APPLICATION AND EFFICIENCY OF THERMAL ANALYSIS IN A PRODUCTION LABORATORY

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ABSTRACT

The application of thermoanalytical methods to technical products in a production laboratory is characterised by a close connection with the specific production process and therefore it is frequently confronted with a large variety of samples. Contrary to research laboratories there are almost no pure material systems to be tested. This means that in harsh environments thermoanalytical methods must provide results with high sensitivity and reproducibility in order to detect reacting components. The example of technical plastics shows not only the efficiency but also the problems of Thermal Analysis for materials testing. Discussed are polyethylene for cable insulation and for pipes, and epoxy resins for injection moulded parts in the electrical engineering field. Demonstrated is the routine application of DSC to determine the crystallinity, curing, and oxydation stability. TG to determine the temperature stability and TMA to measure the degree of curing. A comparison is made between results obtained from different Thermal Analysis methods.

INTRODUCTION

The aim of an industrial production laboratory varies considerably, depending on product specifications. Possible interactions to the production processes are shown in scheme 1.
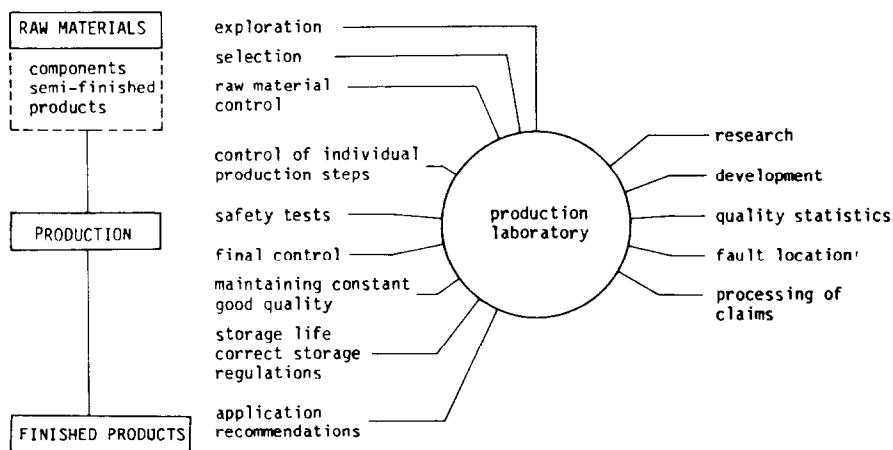
Scheme 1: Classification and problems in a production laboratory

The difference to research laboratories may be seen thematically, the staff employed, the time pressure and the variety of samples. Therefore, it is not necessarily the task of a production laboratory to obtain absolute results but of greater importance are reproducible comparisons to internal standards. The equipment must be operable by assistants as highly-qualified specialists are not very often working directly in the laboratory. Therefore, the standardisation of test instructions and evaluation processes is of great importance. New raw materials and production problems which are found daily, hardly allow a complete clarification of basic material properties; therefore the statistical sampling and quality control have precedence. For technical products the effects known from pure materials only rarely can be clearly shown, as the reacting components are available in reduced concentration and can be influenced and disguised by other components and fillers. Therefore, the instruments and test methods in the production laboratory need to have a very high sensitivity and reproducibility, although for the installation conditions because of the locally close connection to the production process, optimal conditions seldom exist.

Nevertheless, Thermal Analysis is virtually almost without competition in the field of material testing in terms of speed, easy sample preparation and applicable information. The standardisation of the thermoanalytical test conditions and evaluations needs the comparison of results between laboratories. First steps towards standardisation can now be seen nationally and internationally. (ref. 1 and 2)

SAMPLES AND METHODS

Of the important polymers in industrial application here polyethylene (PE) and epoxy resin have been thermoanalytically measured. Measurements were made with polyethylene and cross-linked polyethylene for cable insulations as well as for dense PE pipes with DSC/DTA and TG to study crystallinity, oxydation stability and decomposition behaviour. Die-casting parts of epoxy resin basis for application in electrical engineering were studied to find out the degree of curing in order to optimise the curing temperatures and times using DSC and TMA.

MEASUREMENTS AND RESULTS

The endothermal melting range of the crystalline portion of a PE sample is mainly a material property and therefore is also used for identification of polymers. An exact sample temperature record can be made with the NETZSCH Heat Flux DSC 444 which has a thermocouple at the bottom of the reference cell and is ideally suited for routine measurements of melting endotherms.

