↔ morphology [46]: there are clear gaps in our knowledge in this area. Techniques such as scanning probe microscopy are likely to be of help in bridging these gaps [47]. This applies to the study of crystallization and morphology in general: recently, lamellae growth during isotherm crystallization was monitored for the first time [48]. For the time being, a great deal of progress can be made by combining different techniques and conducting the various measurements under the same conditions, particularly on samples with the same thermal history.

Metastability of polymer systems

Polymers are generally highly metastable [49, 50]: the substances and materials studied by DSC are seldom in thermodynamic equilibrium. Hence all kinds of changes are possible as a function of time and temperature: reorganization by means of recrystallization and annealing; cold crystallization; solid–solid transitions; superheating, etc. [22, 51, 52]. The same applies to pharmaceutical raw materials and products. This calls for research on the kinetics in the systems to be studied and on the metastability of these systems. Such research will also yield a better insight into the behaviour of materials in real-life conditions.

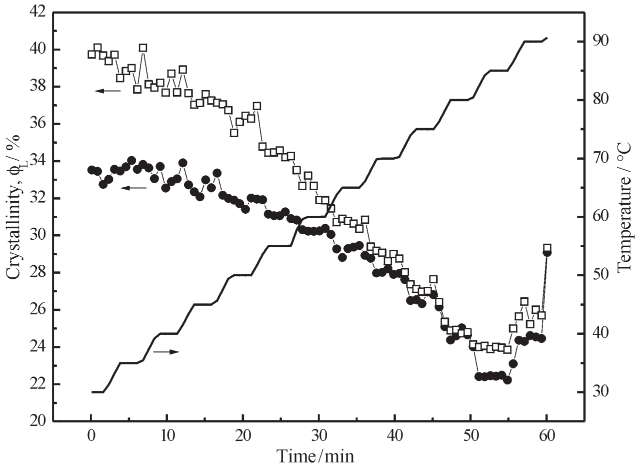

Fig. 4 The local volume crystallinity ϕ_L in the semi-crystalline regions, calculated on the basis of SAXS results, of the homogeneous metallocene-based ethylene-1-butene copolymer EB 2 cooled at –1°C min^{-1} (□) or quenched (•) from the melt during a (heating) scan-iso temperature-time program; (—) temperature

Figure 4 gives an example of metastability and also shows that for the interpretation of DSC results other techniques are indispensable. The figure includes ‘scan-iso’ real-time (synchrotron) SAXS measurements [24] according to a temperature-time ramp that is comparable to a ramp that is also used in temperature-modulated DSC. Recently such measurements – which are essentially the same as the classical step-wise procedure for heat capacity measurements [1, 18] – have also become known as ‘step-scan’ programs, and they can now be programmed via commercial software [53]. There are various interesting aspects to be observed. First of all, the local (volume-fraction) crystallinity ϕ_L – which is the crystallinity in the semi-crystalline stacks of the homogeneous ethylene-1-butene copolymer – broadly decreases with increasing temperature, as is to be expected. It is striking, however, that in the quenched sample the crystallinity decreases less quickly than in the slowly cooled sample. The result is that, although the slowly cooled sample (naturally) starts with a higher crystallinity, the difference disappears at higher temperatures. This is confirmed by DSC and SAXS measurements [54–56] on other copolymers, in which, over a certain small temperature range, the crystallinity of the quenched sample is even larger than that of the slowly cooled sample, and the same holds for the melting peak temperature. It was demonstrated this was due to extensive recrystallization of the quenched sample during heating, as a result of which this sample 'caught up with the slowly cooled sample' in terms of crystal thickness, crystallinity and melting temperature. Obviously, in such cases there is no point in trying to relate a crystal thickness at room temperature to a melting point via the Gibbs–Thomson equation [52]. Apparently, there is a lot of reorganization going on in the sample – in this case via recrystallization – during heating. This is by no means exceptional, so it is important not only to detect reorganization, as in this case with the aid of X-ray analysis, but to prevent it where possible. This can be done, for example, by crosslinking the amorphous phase [6, 57, 58] and in particular by increasing the heating rate [6, 59–64] (see below: HPer DSC).

