Journal of Thermal Analysis, Vol. 40 (1993) 587-596

CHARACTERISATION OF POLYMER MASTERBATCHES BY MODERN THERMAL METHODS OF ANALYSIS

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Thermoplastic masterbatches are a complex blend of the base thermoplastic resin, a pigment and a range of additive materials. End use applications of masterbatches include agricultural film, packaging film, injection moulding of small and large bottles, boxes and crates and extrusion of pipe and sheet.

Thermal analysis is a very useful tool for the characterisation of the physical properties of both masterbatches and finished product. This report will show the use of differential scanning calorimetry (DSC) to identify the melt profiles of masterbatches and to determine oxidative stability. Thermogravimetric analysis (TG) is very useful for the determination of the composition of masterbatches, for the study of batch to batch variability and for a comparison of a material with competitive products.

The use of High Resolution TGA (Hi-Res TGA) will be shown to give greater resolution between overlapping weight loss steps leading to better quantification of components within the masterbatch when compared to conventional TG.

Keywords: DSC, Hi-Res TGA, oxidative stability, polymer masterbatches, thermoplastics

Introduction

Thermoplastic masterbatches are a complex blend of the base thermoplastic resin (for example polyethylene, polypropylene PVC or a polymer blend), a pigment (carbon black, titanium dioxide (white) or any other pigmented material) and a range of additive materials used to improve the physical properties of the polymers with which the masterbatch will be blended to produce the final product. These properties include anti-blocking, slip properties of polyethylene film, anti-fibrillation, antistatic, stability against uv light and oxidation, and for ir absorption.

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Akadémiai Kiadó, Budapest

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Thermal analysis is a very useful tool for the characterisation of the physical properties of both masterbatches and finished product. This report will show the use of differential scanning calorimetry (DSC) to identify the melt profiles of masterbatches and to determine oxidative stability. Thermogravimetric analysis (TG) is very useful for the determination of the composition of masterbatches, for the study of batch to batch variability and for a comparison of a material with competitive products.

Experimental

All instrumentation used to produce the results discussed in this report is manufactured by TA Instruments (formerly DuPont) of New Castle, Delaware, USA.

TG analyses were undertaken using the model 2950 TGA in conventional (constant heating rate) and Hi–Res modes. DSC analyses were undertaken using the DSC10 under dynamic and isothermal conditions. Experimental set-up and control and all subsequent data manipulation were facilitated using the Thermal Analyst 2000 controller.

For TG analyses all samples were analysed under either a nitrogen or air atmosphere at a flow rate of 100 ml/min. In all analyses a nominal 30 mg of sample was used. The temperature profile for each analysis was selected dependent upon the sample under investigation.

For DSC analyses an atmosphere of nitrogen or oxygen at a flow rate of 50 ml/min or 100 ml/min respectively was employed. All dynamic analyses were undertaken at a constant heating rate of 10 deg·min^{-1}. Isothermal temperatures for the study of oxidative stability were selected dependent upon the material under investigation.

Results

Figure 1 shows the thermogram resulting from the analysis of a black masterbatch heated at 20 deg·min^{-1} under an inert nitrogen atmosphere. The derivative profile shows that the polymer decomposes in a single step between room temperature and 530°C, with the main decomposition over the narrow range 420°

