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CHARACTERIZATION OF PROCESSING PARAMETERS FOR INJECTION MOLDING OF THERMOPLASTICS AND THERMOSETTING PLASTICS USING THERMAL ANALYSIS

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ABSTRACT

The purpose of this work was to present the possibilities of thermal analysis to characterize injection molding parameters. Two significantly differing examples were selected:

- characterization of the microstructure by taking specimens from the injection-molded thermoplastic piece, e.g., after processing, and
- reaction behavior of the molding mass for thermosetting injection molding, i.e., before processing
- Morphology and differential scanning calorimetry (DSC) of an injection-molded stepped plate of polybutylenterephthalate

1. INTRODUCTION

Polybutylenterephthalate (PBT) is a partially crystalline, thermoplastic polyester. In order to exclude the influence of the glass fibers on the morphology, a non-reinforced material - a B-type Pocan from Bayer AG in Leverkusen, W. Ger., was used. The dimensions and manufacturing conditions of molded parts determine their microstructure (morphology) to a high degree. The cool-down rate in the mold nest and the resulting crystal formation (degree of crystalization, crystal size) are determined primarily by the temperature of the mass and the mold wall, and the wall thickness of the molded part. It therefore appears possible to investigate these influential variables on the DSC curve using the stepped plate. In addition of course, the variables affecting mold filling, such as injection pressure and flow cross section (of the feedhead runner and the molded part), and therefore the shear speed, any possible alteration of the temperature of the mass, and the filling pressure in the individual mold nest sections must also be observed.

2. EXPERIMENT

2.1 MANUFACTURING THE TEST PART

A stepped plate (mold insert with two mold nests) was selected as test part (Fig. 1) :1:. The injection trials were performed on a 50-ton Arburg model 270-210-500 "Allrounder" machine. The feed-screw diameter (L) was 30 mm, and the feed-screw length (L) resulted in an L/D ratio of 20:1.

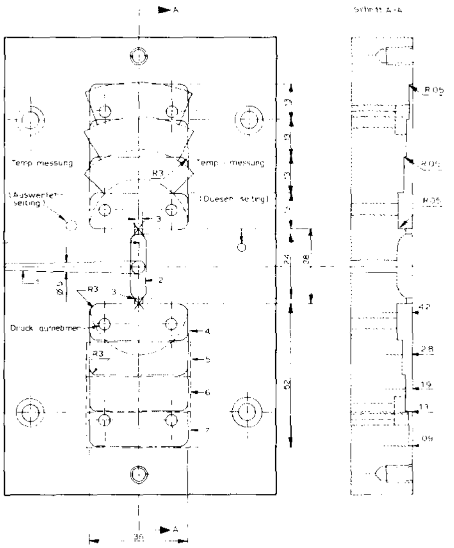


Fig. 1. Stepped plate with allocation of sections for Moldflow.

As Fig. 2 show, the most important process parameters such as interior mold pressure and hydraulic pressure are continuously recorded. With increasing mass and mold-wall temperatures, the time (calculated from the moment of injection) for the secondary-pressure plateau with subsequent drop of the mold inner pressure due to crystallization and the height of the secondary-pressure plateau also increase. In other words, two of the variables mentioned above which influence crystallization, change simultaneously conclusion of the filling process: pressure and stress respectively shear rate are changed by further densification in the molded part - even if one always takes specimens for subsequent thermal analysis from the same section and layer (edge surface or core). These values overlap thereby, e.g., under the conditions of 250/90°C and 260/70°C, so that even when the Moldflow method :2: is used to calculate the mold-Filling process, it could be difficult (as it later in fact proved to be) to always derive unequivocal explanations for the thermoanalytic values from the injection-molding parameters. The moldfilling process is completed upon reaching the first shoulder of the hydraulic pressure, i.e., by an inner mold pressure of approx. 115 bar, so the Moldflow calculation can describe only this very small portion of the complete processing cycle. It should also be considered that the orientations forced upon the material by the injection molding process can also lead to thermal effects.

