Modern DSC
measuring cell

DSC – More than Just Identifying Materials

Failure Analysis. Integrating the melting peaks of semi–crystalline polyolefins determines more than just the degree of crystallinity. Continuous monitoring of softening and melting behavior into the processing temperature range also provides information on additional components or contaminants. The so–called OIT test often provides reliable criteria for distinguishing oxidation–sensitive polyolefins.

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Thin, flexible packaging films have something in common with thick-walled, rigid pipes and containers: They are made from polyethylene (PE). This semicrystalline thermoplastic comes in various types usually distinguished according to their density as Low Density (PE-LD), Linear Low Density (PE-LLD) and High Density (PE-HD). Above and beyond these, there are special types with higher molecular weights, e. g. Ultra High Molecular Weight Polyethylene (PE-UHMW) as well as cross-linked PE types designated PE-X (formerly VPE). The latter are used mainly for gas and warm water pipes as well as for cable insulations due to their enhanced temperature resistance. Mixing, blending or copolymerizing them with polypropylene (PP) results in a stronger and stiffer material due to the increase in crystallinity. Modification with an elastomer component achieves the enhanced cold flexibility sought for exterior applications in automobile construction (e. g. PP/EPDM for bumper covers).

Conventional Thermoplastics Testing

In quality control and assurance, it is common practice to rely on conventional test data from the granulate before putting it in an injection molding machine or an extruder. Thus the Melt Flow Index, MFI, according to DIN 53735, ASTM D1238 and the Melt Mass-Flow Rate (DIN ISO 1133) describe the flow behavior of thermoplastic materials. The advantage of this rheological test data is its short measuring time. The mass of melted thermoplastic polymer squeezed through a nozzle (aperture) under a certain pressure is measured after 10 min. This value correlates with the molecular weight or molecular weight distribution. The melt flow index falls off sharply fundamentally as the degree of polymerization, i. e. molecular weight, rises. However, this provides only an approximate indication for processability (flow behavior), since neither nozzle dimensions (length/diameter), shear rate, nor temperature can be varied as they are during production [1].

MFI has the essential drawback that it detects single point values only and fails to identify the material or even distinguish different types of polyolefins. To-tally missing is any comprehensive failure analysis of films produced by calendering or blow molding, or of extruded, blow or injection molded pipes and technical parts.

Analyzing Polyolefin Melting Behavior with DSC

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The measurement techniques now being used more frequently in polymer processing continuously detect thermal property data of the investigated polymer material at defined heating or cooling rates. By means of meanwhile established Differential Scanning Calorimetry (DSC, according to ISO 11357 and DIN 53765), an amorphous thermoplastic can be identified and characterized via its glass tran- ▶

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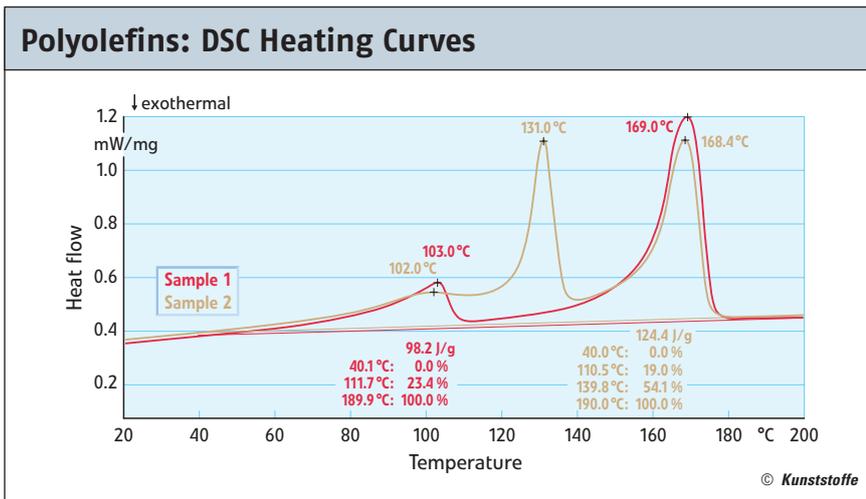
Polyolefins: DSC Heating Curves

Fig. 1. Melting behavior of two polyolefin films, heating rate: 10 K/min

sition, and a semicrystalline thermoplastic via its melting peak temperature. By integrating the area under the melting peak, the heat is determined that is required for melting. The greater the melting peak area, the higher the degree of crystallinity. The shape of the DSC melt curve permits conclusions as to the distribution of crystallite sizes [2]. Thus a flat, wide melting peak describes a wide distribution of crystallite sizes. A melting peak in a narrow temperature range at high melting peak temperature indicates well formed, large crystallites. That is why the ratio of peak height to peak width is often evaluated in DSC analysis.