In the figure it is clear that the crystallinity closely follows the temperature-time program: it decreases during the heating scan and is constant during the isothermal stay. Characteristic quantities such as the amorphous layer thickness, and hence the long period, also closely follow the temperature-time program, and the same holds for the fraction of semi-crystalline regions. It can be concluded that in the absence of additional morphological information [56, 65], such as WAXD and SAXS measurements under the same conditions [66], it is impossible to interpret DSC results correctly.

The need for high scan rates

In the introduction it was observed that in specific subareas of TA&C, and specifically in combination with DSC, a large number of new developments take place. One aspect of DSC that certainly has contributed to its great popularity is that it intrinsically offers the possibility to measure at a high (relative to other techniques) and linear rate, for example 20°C min^{-1}. This means it has a high output, which is greatly valued in industrial applications. What is much more important is, however, it offers perspectives for mimicking cooling and heating rates under practical conditions, although conventional DSC experiments are admittedly still far from 'mimicking' [67, 68] the extremely high cooling rates that occur during, for example, injection molding [69].

Nevertheless, DSC is one of the few techniques that have such a large dynamic range in relation to measuring rates – varying from ('quasi') isothermic measurement to measurement at relatively high rates – that it can cover an experimental time domain that matches the kinetics relating to the many possible metastable states of polymer systems, such as the above example of a metastable system in which considerable reorganization occurs during heating.

High Performance DSC (HPer DSC)

High rate DSC: a tool to study metastability

We shall now report on measurements performed with a so-called High Performance DSC (HPer DSC), which was recently developed [70] specifically for the study of

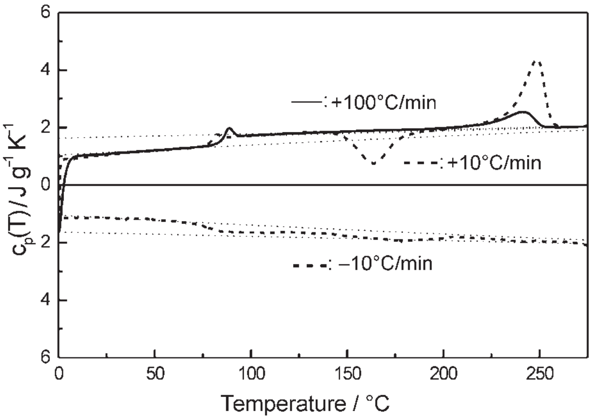

Fig. 5 High Performance DSC (HPer DSC), using a modified Perkin Elmer Pyris-1 calorimeter, on a poly(ethylene terephthalate) sample. Crystallization and vitrification during cooling at 10°C min^{-1}; devitrification, cold crystallization and melting during subsequent heating at 10°C min^{-1}. Heating at 100°C min^{-1} suppresses cold crystallization: only melting is seen. Samle mass: 1.285 mg

metastable systems. To this end the dynamic range of conventional DSC was considerably extended to include rates of a few hundreds degrees per minute: this aspect of HPer DSC can be referred to as high rate DSC. In heating it does not seem spectacular, any power compensating DSC or heat flux DSC can achieve such rates. However, in contrast with existing equipment, the HPer DSC enables us to achieve *high controlled and linear scan rates in heating as well in cooling*. Calibrants such as indium, lead, zinc, adamantane, azoxy anisole etc. retain the peak shape recorded at low rates. It is necessary, however, to adapt the sample mass to (sub) milligram level. Furthermore, hardware and software adaptations are required.