The Moldflow system is a program for rheological calculation of the mold filling process; a molded part is divided into sections (Fig. 1), and the dimensions and types of flow - as well as the material characteristics - are entered into the computer. The following model was postulated for the calculations in question: radial flow for sections 3 and 4, rectangular flow in sections 5, 6 and 7 of the molded part.

Table 1 shows the values compiled for mold filling with a mass temperature of 260°C, mold wall temperature of 80°C and an injection time of 1.3 sec.

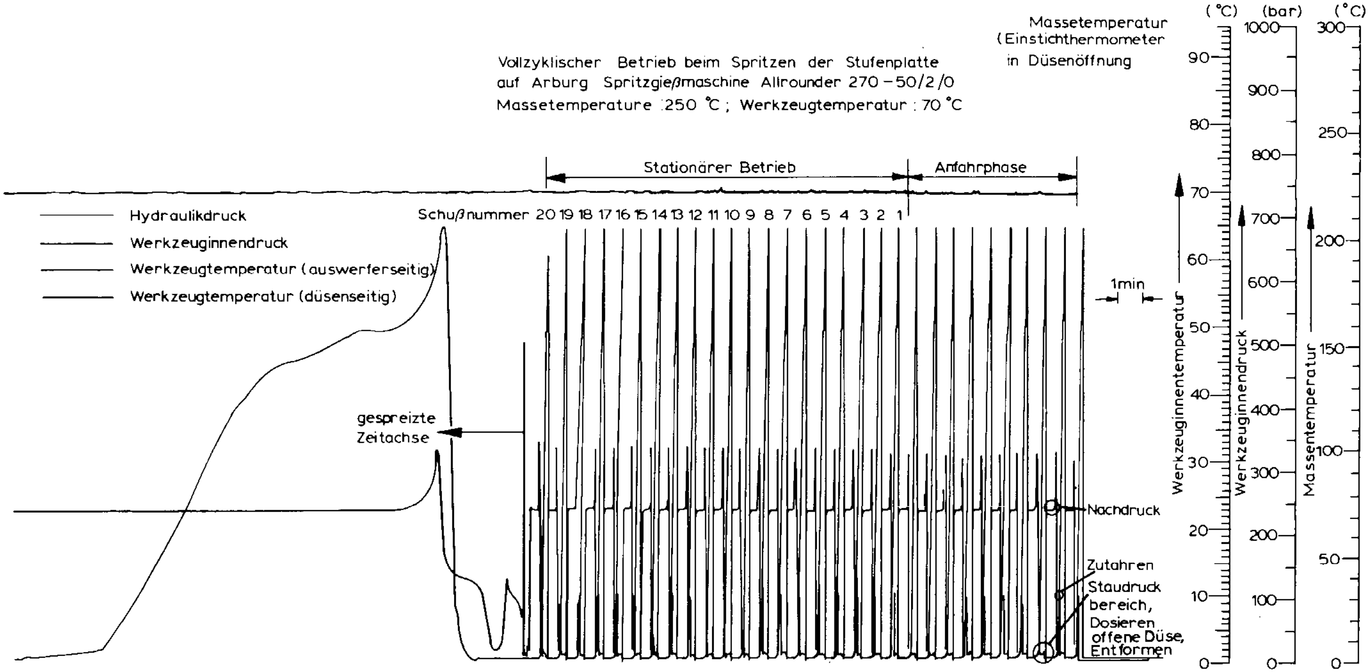


Fig. 2. Typical injection cycle for stepped plate on Arburg 270-50/210 Allrounder.

TABLE 1: Rheological Calculation for Mold Filling with the Moldflow System

Mold section No.	Filling press. (bar)	Press.gradient (bar/mm)	Shear rate (1/sec)	Avg. mass temp. (°C)	Cooling time (sec)
1	284.0	2.187	717	265	21.5
2	163.7	2.957	817	266	13.2
3	134.2	1.714	359	265	12.2
4	117.0	0.384	42	262	29.6
5	112.0	0.925	94	257	14.4
6	100.0	2.229	203	253	7.5
7	71.0	5.464	434	250	4.2

The values represent averages for the individual sections, i.e., other values actually occur in the various layers (edge, core); our experience indicates that these calculated values are more applicable to the edge areas.