The melting peak for PE is found between 100 and 140°C depending upon the crystallinity, density and purity. If there is a bad crystal formation, the melting onset can in some cases be found only a few degrees above Tg (Tg below -20°C). If the start temperature of the measurement is low enough (preferrably < 20°C: therefore low temperature equipment) it is usually possible to determine the melting onset and also to choose sensible integration limits for determination of the peak areas. The degree of crystallinity of a pure PE sample can be determined by comparison of the melting enthalpy with the enthalpy of a 100% crystalline sample (literature value for PE 293,3 J/g or 70 cal/g):

$$\text{crystallinity } C = \frac{\Delta H_{sample} \ (J/g)}{293,3 \ (J/g)} \cdot 100\%$$

Increasing crystallinity results in higher mechanical strength of the polymer.

With the DSC it is also possible to measure small crystalline differences (Fig. 1 a, b) on PE samples from the same piece of pipe sampled at different places.
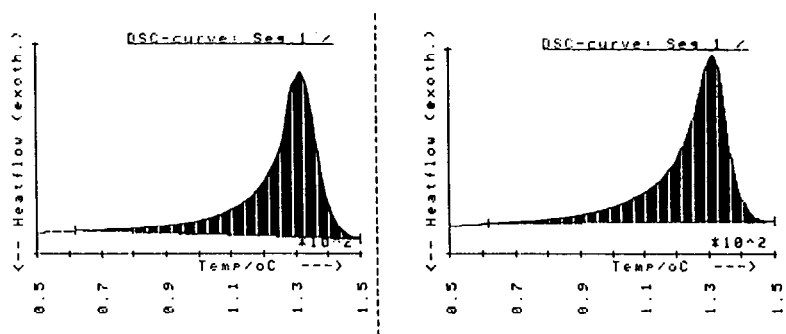
Enthalpy ΔH = 140.0 J/g   Enthalpy ΔH = 147,3 J/g

Fig. 1 a   Fig. 1 b

Fig. 1: DSC melting curves of PE from dense PE-pipe, samples taken on
        outside of tube (1a) and inside of tube (1b)

The samples taken from a dense PE pipe (Ø 20 mm) show different melting enthalpies, therefore different crystallinity. The inside of the pipe is more crystalline as it is recrystallised slower during production.

degree of crystallinity pipe outside 47,7%
degree of crystallinity pipe inside 50,2%.

The DSC 444 with data acquisition system 414 and computer evaluation offers a quick and exact determination of the PE melting enthalpy together with the

degree of crystallisation.

Melting range and melting enthalpy are also influenced by additives (softeners, plasticizers, antioxidants, cross-linking media) and fillers (colours, carbonate) (see Fig. 2). The influence of mechanical pretreatment of PE is usually lost before melting and therefore cannot be seen from the melting peak.

Cross-linking

The mechanical properties of PE can be significantly changed by cross-linking of the polymer chains, i.e. the strength is increased by hindering the movement of the macro molecules. The cross-linking of PE can be initiated chemically (radical formation by dicumylperoxide) or physically (high energy radiation) and results in a chemical interconnection of the macro molecules by co-valent bonds. Consequently cross-linked PE (XLPE) shows a rubber like behaviour above the glass transition and is most suitable for cable production.

Cross-linking improves the mechanical characteristics of PE - but how is the thermal stability influenced particularly in oxidising atmosphere? Oxidation stability was measured on four samples (chemically cross-linked) using two of the possible TA techniques: -

Dynamic testing of a sample in oxidising atmosphere (air, oxygen) with linear heating rate from ambient temperature to the measured onset of oxidation (oxygen absorption) (ref. 1).
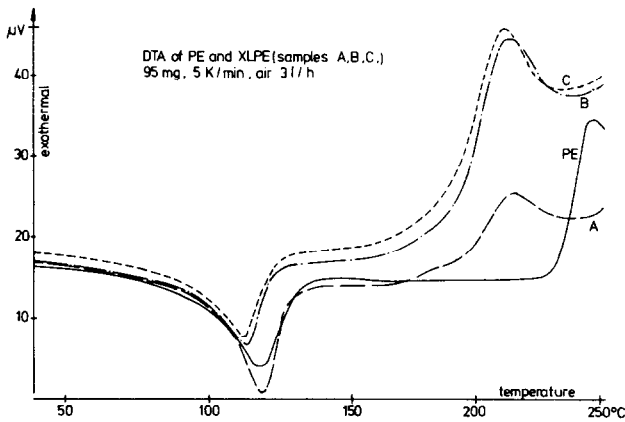

Fig. 2: Melting and oxidation curve for PE and cross-linked PE (XLPE)
samples A. B. C., dynamic test method, 5 K/min

The samples A, B, C are: -

A: PE + cross-linking activator (not cross-linked)
B: PE   partially cross-linked
C: PE   highly cross-linked