In addition, contaminants or foreign components can be clearly detected by DSC if they show exhibit thermal effects in a temperature range different from that of the thermoplastic under investigation. Information on the crystallization behavior of semicrystalline thermoplastics can be gained by DSC measuring under controlled cooling. [3] describes in detail the wide ranging use of DSC in quality assurance and failure analysis.

Distinguishing Individual Melting Phases Better

Fig. 1 shows two heating curves following controlled cooling of each of two samples from different film materials. The missing melting peak at 131 °C can be clearly recognized in the red DSC curve (sample 1) and correlated with PE-HD. However, both samples have PE-LD content (melting at 103 °C) as well as one PP component each (melting at 169 °C). The total heat of melting of 98 J/g for sample 1 was evaluated by integrating partial peak areas, whereby the portion of the PE-LD component is approx. 23 %. It can

Separation of Melting Peaks

Fig. 2. Peak separation of individual melting peaks of a PE-LD-HD-/PP film using Netzsch Software

be seen that the quantitative portions are not involved here, since the degree of crystallinity is unknown, on the one hand, and the compatibility of the two polyolefin components has to be considered.

This becomes even more important for the three-component film (sample 2, beige). Total heat of melting here is 124 J/g. Approx. 19 % can be attributed to PE-LD, 35 % to the PE-HD components. The PP component contributes approx. 46 % to total melt heat of melting.

With the aid of peak separation software [4], individually overlapping melting peaks of semi-compatible individual components can be better distinguished (Fig. 2). Here use is made of curve adaptation via the Fraser-Suzuki model (asymmetric Gauss curves). Peak separation using 3rd degree polynomial fit calculates the PE-LD melting area portion to be 22 %, the PE-HD portion being 28 %. The PP component portion thus

stands at 50 %, instead of at the above 46 % evaluated via simple partial peak area. In the blue single peak, it can be clearly seen that the PP component already begins to melt at a significantly lower temperature. At 131 °C (melting peak temperature of PE-HD components), the smaller polypropylene crystallites have already melted.

Evaluating Oxidation Stability by DSC

For packaging films, pipes and fittings from PE, PP or thermoplastic olefin-based elastomers (TPO), information on oxidation stability is becoming more im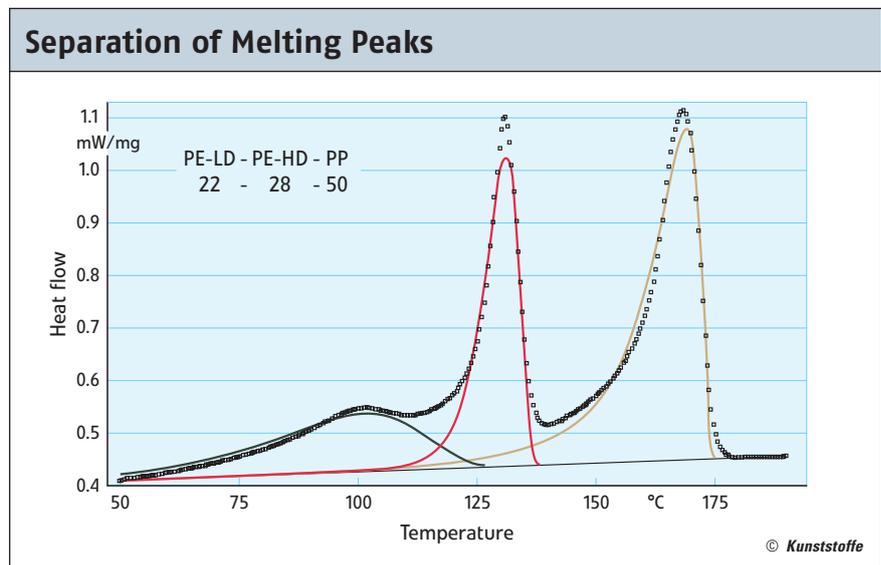portant, since it correlates with product service life. DSC can be utilized for this, too. So-called oxidation induction time (OIT, Oxidative Induction Time) is precisely described in e.g. DIN EN ISO 728 or ASTM D 3895. As determined in co-operative tests [5], the important items are comparable sample weight and removal from the part, good sample preparation, reproducible gas switch from nitrogen to oxygen in the DSC cell and an exact oxygen flow usually controlled and displayed via so-called Mass Flow Controllers (MFC). Modern DSC measurement software also enables OIT detection and monitoring. Here the operator defines a threshold value for exothermic oxidation. If this threshold is exceeded, DSC measurement is automatically interrupted or the next temperature segment called instead [6]. In this way, measurement time can be considerably shortened. The DSC measuring cell is spared a corresponding amount of stress.