Under the term "filling pressure", the pressure from the respective section to the end of filling travel is to be understood. Since the values calculated for the filling pressure and colling time correspond well with those derived experimentally, it can be assumed that the remaining values also correctly describe the actual filling process. Unfortunately, the Moldflow system was available only for this one combination of mass and mold nest-wall temperatures, however it can be assumed that although the absolute values change for other combinations, the tendency within the mold nest would not.

The table shows that although there is a continual reduction in the filling pressure and average mass temperature of the section (No. 3) across the step with the greatest wall thickness (section 4 with approx. 4 mm, in which also the pressure sensor (Fig 2) is located for the transition from injection pressure to secondary pressure which is dependent on the mold interior pressure) to the section with the least wall thickness (approx. 1 mm, section 7); the pressure gradient - and therefore also the shear rate - rises very steeply from the minimum in section 4 to the end of the filling travel in section 7.

It is also particularly important to recognize that the cooling time in section 4 is a maximum while that of section 7 is the smallest. Because the variables stated - mass temperature, mold temperature, wall thickness and shear rate - all influence the microstructure :3:, specimens were taken from sections 4 and 7 for the DSC analyses.

2.2 TEST PROCEDURE

2.2.1 OPTICAL MICROSCOPY AND SPECIMEN PREPARATION

With the aid of a "K" microtome (Jung Co., Heidelberg-Nussloch), 10-µm microcuts were taken from section 4; they were cut parallel to the surface of the molded part from the side opposite the step, and from the core approx. 2 mm from the edge.

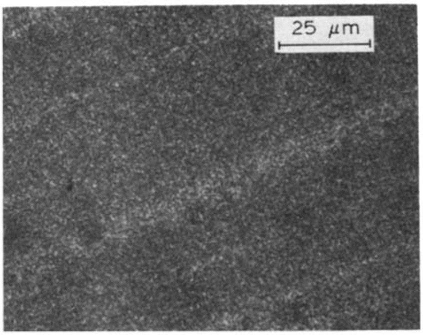
2.2.2 DESCRIPTION OF DSC EQUIPMENT AND SPECIMEN PREPARATION

The DSC analyses were performed with the Perkin-Elmer DSC-4 with a data station. Approx. 100 µm microcuts were taken from the edge surface and core zones of section 4. A scalpel was used to cut the specimens from a corner of section 7, so that for this section, only the exterior of the specimen was examined. Preliminary trials were used to optimize the specimen weight so that all effects relevant to the thermogram would be recognized. With the exception of the injection trials at a mass temperature of 280°C, the molded part related to the 20th shot was analyzed. The heating rate was always 10°C/min.

3. RESULTS AND DISCUSSION

3.1 OPTICAL MICROSCOPY

Looking for various combinations in the microphotographs (Fig. 3 and 4), one can observe primarily microspheres with a diameter of approx. 1 µm, and some of approx. 4 µm, regardless of whether in the edge or core zones.



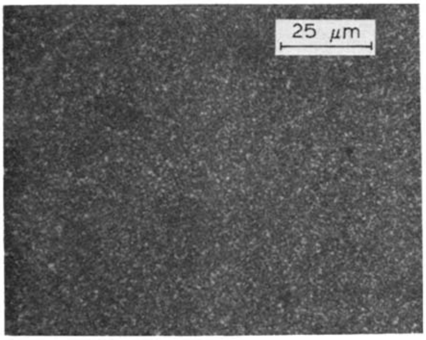


Fig. 3. Microphotograph of a 10-µm specimen between crossed polarizers for 260/70 injection conditions; specimen from edge of stepped plate, section 4.

Fig. 4. As Fig 3; specimen from core of stepped plate, section 4.

