

# THERMAL OXIDATIVE STABILITY OF HEAT-STABILISED POLYAMIDE 66 BY DIFFERENTIAL SCANNING CALORIMETRY

*P.-A. Eriksson*<sup>1</sup>, *A.-C. Albertsson*<sup>1</sup>, *K. Eriksson*<sup>2</sup> and *J.-A. E. Månson*<sup>3\*</sup>

<sup>1</sup>Department of Polymer Technology, Royal Institute of Technology, S-100 44 Stockholm Sweden

<sup>2</sup>AB Konstruktions-Bakelit, S-286 85 Örkelljunga, Sweden

<sup>3</sup>Ecole Polytechnique Fédérale de Lausanne, Laboratoire de Technologie des Composites et Polymères, CH-1015 Lausanne, Switzerland

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## Abstract

The thermal stability of heat-stabilised polyamide 66 in an oxidative environment is evaluated by DSC. The oxidative stability of the polyamide decreases as a result of repeated injection moulding. The results also indicate that the presence of glass fibres in the polyamide has a negative influence on the oxidative stability. Both isothermal and dynamic DSC measurements seem to be useful tools for assessing the stability of polyamides and there is a relationship between data determined using both procedures.

**Keywords:** differential scanning calorimetry, glass fibre reinforced, oxidative stability, polyamide 66, reprocessing

## Introduction

The long term application performance of a polymer is often related to its resistance to oxidative decomposition. Thermoanalytical techniques has frequently been used to study the thermal stability of polymers. DSC has been used to study the oxidation of a wide variety of polymers [1–10] and much of this work has been performed on polyolefins to assess of the relative performance of anti-oxidants or to determine the antioxidant concentration [1–3, 5, 8]. Furthermore, most of the work reported in the literature has been performed under isothermal conditions at elevated temperature well above the melting region. A typical procedure involves:

\* Author to whom all correspondence should be addressed.

- i) the establishment of isothermal conditions
- ii) changing the purge gas from nitrogen to the reactive gas, usually oxygen
- iii) measuring the induction time for the exothermic oxidation process.

The effects of reactions during the induction period are too small to be detected, but these reactions eventually 'consume' the stabiliser and exothermic oxidation of the polymer follows.

The oxidative stability can also be evaluated by heating from an ambient temperature in air or oxygen [2, 5–8, 10–11]. The temperature at, for example, the onset of oxidation is taken as a measure of oxidative stability. The attraction of this dynamic measurement, where the temperature is raised at a constant rate, is its simplicity [8].

Heat-stabilised polyamide 66 has been used successfully for a number of years in critical applications. The glass fibre reinforced grades are, for example, a commonly used material for automotive under-the-hood applications. It is more difficult to study the oxidation of heat-stabilised polyamide 66 than polyolefines by DSC because the measurable exothermic oxidation process usually starts at temperatures within, or just above, the melting region. In unstabilised polyamide 66, however, the measurable oxidation process already starts in the solid phase [11].

In the present work, experiments were carried out to investigate and to determine a reliable method for assessment of thermal oxidative stability of heat-stabilised polyamide 66. Both isothermal and dynamic calorimetric analyses were performed in an oxygen atmosphere on unreinforced and glass fibre reinforced samples. In addition, the influence of repeated injection moulding on stability was investigated.

## Experimental

The test materials were commercial heat-stabilised polyamide (PA) 66. The heat-stabiliser consists of a combination of a copper salt and a halogen compound. The probable mechanism of stabilisation has been reported by Janssen *et al.* [12]. Both unreinforced resin (Rhône-Poulenc Technyl A218) and material reinforced with 30% by mass of short glass fibres (Rhône-Poulenc Technyl A218 V30) were investigated. In order to study the influence of repeated processing, reference samples were injection moulded from virgin PA resin and reprocessed samples were obtained from virgin resin by repeated injection moulding and grinding. All examined samples are listed in Table 1.