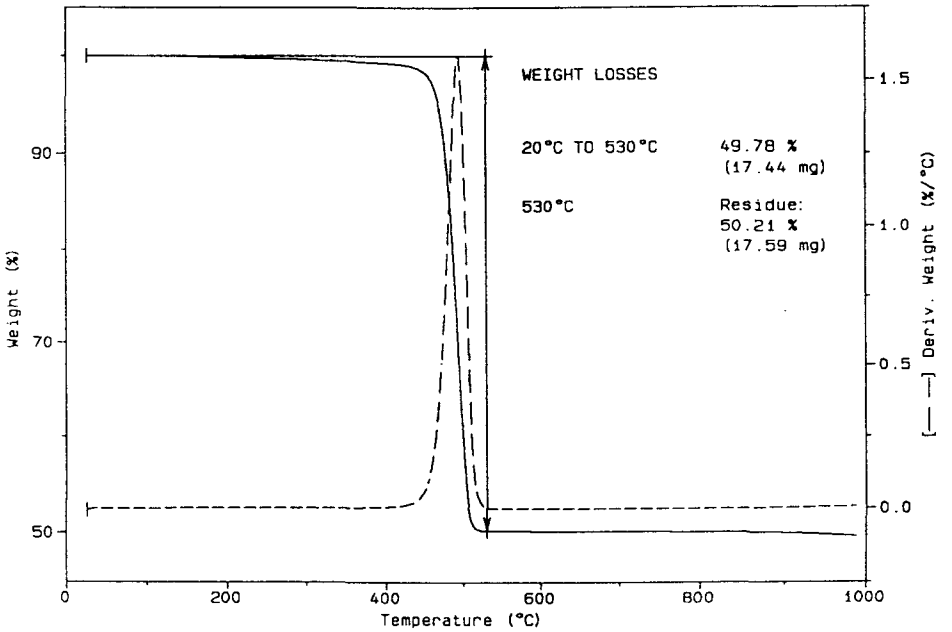

Fig. 1 TG of a black masterbatch under a nitrogen atmosphere

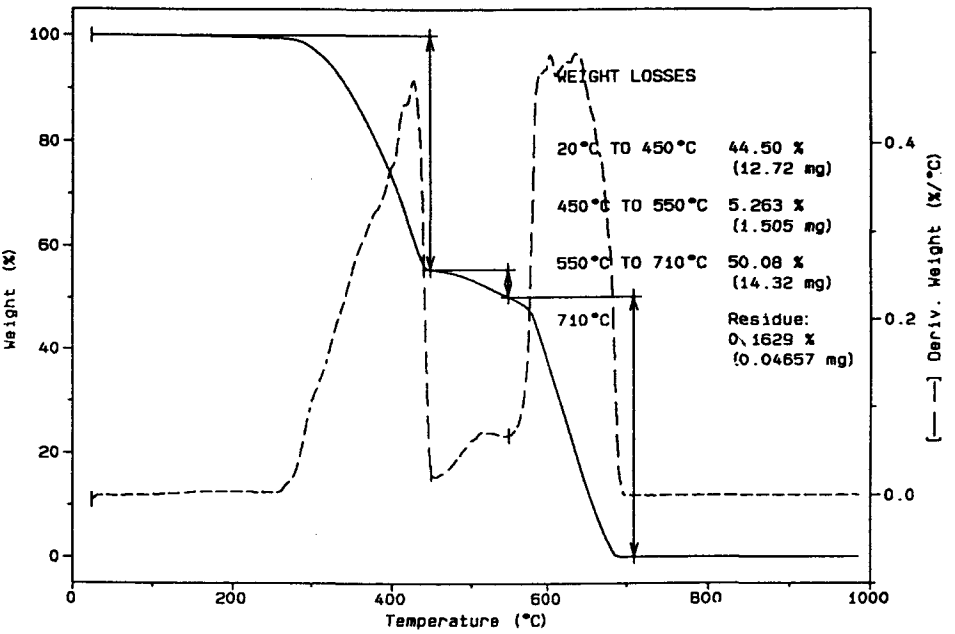

Fig. 2 TG of a black masterbatch under an oxidising atmosphere

to 530°C, to leave behind any carbon char from the polymer along with the carbon black pigment and any inert residue.