As is known, formation and growth of nuclei are controlled via the thermodynamic energy of crystalization if the pressure relationships - and therefore the shear rates - remain constant. For isobaric production of specimens. The reduced cooling parameter $\frac{Tm - Tk}{Tm}$, serves as standard for this.

Although is not the case for the cross section of the part as well as for differing wall thicknesses with injection molding, this parameter is used for characterization of the cooling conditions of the injection trials (Tm is the mass temperature and Tk is the crystallization temperature). One can see now - whether at the edge or in the core - at a constant mass temperature (Fig. 3 and 4), the expected homogeneous microstructure with slightly reduced cool-down rate (0.68 to 0.64). However, these relationships can invert (0.731 to 0.714) at other mass and mold-nest temperatures. In addition to the mold-filling process, it is certain that the secondary-pressure plateau and the drop of mold inner pressure due to crystallization are also playing a role. This was also shown by the investigations of crystallization under high pressure, for which the specimens were produced in autoclaves under known conditions :4:. This indicates that future investigations should couple the rheological calculation of the mold-filling process with that of the area of secondary-pressure. Because of the very fine crystalline microstructure, an unequivocal characterization or differentiation of the injection-molding parameters was not possible with the optical microscope - even at very high enlarging powers. Therefore a numerical expression of the crystal formation is of course hardly possible with the microscope, which is why the DSC investigations were added.

3.2 DSC INVESTIGATIONS

As can be seen by comparing the thermograms of Fig. 5 a small endothermic peak occurs at 221.4°C, with a main peak at 223.3 °C with specimens from the core, while a weakly exothermic peak occurs at 205 °C to 206°C, which turns into the main peak at 222°C, which is joined by an additional, small endothermic peak at 228.2°C. In an earlier investigation :5:, it has already been shown that the small endothermic peak at 212.4°C occurs with a low cooling rate, i. e., in specimens from the core, while the exothermic peak at 205°C to 206°C occurs with a high cooling rate from the melt state, i.e., in specimens from the edge. The other endothermic peak at 228.2°C found here could not be found at that time. This is apparently a form of crystallization mentioned in the literature, which is completely re-crystallizable :6: and which therefore only forms during a DSC measurement :7:.

These effects occur with all specimens investigated from section 4 of the molded part. Also, the endothermic rise of the base line between 150 and approx. 200°C is usually clearly higher with specimens from the core than with those from the edge; this is caused by re-crystallization in specimens from the edge zone - which effect is reduced as specific heat increases with increasing temperature :8:. In Table 2, it can be seen that the tendency of Tmax (temperature of the major endothermic maximum) is somewhat lower on the edge than in the core, however there are also some inversions, particularly in the injection trials with mass temperatures of 260 and 270°C. Taken together however, the differences are so slight that they disappear in the tolerance range when the measurements are repeated. The total enthalpy, Δ H6, behaves similarly. Here, it can only be seen that the values on the edge are higher than in the core; neither value is predictive for variation of the injection parameters. The following evaluations therefore seemed advisable for characterization of the processing parameters:

- Determination of the melt enthalpy ΔHs between 199°C and 233°C (with respect to the exothermic re-crystallization peaks) as standard for crystal formation (degree of crystallization, crystal size);
- Determination of the "rise" enthalpy (between 150 and 199°C) referenced to the total enthalpy ΔH6 (between 150 and 233°C) as standard for the counteracting effect of increasing enthalpy with rising temperature and the exothermic post-crystallization;
- Determination of the endothermic "re-crystallization" enthalpy (between 226.8°C and 233°C) referenced to the total enthalpy ΔH6 as standard for the re-crystallized portion (Fig. 6).