Figure 5 illustrates an advantage of the use of a high heating rate, in this case 100°C min^{-1} (HPer DSC), compared with 10°C min^{-1} (conventional DSC). After cooling of a polyethylene terephthalate (PET) at 10°C min^{-1}, during which the sample partially crystallizes and subsequently vitrifies below approximately 85°C, it can be clearly observed that in heating at 10°C min^{-1} cold crystallization occurs to a considerable degree, followed by melting of the sample. Of course, we know how to interpret such a situation [1], and also how to correct the enthalpy of fusion for the contribution relating to cold crystallization. This is not difficult, certainly if the above-mentioned software package [19] is used. However, things can be simplified much further, see the heating curve measured at 100°C min^{-1}. Evidently this rate is high enough to simply *prevent* cold crystallization. As a result, the endotherm that is measured gives a straightforward representation of the melting of crystals formed during cooling. So, there is no longer any interference with cold crystallization processes resulting from the macromolecular chains' ability to crystallize during heating. Of course, it is still meaningful to measure at different heating rates if one wants to chart the kinetics and metastability of the sample. After all, here too, it is very interesting to compare the two heating curves. It is clear, however, that a high heating rate adds considerable value.

High Performance DSC: heat capacity measurement at high rate

The answer to the question as to which combinations of scan rates provide useful information depends on the research objective and on the specific sample. If, in the case of the PET sample, the aim is to relate the DSC results to, for example, the material's behaviour under injection molding conditions, higher cooling rates should, of course, be applied. At a cooling rate of 100°C min^{-1} the sample in question already appears not to crystallize all the way down to the glass transition [70]. It need not always be the case: addition of nucleating agents, etc. can induce crystallization even at this cooling rate. The sample mass is typical: 1.285 mg. Comparison with the reference values for amorphous and completely crystalline PET according to the ATHAS data bank (see dotted curves) [14] shows that the cooling curve at 10°C min^{-1} is not quantitative, while the heating curve is quite good. This is typical of measurements of this kind with conventional DSC equipment: cooling imposes greater demands on the equipment. In this case the low sample mass is the cause of the problem: for a heat capacity measurement in cooling at 10°C min^{-1} a higher sample mass must be used and/or the DSC must be stabilized further. However, this experiment was not aimed at performing a heat capacity measurement in cooling at 10°C min^{-1}; the c_p axis refers to the measurement at 100°C min^{-1}.

It highlights another important advantage of HPer DSC: the sensitivity resulting from a low sample mass is compensated for by the high scan rate. Moreover, since the measuring time has been shortened drastically (in this case to less than 3 min), instrumental drift is effectively suppressed, so quantitative measurements are possible. Thus, the technique offers the unique possibility to *perform heat capacity measurements at rates of more than a hundred degrees per min, both in cooling and in heating*! In this way, an important aim is achieved: HPer DSC indeed offers a *high performance at high rates*.

The fact that a heat capacity is measured offers opportunities for a further, quantitative analysis of the curve measured at 100°C min^{-1}. Integration of this curve yields the enthalpy curve, and by comparing the results with the reference values we can calculate the crystallinity as a function of temperature.

High performance DSC: a tool for fast characterization of minute amounts of material

Figures 6 and 7 show that HPer DSC also offers an advantage when small amounts of material need to be characterized rapidly. The figure shows an edge-on picture of a sausage packaging film with a total thickness of 46 μm as obtained via optical microscopy [71]. This sample is being used in a European Community sponsored project [71, 72] on the 3D-Image reconstruction of the morphology of layers via scanning probe microscopy using a thermal tip. To this end the sample is scanned at a number of modulation frequencies. The reconstruction is based on the Sensitivity

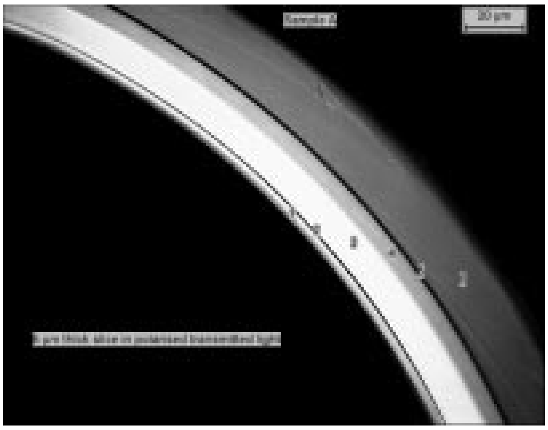

Fig. 6 A cross section of a multi-layered wrap film used for sausage packaging, as viewed by optical microscopy, consisting of different polymers and adhesives. Thicknesses of layers 1–6: 3, 0.5, 11, 6.5, 1 and 24 µm, respectively