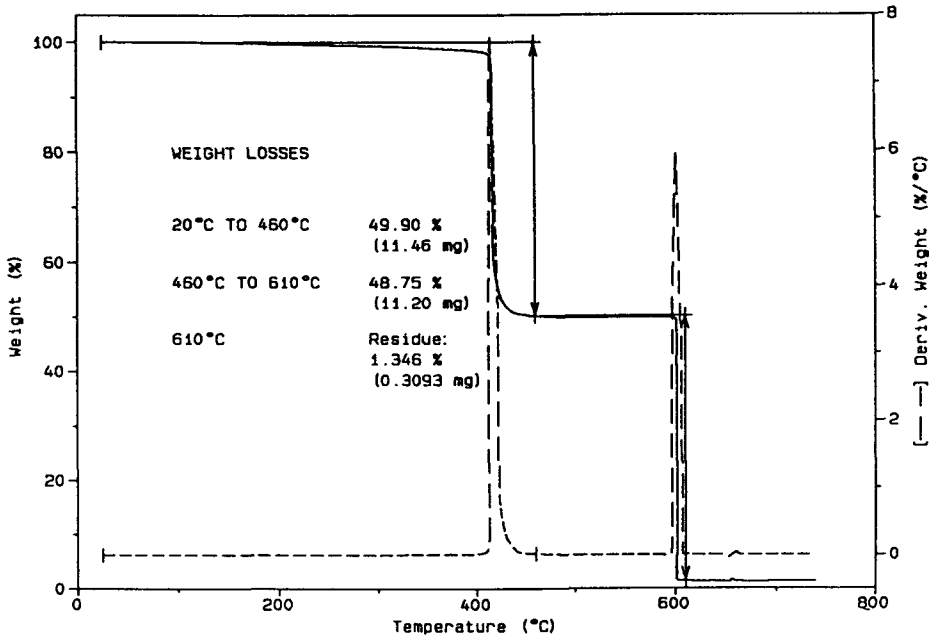

Fig. 3 Hi–Res TG of a finished pellet switching purge atmosphere from nitrogen to air at 600°C

In a flowing air atmosphere the same black masterbatch decomposes in three main steps as shown in Fig. 2. The first weight loss is broader and begins at a lower temperature than is seen under nitrogen, occurring between 260° and 450°C and is not complete before the second weight loss begins and runs into the third weight loss starting at 550° and finishing at 710°C.

It is suggested that the first weight loss is due to the oxidative decomposition of the polymer (this is not a simple process as shown by the detail on the leading edge of the derivative peak), the second due to the combined decomposition of the carbon char from the polymer along with the start of the oxidation of the carbon black pigment which continues through to 710°C. All three steps have been quantified along with a small amount of inert residue.

An estimate of the amount of carbon (char plus carbon black) present in the masterbatch can be obtained by subtracting the amount of residue found under air from that found under nitrogen – in this case 50.05%.

The ability to determine the amount of carbon black present in a finished pellet is elegantly demonstrated by analysing the sample and switching from an inert to an oxidising atmosphere during the analysis as shown in Fig. 3.

A sample of a finished pellet, containing a different polymeric component to the master batch discussed above, was analysed at 20 deg·min^{-1} from room temperature to 600°C at which point the purge gas was automatically changed to air. This analysis was undertaken in High Resolution mode at a Resolution Index of 6.0.

The effect of working under High Resolution is to allow significant decomposition steps to occur at lower temperatures and over smaller temperature ranges because the heating rate is reduced during significant weight loss steps. Additionally, derivative weight loss peaks are narrower and more intense than can be obtained from conventional TG with the result that greater resolution can be obtained from competing and overlapping weight losses. Hi–Res TGA has been described in detail elsewhere [1].

The results show that the sample begins to lose weight from around 200°C with significant decomposition of the polymer at 410°C. Note how sharply resolved this decomposition is. Between 460° and 600°C the weight loss shows a plateau once all the polymer has been oxidised. At 600°C the purge gas is switched to air and the carbon black immediately oxidises to leave a small amount of inert residue. The amounts of polymer, carbon black and residue have been quantified as 49.90, 48.75 and 1.35% respectively.