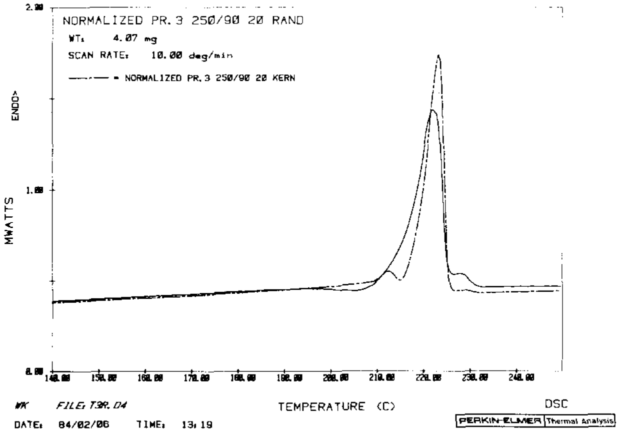


Fig. 5. DSC thermograms for 250/90 injection conditions with specimens from edge and core of section 4 of stepped plate.

Table 2 Mass/mold Temperatures and Thermoanalytical Parameters for Section 4 of the stopped Plate

Specimen designation	reduced cool-down	specimen weight (mg)	Tmax (°C)	H_S (J/g)	H_6 (J/g)	$\frac{H150-199}{H_6}$ (%)	$\frac{H226,8-233}{H_6}$ (%)
250/70/20 Edge	0.720	3.39	221.9	45.9	47.7	5.6	4.6
250/70/20 Core		4.15	222.8	40.7	51.9	12.1	
250/80/20 Edge	0.680	4.57	221.9	44.6	46.5	4.2	3.8
250/80/20 Core		4.31	222.7	40.6	51.5	12.1	
250/90/20 Edge	0.640	4.07	222.0	42.7	48.0	7.7	3.2
250/90/20 Core		4.12	223.2	40.0	51.4	12.2	
260/70/20 Edge	0.731	4.20	222.8	43.1	45.5	4.7	3.4
260/70/20 Core		4.36	222.8	40.6	50.0	10.4	
260/80/20 Edge	0.692	4.33	222.0	43.4	46.1	4.7	3.2
260/80/20 Core		4.24	223.1	39.8	50.3	11.7	
260/90/20 Edge	0.654	4.12	222.9	46.2	45.6	0.8	5.2
260/90/20 Core		4.30	222.5	40.7	44.2	3.4	
270/70/20 Edge	0.741	3.99	222.8	43.6	46.6	6.3	3.1
270/70/20 Core		4.01	222.2	42.0	49.8	9.2	
270/80/20 Edge	0.704	4.52	223.0	43.9	46.4	4.7	3.5
270/80/20 Core		4.32	222.7	41.5	50.7	10.3	
270/90/20 Edge	0.667	4.21	222.6	45.1	45.0	3.5	4.1
270/90/20 Core		4.56	223.1	41.4	51.5	10.6	
280/70/20 Edge	0.750	4.29	223.8	49.0	46.9	4.5	6.9
280/70/20 Core		4.04	223.4	46.9	52.9	6.4	
280/80/20 Edge	0.714	4.48	223.4	46.0	48.2	5.0	4.2
280/80/20 Core		4.98	223.0	43.3	50.7	8.4	