The number-average ( $M_n$ ) and weight-average ( $M_w$ ) molecular mass of the studied materials are typically 22.500 g mol<sup>-1</sup> and 45.000 g mol<sup>-1</sup>, respectively. The molecular mass of all studied samples are assumed to be of the same order, since it has been reported [13] that processing/reprocessing utilising normal (optimal) processing parameters only slightly affect the molecular mass. In fact, the

differences in molecular mass between virgin and reprocessed material were within  $\pm 500 \text{ g mol}^{-1}$ .

**Table 1** Examined samples

Sample designation	Grade	Fibreglass reinforced	Reprocessed
1	Technyl A218	No	No
2	Technyl A218	No	Yes
3	Technyl A218 V30	Yes	No
4	Technyl A218 V30	Yes	Yes

A TA Instruments thermal analyser having a 910 DSC module was used to assess the thermal oxidative stability. The sample mass was  $10 \pm 0.2 \text{ mg}$ , cut from injection-moulded test bars according to ASTM D-638M. During operation, the instrument was purged with a constant oxygen flow of  $4.0 \text{ l h}^{-1}$ .

Isothermal measurements were performed at 260, 265 and  $270^\circ\text{C}$ . For this purpose, the samples were 'dropped' in the DSC cell at pre-set temperatures.

Dynamic measurements were carried out starting at  $50^\circ\text{C}$ . Three different heating rates were employed: 10, 15 and  $20^\circ\text{C min}^{-1}$ . The samples were heated to above the oxidation peak temperature.

## Results and discussion

The effect of the isothermal temperature on the exothermic behaviour of sample 1 is shown in Fig. 1. During a run the initial breakdown of stabilisation protection and oxidation of the polyamide resin is accompanied by an exothermic reaction causing a deflection of the heat-flow curve. This exothermic effect is the signature of a severe degradation of the polymer. It can be seen that, as the isothermal temperature is raised, the peak height is increased and the peak width decreases. From these isothermal DSC scans, the oxidation induction time (OIT) was determined. The deviation from the baseline when oxidation starts was used as a criterion for induction time. This is defined as the intersection of the extrapolated baseline and the tangent at a point on the heat-flow curve with the steepest portion. As expected, the induction time decreased with increase in temperature. Usually, the induction period follows an Arrhenius-type dependence on temperature, i.e. plots of induction time against reciprocal temperature being linear. The OIT was determined to be 21.4 and 12.1 min at temperatures of 260 and  $265^\circ\text{C}$ , respectively. An increase in temperature of  $5^\circ\text{C}$  corresponds to about a 50% decrease in induction time. At  $270^\circ\text{C}$  it was not possible to detect an OIT. The shortest induction periods which can be measured are limited to a few minutes because of the time taken to establish thermal equilibrium.

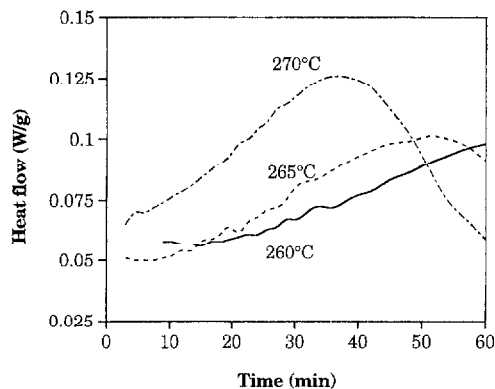


Fig. 1 Heat flow of sample 1 at isothermal temperatures of 260, 265 and 270°C

A typical dynamic DSC scan of heat-stabilised polyamide 66 is shown in Fig. 2. The endotherm at approximately 260°C is due to the crystalline melting of the polyamide. The onset temperature of oxidation (TOX), where the exothermic reaction causes a shift in the baseline which was observed by extrapolation at approximately 305°C. The oxidation peak temperature (OPT) was determined to be about 330°C.