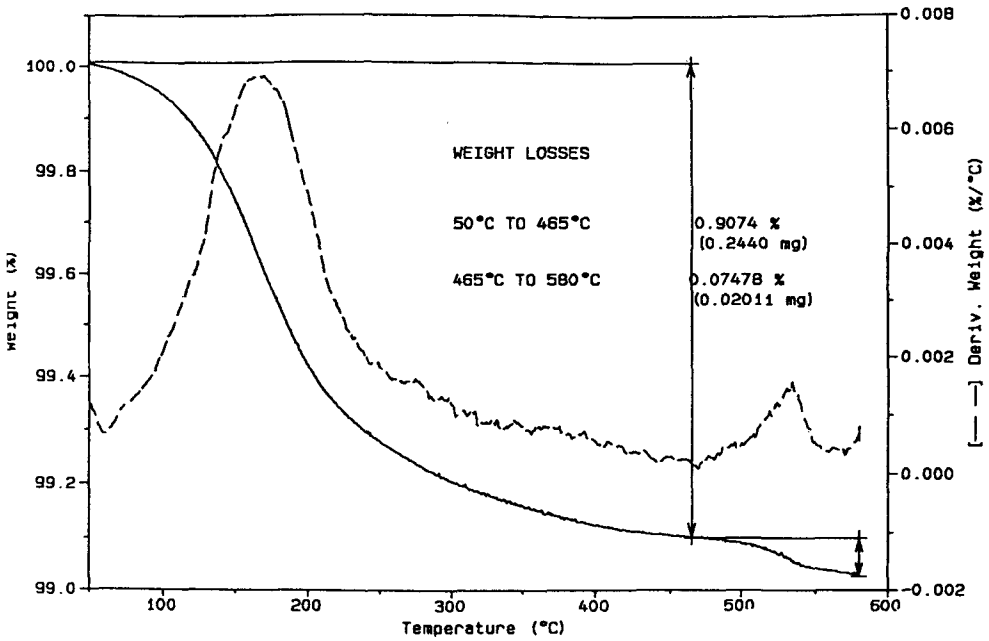

Fig. 4 Hi–Res TG of a polymer additive coated onto carbon black pigment

The sensitivity of the High Resolution TGA technique is displayed in Fig. 4 which shows the results from the analysis of a sample of carbon black, used as a pigment in the masterbatch, at a Resolution Index of 6.0, between room temperature and 580°C. Note that the total weight loss, which is less than 1.00%, occurs in two discreet steps from ambient to 465° and 465° to 580°C in the amounts of 0.9 and 0.07% respectively. Note the sensitivity of the derivative weight signal and how the derivative peaks clearly define the two weight loss steps. It is suggested that this two stage decomposition arises from the breakdown of an organic additive used to enhance the processing of the masterbatch and/or finished pellet. It is further suggested that the analysis of this material by conventional TG would not have resolved these two clear decomposition processes.

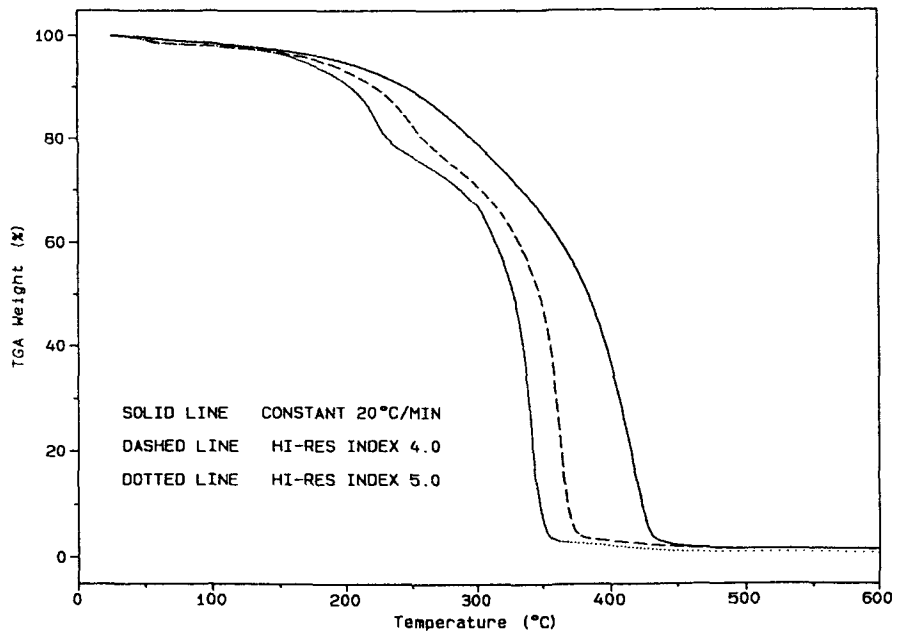

Fig. 5 Comparison of conventional TG *v.s.* Hi-Res TG of a polymer additive

Figure 5 shows the overlay of three curves resulting from the analysis of another organic additive that forms part of the masterbatch recipe. The three plots represent conventional TG under a heating rate of 20 deg·min^{-1} along with High Resolution analyses at Resolution Index 4.0 and 5.0. Note how greater resolution and detail is achieved in the decomposition profile as the analysis goes from conventional, constant heating rate, through to High Resolution under increasing Resolution Indices. Between 160° and 240°C a clear decomposition step evident

at Resolution Index 5.0 is not seen at all under conventional, constant heating rate, conditions. The derivative profile is a very elegant way of 'fingerprinting' the various weight loss steps produced under Hi–Res conditions.

The study of the oxidative stability of masterbatch recipes is important since valuable information can be derived that can be related to process conditions. In addition, depending on the end use of the material, an estimate can be made of the likely useful life of the plastic since correlations can be drawn between oxidation induction times (OIT) at high temperatures and expected time to oxidation at temperatures that the plastic will experience in use.