Repeatability for enthalpies/relative enthalpy components : ± 3 %

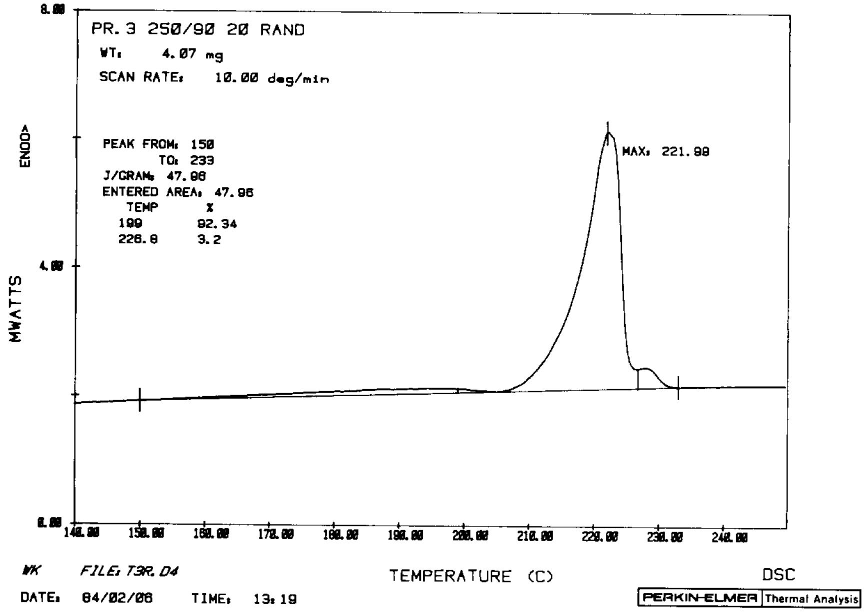


Fig. 6. Allocation of a DSC thermogram for calculating the relative enthalpy portions for the "rise range" (150-199°C) and the "re-crystallization range" (226.8-233°C).

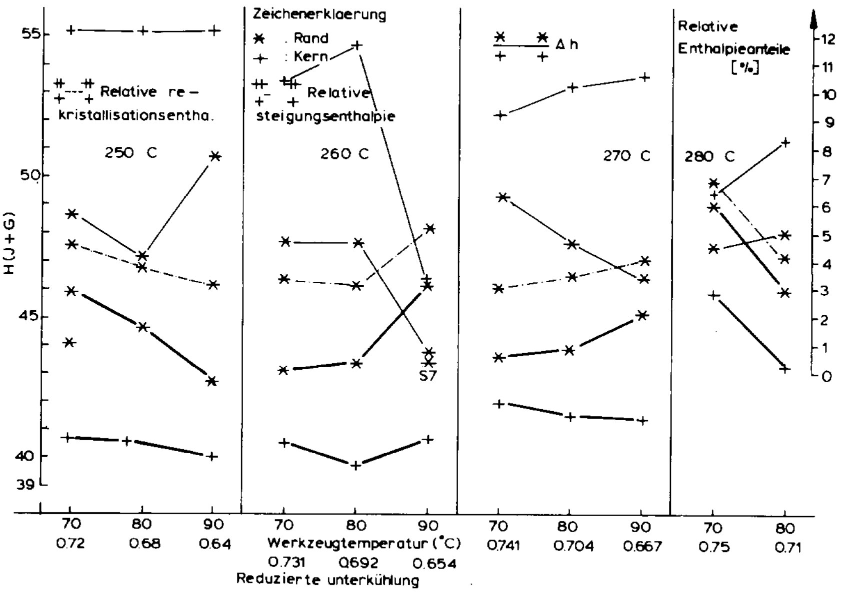


Fig. 7. Melt enthalpy (ΔH_s) and relative "rise/recrystallization" enthalpy for the edge and core as a function of mass/mold-nest-wall temperature/reduced cooling parameter.

In Fig. 7, one can see a reduction for ΔH_S with reduced cooling parameter at the mass temperature of 250 and 280°C, while the relationships at 260 and 270°C are exactly the opposite. The following interrelationships are known from :4::

- The size of the microspheres and the melt heat grow as the cooling parameter is reduced under constant crystallization pressure.
- The melt heat rises as crystallization pressure drops at constant reduced cooling parameter.

If the tendency of the change in shear ratios during the mold filling process is essentially independent of the temperatures of mass or mold nest, there is an increase in the specific melt enthalpy as well as the relative recrystallization enthalpy at a slightly reduced cooling parameter for 260 and 270°C mass temperature. This is in good correspondence with :4:. The premise above should be valid as long as the specimen is always taken from the same location in the molded part. This seems reasonable because if the reduced cooling parameter is reduced, the crystals can form better. At 250 and 280°C, the relationships are exactly the opposite. There is just as little explanation for this by observing the shear ratios from the Moldflow calculation and the pressure curves of the mold interior, as there is for the low enthalpy values in the core, unless the higher shear rate at the edge is responsible. The high reduction in the cooling time is probably responsible for the low values in section 7, in spite of the higher shear rate in comparison with section 4. The relative "rise" enthalpy does not offer a uniform picture. To get a better explanation especially at 250°C and 280°C the Moldflow calculations would be necessary for all injection trials.