It is generally the case that longer OIT time indicates better oxidation stability and thus longer part or film service life. Extensive measurement results on new and aged PE pipe as well as the corresponding granulates were presented in [7].

As part of failure analysis, the OIT test can be directly connected to the second heating following gas switch to an oxygen atmosphere (dynamic OIT or OOT, Oxidative Onset Temperature) by dynamically continued heating at a lower heating rate.

Of course, a broken part from a thermoplastic elastomer cannot be significantly distinguished from a good part during heating (Fig. 3), but a clear difference in their oxidation behavior can be evaluated (Fig. 4). The sample from the
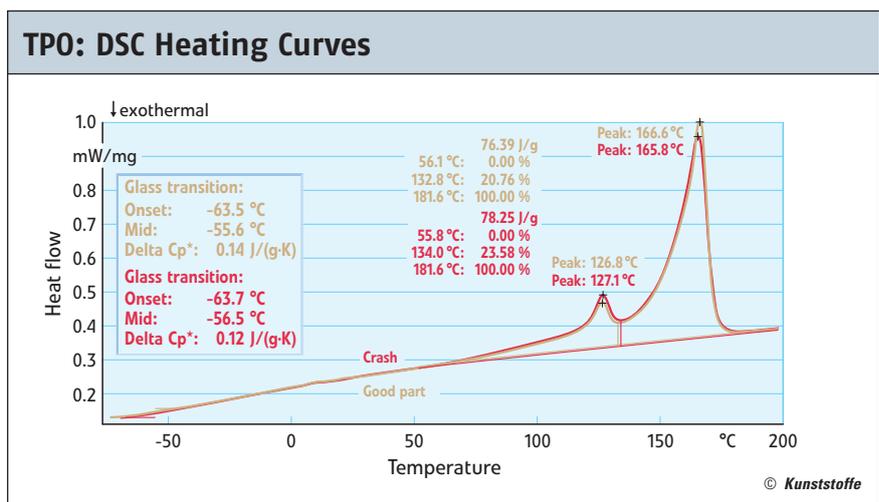

Fig. 3. Glass transition and melting behavior of a broken TPO part (red curve) compared with a good part (beige curve); two heatings following controlled cooling, heating rate 10 K/min each, nitrogen atmosphere 20 ml/min
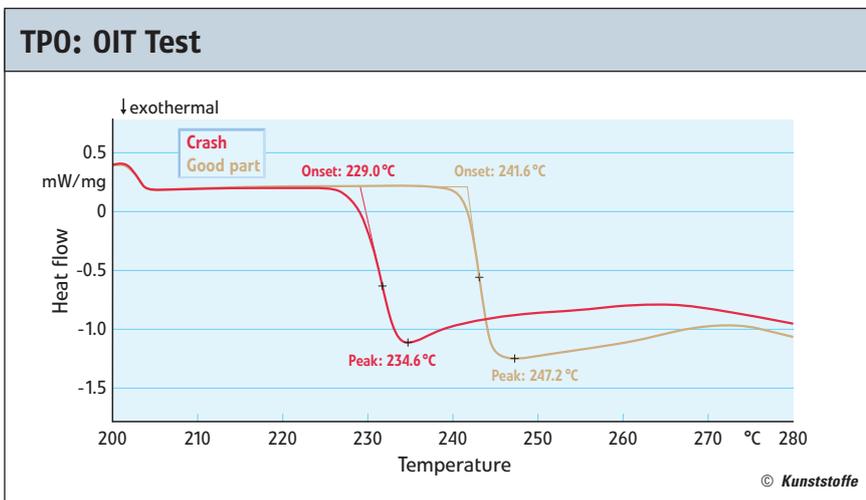

Fig. 4. Oxidation behavior in dynamic OIT testing of the broken TPO part (red curve) compared with the good part (beige curve); heating rate 5 K/min each, oxygen flow 50 ml/min, punched aluminum covers

broken part (red curve) already produces an exothermic peak in the DSC curve at 229°C, thus indicating oxidation onset. By contrast, the sample from a good part is clearly more stable in oxygen flow: its extrapolated onset temperature is significantly higher at 242°C.

Conclusion

The use of Differential Scanning Calorimetry (DSC) as an element of quality control in polymer processing has essential advantages over traditional single point tests, such as melt flow index (MFI). Integrating the melting peaks of semi-crystalline polyolefins determines more than the degree of crystallinity and thereby correlations with strength and stiffness. Instead, continuous monitoring of softening and melting behavior into the

processing temperature range also provides information on additional components or contaminants. Semi-compatibility of blend components can be even better differentiated using Netzsch Peak Separation. Dynamic application of the usually isothermal OIT tests in failure analysis provides excellent criteria for distinguishing oxidation-sensitive materials such as polyethylene, polypropylene or thermoplastic olefin-based elastomers. ■

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