The cross-linked samples show a displacement of the melting range to lower temperatures and a clearly reduced oxidation stability compared to uncross-linked PE. The cross-linking of sample A is initiated during heating. Isothermal test to measure the induction time between supply of oxygen and onset of oxidation exotherm. The sample is heated to the test temperature in inert gas flow.
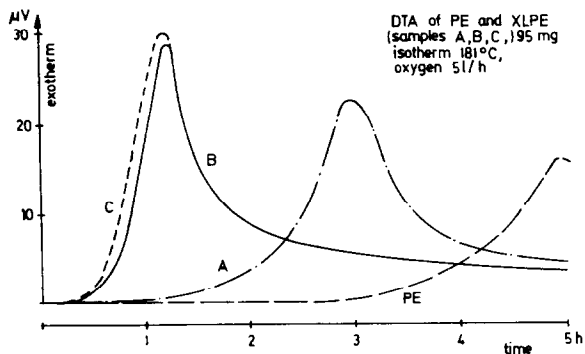

Fig. 3: Isothermal oxidation of PE and XLPE
DTA results of a simultaneous TG-DTA-DTG measurement

The changing from N_2-atmosphere (during the heating phase to the isothermal at 181°C) to pure oxygen atmosphere is made at time t = 0.

Results	oxidation onset dynamic method		oxidation onset isothermal method oxidative induction time (O.I.T.)	
	T_{onset}	$T_{extrapol. onset}$	t_{onset}	$t_{extrapol. onset}$
PE	228°C	237°C	160 min	233 min
PE A	158	190	70	125
PE B	154	193	25	40
PE C	154	189	19	36

The degree of cross-linking is directly related to the thermal stability, the stability of the tested PE samples decreases with increased cross-linking.
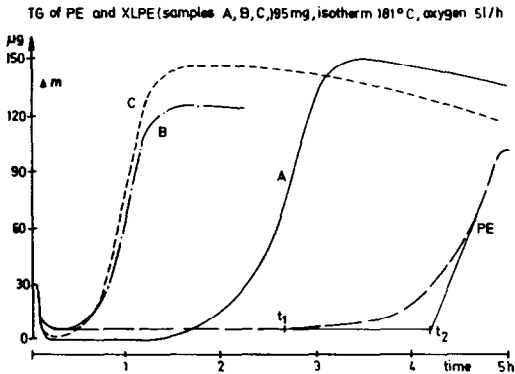
Fig. 4: Isothermal oxidation of PE and XLPE
TG results of a simultaneous TG-DTA-DTG measurement

Changing the atmosphere from N_2 to O_2 at t = 0 first results in an apparant weight loss caused by the buoyancy of the sample carrier system in the higher density atmosphere.

According to Morisaki (ref. 3) the easier oxidation of cross-linked PE is caused by the higher concentration of ternary carbon atoms.

For the tested samples (Fig. 2 - 4) the resolution of the isothermal oxidative induction time measurements is better than the dynamic method (contrary to ref. 1).

The onset of PE oxidation is combined with an increase of mass (Fig. 4) which can be explained by the formation of peroxides and hydroperoxides (ref. 4). The formation of these compounds is exothermal, therefore the evaluation of the TG curves and of the DSC/DTA curves results in similar values for the O.I.T. (isothermal method) or oxidation resistance. This also applies to comparison with the oxygen absorption method to determine the induction period (ref. 5).

The atmosphere also greatly influences the thermal stability of PE. Thermoanalytical measurements made in helium atmosphere indicate a single stage decomposition (endothermal) between 400 and 500°C, before complete weight stability. As shown (see oxidation stability) PE dependent on its structure can be decomposed from 150°C (XLPE) if oxygen is present. The thermogravimetric comparison of PE in helium and pure oxygen atmosphere in the latter case shows at least two stages for the decomposition with onset of the first stage at 250°C and the second stage at 385°C. As with helium atmosphere the total decomposition is only complete at 500°C. Therefore in routine application an exact atmosphere control is necessary for TG tests.

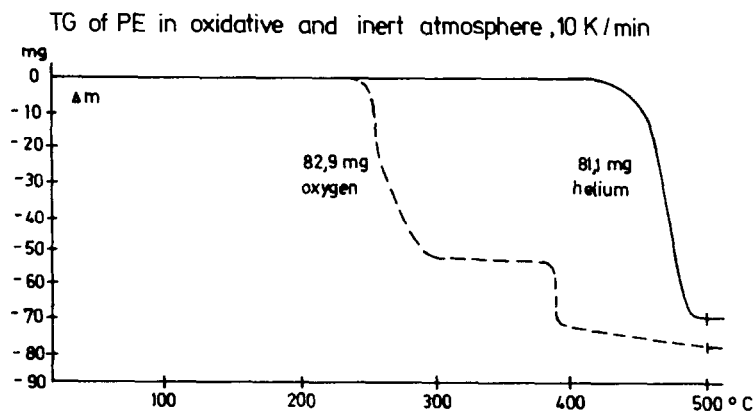TG of PE in oxidative and inert atmosphere ,10 K/min