Based on these results, one can say that the zonal (edge, core) DSC analysis is a suitable method for characterizing the processing parameters investigated here, in spite of these unclarified questions. For future investigations, an attempt should be made at modifying Moldflow (also zonal calculation).

II OPTIMIZATION OF MASS AND MOLD-WALL TEMPERATURES FOR THERMOSETTING INJECTION MOLDING USING THERMAL ANALYSIS

1 INTRODUCTION

Within the scope of a larger investigation :9: theses consisted of manufacturing high-quality molded parts from a Novolak phenolic molding mass with hexamethylentetramine hardener in a four-piece injection mold. As will be seen here, such tasks can be solved with considerably more ease by using thermal analysis (TA) than for thermoplastics injection molding, particularly when it is a poly-condensation cross-linking reaction, as it is here. The following problem occured after the initial injection trials:

- Depending on the mass or mold-wall temperature, the material foamed either in the injection cylinder or in the mold nests. It appeared that optimization directly on the injection molder would be time consuming and accordingly expensive, and would require large amounts of material. The task therefore consisted of determining the most accurate indications of the optimum temperatures via thermal analysis of the raw materials, so that only the remaining injection molding parameters such as injection pressure would have to be optimized on the machine.

2 TEST PROCEDURE, RESULTS, DISCUSSION

2.1 SIZING TEST COMPLYING WITH DIN 53 477

Due to the requirement of a high cross-linking density, the material had to be relatively fine-grained (particle size less than 2 mm with approx. 5% powder) and a sizing test always had to be performed to avoid too high a proportion of fines which would lead to bridge formation in the granulate container and in the feed-screw induction area.

2.2 THERMAL ANALYSIS

The combined use of DSC and TGA is always recommended for poly-condensation reactions. Looking at the TGA thermograms in Fig. 8, two weight-change stages can be seen. The first stage corresponds with the escape of moisture and the second, the formation of formaldehyde out of hexamethylentetramine and water as ammonia leaves. The formaldehyde promotes the poly-condensation cross-linking of the Novolak phenolic resin molding mass, whereby water again occurs. It is obvious that water content initially present in the molding mass must be precisely matched to the hardener content for an optimal cross-linking reaction, which can be easily tolerated via the relationship of the two weight-change stages. Furthermore, it is also obvious that for the investigated test one cannot heat the mass in the injection cylinder - as is usual with thermosetting injection molding - as near as possible to that required for the start of the reaction, or the material will foam in the cylinder as ammonia forms. Contrary to the data provided by the manufacturer therefore, the selected molding-mass temperature was between 105 and 110°C.

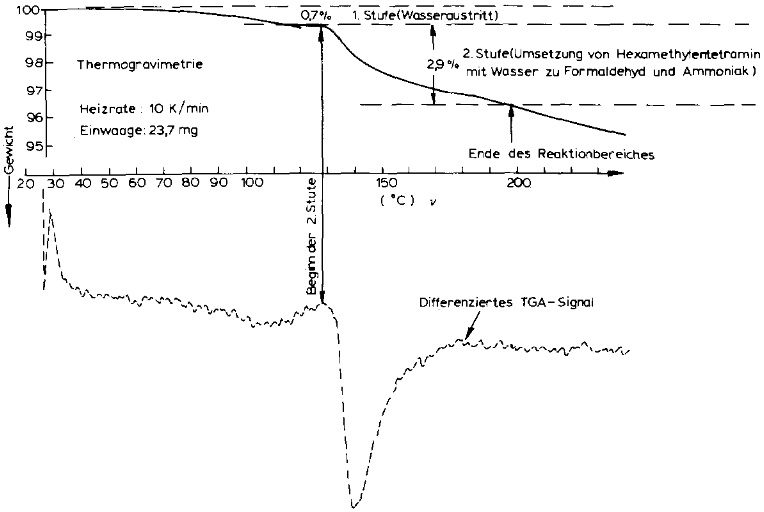


Fig 8. TGA thermogram of a Novolak phenolic molding mass with hexamethylentetramine as hardener.