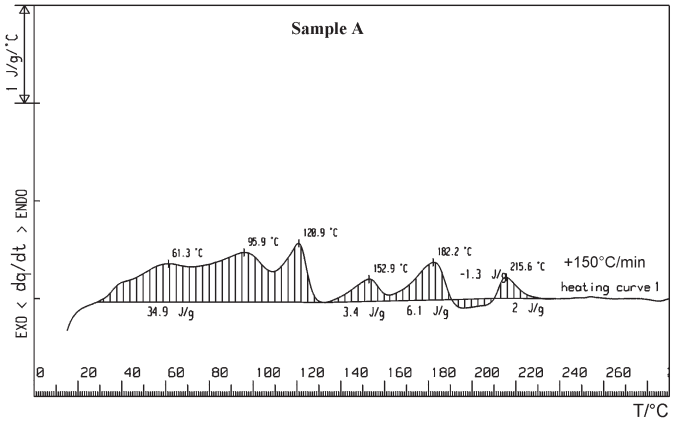

Fig. 7 A HPer DSC first heating curve at 150°C min^{-1} for the film presented in Fig. 6. Various melting peaks result from the different polymers and adhesives constituting the layers. Samle mass: 1.219 mg

Matrix approach adapted from Electrical Impedance Tomography, a medical imaging technique. The different layers in the packaging film are composed of different polymers and adhesives, each having a specific function: as a permeable or impermeable layer; as a layer affording certain optical properties; as a carrier, etc. A complete analysis of the composition is possible in combination with FTIR and DSC. FTIR provides clues to the components present, such as polymers, adhesives etc. DSC gives a good indication of the nature of the polymers present via analysis of melting and crystallization temperature distributions; microscopy reveals which layer melts at which temperature during a heating run, and can thus provide clues to the nature of each layer. Figure 7 gives the result of a HPer DSC heating curve obtained at 150°C min^{-1}.

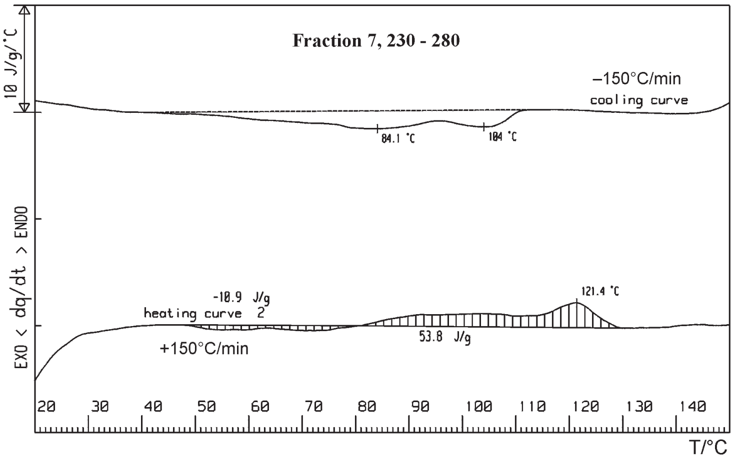

Fig. 8 HPer DSC cooling and subsequent heating curves at 150°C min^{-1} for a 29 μg HDPE sample, obtained by fractionation of a butene-containing high density polyethylene (HDPE), of 0.45 mg in total, by size exclusion chromatography (SEC). Sample mass: 29 μg

The different melting peaks point to the presence of various polyethylenes; polypropylene; polyvinyl alcohol and polyamide.