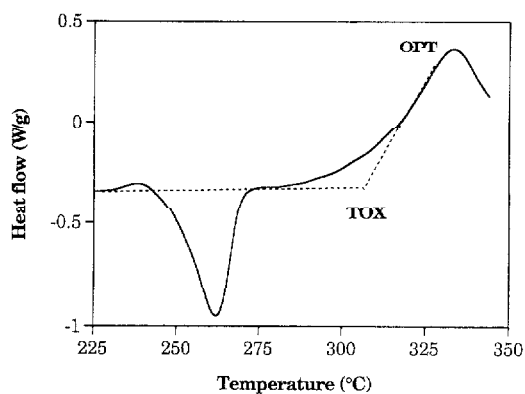
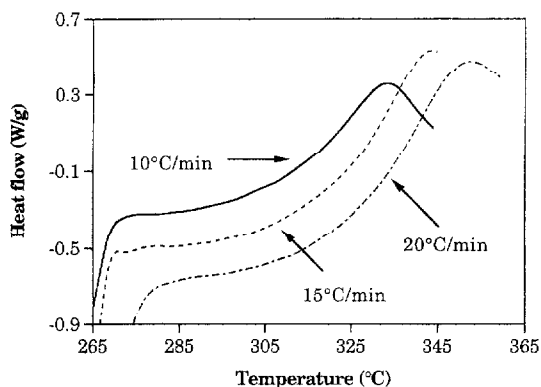


Fig. 2 Typical dynamic DSC scan of heat-stabilised polyamide 66

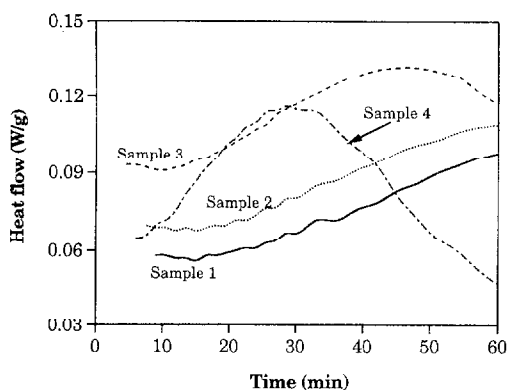
In Fig. 3, the heat flow of sample 1 at different heating rates is shown as a function of temperature above the melting region. As the heating rate is raised, the peak height, the onset temperature of oxidation and the oxidation peak temperature are increased. The activation energies were calculated from the slopes in a logarithmic plot of the heating rate vs. the reciprocal onset and peak temperature. Correction for the error introduced by using a linear approximation in the calculation of the activation energy was performed [14]. The activation energy based on TOX and OPT was calculated to be 140 and 105 kJ mol<sup>-1</sup>, respectively.



**Fig. 3** Heat flow of sample 1 as a function of temperature (heating rate 10, 15 and 20°C min<sup>-1</sup>)

The results shown in Figs 1–3 illustrates the sensitivity of polyamide 66 to oxidative decomposition at elevated temperatures. Considering that the melting peak temperature of polyamide 66 is approximately 260°C and that the processing temperature is in the region 265° to 290°C, thermal oxidative degradation might occur immediately after melting and at temperatures similar to the processing temperature. Fortunately, polymers are usually processed under conditions where the oxygen concentration is low, as in the case with injection moulding. Therefore, these measurements are not very relevant to moulding conditions. However, the sensitivity to oxidative decomposition makes stability studies of polyamides difficult.

Figure 4 shows a set of DSC traces for samples 1–4 as a function of time at an isothermal temperature of 260°C. The oxidation induction time was determined to be 21.4, 17.8, 14.1 and 8.6 min for samples 1 to 4, respectively. Reprocessed samples exhibit lower OIT values compared to that of the virgin reference sam-



**Fig. 4** DSC traces for samples 1–4 as a function of time at an isothermal temperature of 260°C

ples. Furthermore, the presence of glass fibres in the polyamide matrix seems to decrease the thermal oxidative stability