Also contrary to the molding mass manufacturer's recommendations, a higher mold-wall temperature was selected, between 170 and 180°C, i.e., at the end of the exothermic reaction peak (Fig. 9). That lead to a higher reaction speed of the very thin material injected into the mold, and therefore avoided over-injection and the formation of webs on the molded part. Furthermore, cycling time could be considerably reduced and the molded parts were of high quality and uniformity. The process described here is now used with great success in the incoming inspection.

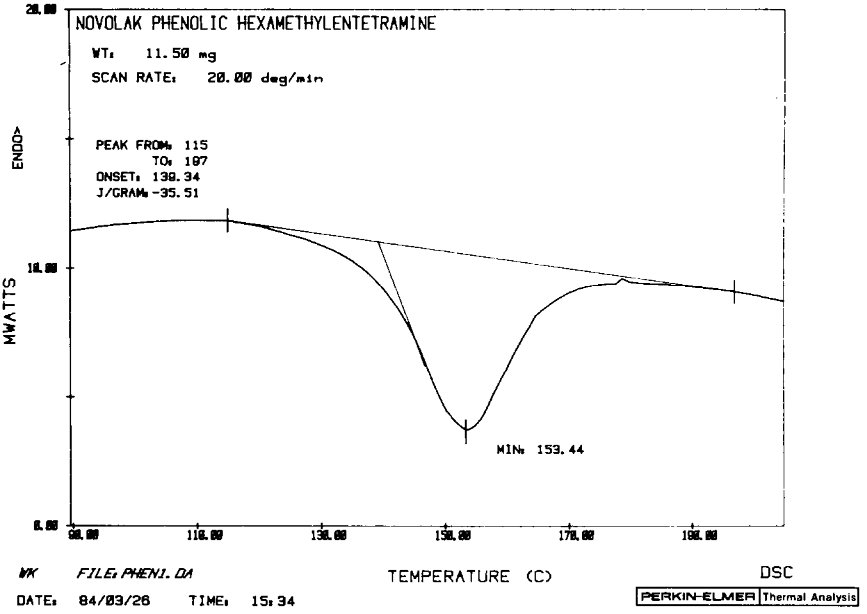


Fig. 9. DSC thermogram of a Novolak phenolic molding mass with hexamethylentetramine as hardener.

III SUMMARY

The possiblities for using TA for optimization and characterization of injection molding processes were represented by two significant examples, i.e.:

- Microstructures based on specimens from various zones of an injection molded thermoplastic part;
- Reaction behavior of a molding mass during injection molding of a thermosetting plastic.

In the first example, polybutylenterephthalate (PBT) without filler was selected, a partially crystalline thermoplastic polyester for injection molding of technical articles.

Through specimens from the edge and core of a stepped plate, characteristic thermoanalytical parameters were determined by assistance of rheological calculations of the mold filling process (Moldflow); these parameters could only partially be correlated with the influences of mass temperature, mold temperature, and the wall thickness - and therefore the pressure and shear rates in various sectors of the molded part, as well as the cooling time.

Additional investigations are necessary in this area; for quality control, the specific melt enthalpy and the relative re-crystallization enthalpy - or instead, simply the DSC thermograms - are suitable.

In the second example, the combined application of DSC and TGA on a Novolak phenolic resin molding mass with hexamethylentetramine as hardener, indications for the optimum mass and mold-wall temperatures for the injection molding process were provided very quickly and at low cost. Furthermore, the dependency of specific reaction enthalpy on the particle size distribution of the molding mass supplied was also shown so that the method described is now used successfully in the incoming materials inspection.

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