Fig. 5: Thermal decomposition of PE (oxidative, inert)

In a production application of DSC and TMA the curing degree had been determined on an epoxy resin mixture to encapsulate electronic components. The problems with a high filler portion ($\approx$70%) are clearly shown in the DSC measurements by low enthalpy changes for the thermal subsequent curing and small c_p changes for the glass transition (Tg).
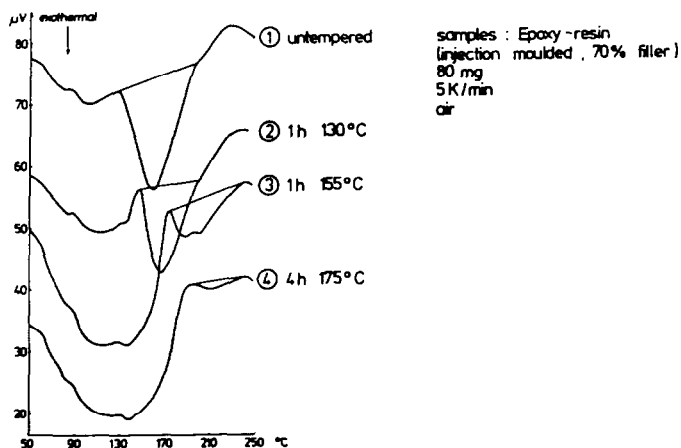
Heat Flux DSC 444

Fig. 6: Glass transition and curing of a technical epoxy mixture, samples with different thermal pretreatment

Evaluation table for DSC tests (Fig. 6) on epoxy resin samples

heat treatment	T_g (onset)	Δc_p	curing from - to	ΔH
untempered	-	-	128 - 230°C	4,33 J/g
1 h 130°C	134,6°C	0,04 J/gK	147 - 230°C	2,51 J/g
1 h 155°C	158,6°C	0,094 J/gK	176 - 236°C	1,12 J/g
4 h 175°C	161,2°C	0,121 J/gK	194 - 240°C	not evalua.

Comparing the changes for T_g, Δc_p and ΔH caused by tempering of the sample, a stronger dependence for Δc_p and ΔH is shown than for T_g. Complete curing of the sample can be achieved with tempering between 175 and 180°C, i.e. Δc_p reaches the maximum value and ΔH gets to zero.

Reason for the distinction between different thermal pretreatment of epoxy resins by means of TMA is the change in volume or change in length of the sample according to its curing conditions (ref. 6). This is clearly indicated when directly comparing an untempered sample with a sample additionally cured at 170°C for 4 h in the differential dilatometer (Fig. 7).
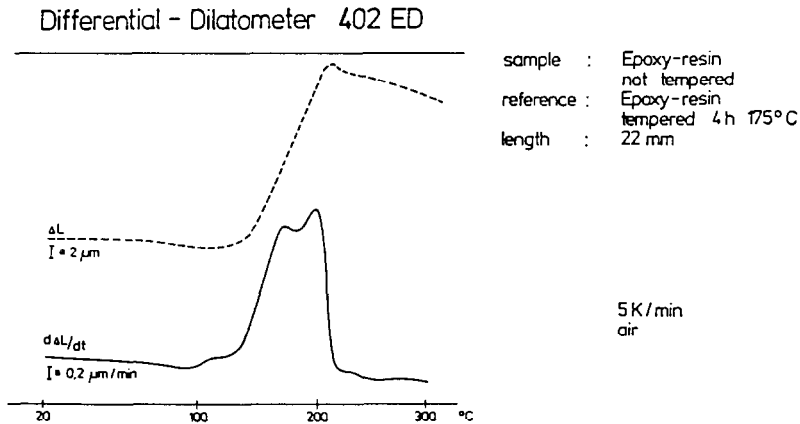

Fig. 7: Expansion difference between untempered and cured injection moulded parts of epoxy resin

Here almost a conformity between DSC and TMA results can be achieved with regard to the curing condition of the epoxy mixture. However, to generalize this is dangerous for a routine application of these TA methods as numerous factors can influence the measurements of epoxy resin mixtures: overlapping of T_g with enthalpy relaxation effect (ref. 7), different ageing and curing behaviour of similar epoxy types from different manufactures (ref. 8).

CONCLUSION

Technical polymeric materials offer versatile application possibilities for TA methods. However, they also require a constant material control in the production laboratory because their properties are easily influenced during an industrial production process. If there are no standards and standardized test specifications available, it is the work of the production laboratory to determine internal standards specific for the material ("example" curves) and tolerances for comparison measurements. Variability of TA methods and present development of TA instruments meet fully the needs of the production laboratory.

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