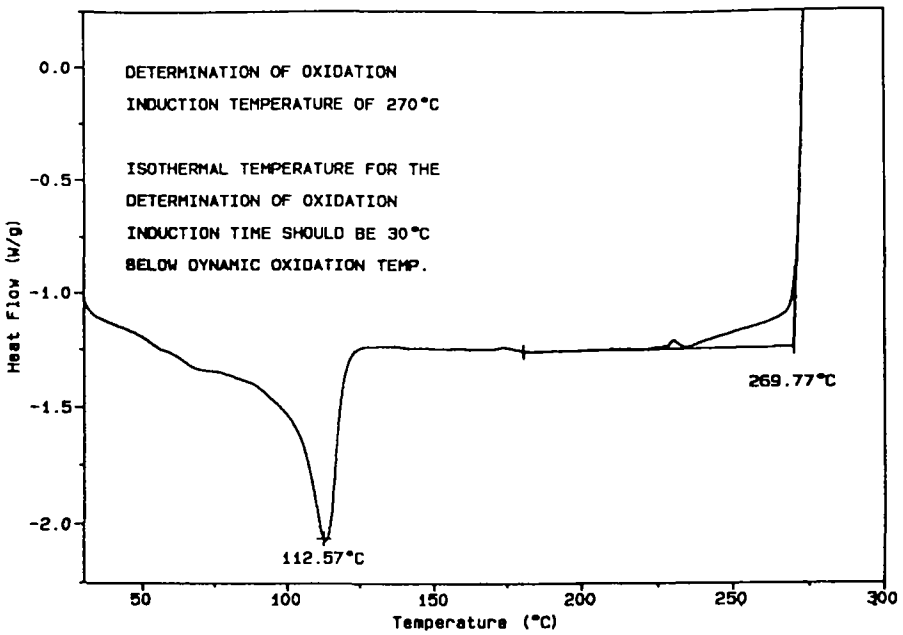

Fig. 6 Determination of oxidation induction temperature using dynamic heating

Oxidation induction of plastics can be studied by differential scanning calorimetry as a function of dynamic heating rate (to give oxidation induction temperatures) or under isothermal conditions (to give oxidation induction times). The most common characterisation of oxidation of plastics uses the oxidation induction time.

In order to identify the most appropriate isothermal temperatures for the study of oxidation induction time the sample must firstly be subjected to a dynamic heating profile under the same oxidising purge gas and flow rate that is to be used in the isothermal studies.

Figure 6 shows the results from the analysis of a black masterbatch at a heating rate of 10 deg·min^{-1} in a flowing oxygen atmosphere at 100 ml/min. Note the endothermic peak with very long leading edge (typical of polymeric melts) and peak temperature of 113°C associated with the melt of the polymer component of the masterbatch recipe. At temperatures above the melt of the polymer the DSC thermogram displays a flat baseline whilst the material remains stable to oxidation. At the critical point however, once all of the anti-oxidant additives have been consumed, the DSC profile shows an excursion in the exothermic direction followed by a very sharp exothermic rise as the material undergoes significant oxidation. The oxidation process releases a large amount of energy, is self propagating and, as a result, the onset is readily identified by extrapolating back from the exotherm to the extrapolated baseline. In this example the oxidation induction temperature is determined at 269.8°C.