An extreme example of a low sample mass measurement is given in Fig. 8, which shows how quantitative information could be obtained from a 29 μg HDPE sample at scan rates of 150°C min^{-1}. Not only the crystallization and melting point distributions could be measured [73], also the heats involved could be established, which is new and unique. The sample was obtained via fractionation of a butene-containing high density polyethylene (HDPE) (0.45 mg in total) using size exclusion chromatography (SEC); the polymer in the elute was solidified on a rotating germanium disk using a Lab Connections (LC) transform module [74]. Thus, seven fractions, ranging in sample mass from 8 to 100 μg, could be measured in a quantitative way by FTIR and HPer DSC. With the aid of FTIR the average branching content along the molar mass distribution was measured, while an analysis of the crystallization/melting behaviour with the aid of HPer DSC provided complementary information about the *distribution* of the branches influencing that behaviour. The fraction (No. 7) shown is the lowest molar mass fraction (200 to 2000 g mol^{-1}) of the HDPE. The method opens up tremendous possibilities for studying the crystallization/melting behaviour of fractions, as obtained by whatever small-scale fractionation method. Recently, a HDPE sample of just 2 μg has been measured and still no problems with signal to noise, curvature etc. were encountered. Of course, careful handling is required in weighing and manipulating such tiny samples.

In general, the low sample mass needed – at *milligram level down to micrograms* – in combination with a high sensitivity and resolution opens up quite different applications. To mention some of the systems brought within reach: coatings and very thin layers, for example in multilayer films as shown above; heterogeneities in samples, such as gels, additives, etc.; and tiny amounts of sample produced by fractionation techniques as shown. In addition, fast screening by high throughput DSC of minute amounts of material as produced in combinatorial chemistry will be possible.

Conclusions

The examples show that interesting new developments take place with respect to scanning calorimetry. First of all, it is clear that modern equipment makes it possible to carry out quantitative measurements, provided the equipment is sufficiently stabilized, the conditions are well chosen, the available models and data banks are used and the results are properly evaluated. A comparison with adiabatic calorimetry confirms once again that DSC can be used to carry out quantitative heat capacity measurements.

DSC has a unique potential for studying the metastability and associated kinetics of polymeric and pharmaceutical systems, owing to the large dynamic range that can be achieved: from (quasi) isothermic to dynamic measurements at hundreds of degrees per minute with the aid of High Performance DSC (HPer DSC).

HPer DSC, a new form of calorimetry, offers the possibility of applying controlled (linear) scan rates up to several hundred degrees per minute in both heating and cooling and will undoubtedly become a very important tool. It will play a crucial role in relating laboratory results to processing conditions, because it offers the possibility of measuring at high cooling rates; it will also be crucial in suppressing reorganization (cold crystallization; recrystallization, annealing, etc.) during heating by means of high heating rates, and, in general, it will be of great value in the study of the temperature-time dependence of important processes such as vitrification and devitrification, crystallization and melting, solid-solid transitions, etc. It can do all this and still offers a high performance: since the measuring time is reduced to minutes, instrumental drift is negligible. Therefore, heat capacity measurements are always possible even at high rates. HPer DSC is also a high rate DSC that can be transformed into a high throughput DSC. As the required sample mass can be extremely low – from milligrams to a few micrograms – it is also possible to analyze impurities, coatings and the yields of analytical fractionations and combinatorial chemistry experiments.

Another development that will be of great practical benefit and scientific interest is high pressure (here up to 550 MPa) DSC. It will be of practical benefit because several important processing techniques (such as injection molding and extrusion) involve high pressures (up to a few hundred MPa). It is of scientific interest because pressure is an important and until now scarcely investigated parameter. It is challenging from an industrial point of view because it may be expected to open up new polymer applications.

Real-time morphological studies – in particular with the aid of scanning probe microscopy (AFM and its variations), small angle light scattering (SALS) and synchrotron X-ray (WAXD and SAXS) – carried out under conditions similar to those usually applied in DSC (incl. TMDSC), provides the required insight into the phenomena measured with DSC.

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