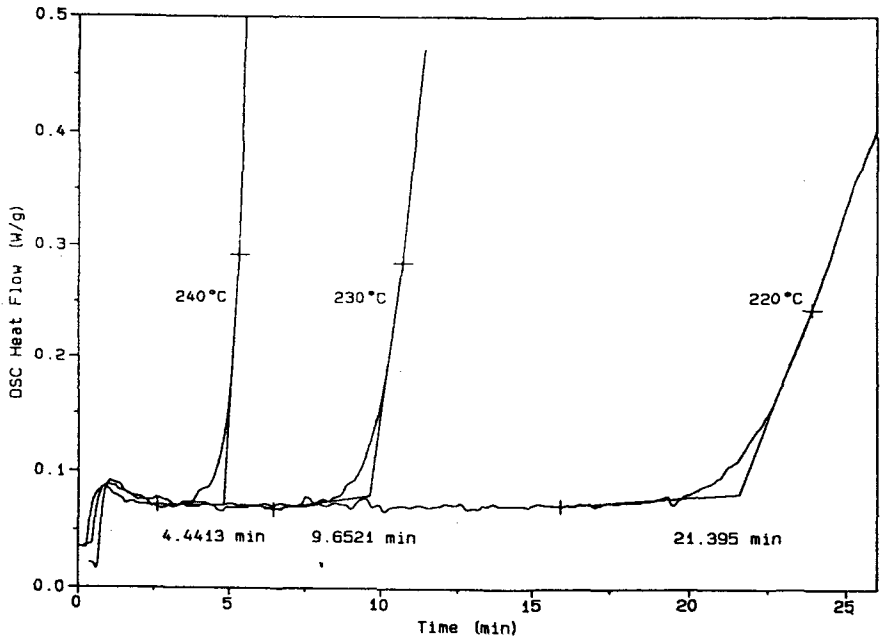

Fig. 7 Comparison of oxidation induction times at different isothermal temperatures

The oxidation induction temperature is used to select the isothermal temperatures at which to hold the plastic in order to determine its oxidation induction time. In general a plastic should be held at least 30°C below its oxidation temperature. In the study of oxidative induction time the plastic is allowed to equilibrate at the isothermal temperature under an inert nitrogen atmosphere. Once temperature equilibration is achieved the purge gas is switched from

nitrogen to oxygen and data collection is begun. In this way zero time is readily identified as the melting point at which data collection commences.

Figure 7 shows the comparison of three oxidation induction time determinations at isothermal temperatures of 240°, 230°, and 220°C. As is expected, the shortest induction time is produced from the highest isothermal temperature and, as a very general guide, the time to oxidation approximately doubles with every 10°C decrease in isothermal temperature. In this example the oxidation induction times have been quantified as 4.4 min, 9.7 min and 21.4 min at isothermal temperatures of 240°, 230° and 220°C respectively. Note also how the gradient of the onset slope is greatest at the highest isothermal temperature showing that the rate of oxidation is also the fastest under these conditions.

Having undertaken oxidation induction time studies the processor will be able to identify the maximum process temperature that he may utilise in the moulding or extrusion process along with the length of time for which he may hold the material at this temperature. Additionally he will be able to specify the maximum in use temperature that will yield an acceptable life expectancy for the finished product.

Another important physical property that will influence the processing conditions of the masterbatch or finished pellet along with the properties of the final product itself is thermal history and its effect on the degree of crystallinity within a polymer. This has been the subject of other studies using DSC [2, 3].

Conclusions

The results discussed here show the potential of the TG and DSC techniques as valuable tools for the characterisation of polymer masterbatches. Information can be obtained quickly and accurately regarding composition along with thermal and oxidative stability. These tools can be used for QC and R&D activities as well as for the identification of competitive products. High Resolution TG, whilst not a panacea, has been shown, in many cases, to yield more detailed information than can be obtained from conventional TG.

* * *

1. Hi-Res TGA is a registered Trade Mark of TA Instruments Inc.
2. This report is a synopsis of a TA Instruments Application Study.

References

1 P. S. Gill, S. R. Saubrunn and B. S. Crowe, J. Thermal Anal, 38 (1992) 255.
2 I. F. Groves, T. J. Lever and N. H. Hawkins, TA Instruments Application Study#3.
3 I. F. Groves, T. J. Lever and N. H. Hawkins, TA Instruments Application Study#4.

Zusammenfassung — Thermoplastische Grundmischungen sind eine komplexe Mischung der thermoplastischen Harzbasis, eines Pigmentes und einer Reihe von Additiven. Zu den Anwendungsmöglichkeiten von Grundmischungen gehören Agrofolie, Verpackungsfolie, Spritzgußteile von kleinen und großen Flaschen, Kartons und Kisten sowie das Strangpressen von Rohren und Platten.

Thermoanalyse ist ein sehr nutzvolles Mittel bei der Beschreibung der physikalischen Eigenschaften von sowohl Grundmischungen als auch Endprodukte. Vorliegende Arbeit zeigt den Einsatz von DSC zur Bestimmung des Schmelzprofiles von Grundmischungen und der Oxidationsbeständigkeit. TGA eignet sich gut zur Bestimmung der Zusammensetzung von Grundmischungen, zur Untersuchung der Unterschiede von Ansatz zu Ansatz und zum Vergleich eines Materiales mit Wettbewerbsprodukten.

Der Einsatz hochauflösender TG liefert eine bessere Auflösung überlappender Masseverluststufen, was im Vergleich zu herkömmlicher TG eine bessere Quantifizierung der Komponenten innerhalb der Grundmischung ermöglicht.