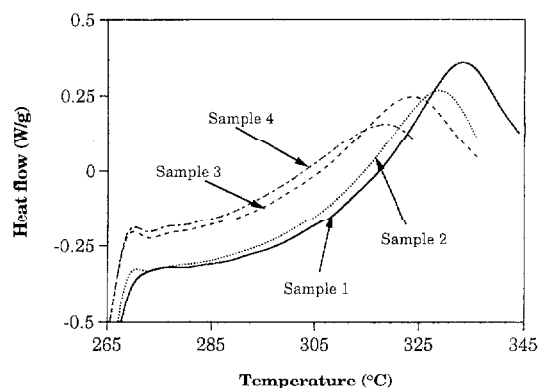


Fig. 5 Dynamic scans for samples 1–4 (heating rate  $10^{\circ}\text{C min}^{-1}$ )

Dynamic scans for samples 1–4 at a heating rate of  $10^{\circ}\text{C min}^{-1}$  are shown in Fig. 5. The onset temperature of oxidation was measured to be  $306.3$ ,  $298.3$ ,  $289.8$  and  $283.0^{\circ}\text{C}$  for samples 1 to 4. The oxidation peak temperature was determined to be  $333.3$ ,  $329.3$ ,  $324.1$  and  $318.7^{\circ}\text{C}$  for the same samples. The order of oxidative stability between the samples determined by dynamic DSC measurements is the same as that based on the induction period during isothermal measurements. Repeated injection moulding and the presence of glass fibres both have a negative influence on the thermal oxidative stability.

The long term performance of a polyamide may be significantly reduced by reprocessing. It is well established that the oxidative stability of a polymer is significantly affected by its previous thermal history. Figures 4, 5 indicate that reprocessed samples exhibit a lower degree of stability compared to that of virgin reference samples as indicated by the lower OIT, TOX and OPT values. This decrease may be explained by process induced consumption of stabilisers during the repeated injection moulding operation because additives such as heat stabilisers are expected to decompose during processing. If this is the case then these measurements may serve as reliable indicators regarding the long term performance of reprocessed items since the results suggest that the degradation will be more intense during, for example, subsequent service in an oxidative environment. This may affect different properties during the service life which may itself be reduced.

The lower stability in glass fibre reinforced samples, compared to that of unreinforced samples, may be explained by the higher processing temperature which conventionally is used for reinforced thermoplastics. A higher processing temperature is expected to increase the decomposition rate of stabilisers. There is a possibility that the surface coating of the fibres, in addition to a higher pro-

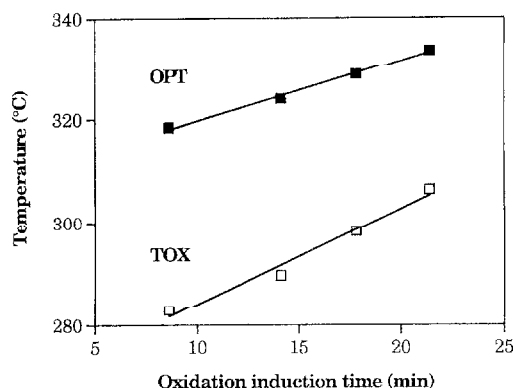


Fig. 6 OPT (Oxidation peak temperature) and TOX (onset temperature of oxidation), determined at  $10^{\circ}\text{C min}^{-1}$ , as a function of oxidation induction time at  $260^{\circ}\text{C}$

cessing temperature, also contributes to the reduced stability. The presence of surface-coated fibres may increase the effect of autocatalytic reactions as a result of extra free radical introduced [9].

The measurement of OIT is rather more time-consuming with very stable materials and less accurate with materials of low stability whereas the OPT measurement is more exact. At a low stability, the induction periods are so short that the reproducibility must be questionable. The induction time is also limited due to the time required to establish thermal equilibrium. To compare data from isothermal and dynamic DSC measurements, dynamic data determined at  $10^{\circ}\text{C min}^{-1}$  was plotted vs. the oxidation induction time at  $260^{\circ}\text{C}$  for samples 1–4. The results are illustrated in Fig. 6. The result indicates that there is a relationship between OPT or TOX and OIT. Both isothermal and dynamic measurements, therefore, seem to be useful for assessment of the polyamide stability. Furthermore, the relationship allows the prediction of the induction period at isothermal conditions using data from the more rapid dynamic DSC method.

## Conclusions

The thermal oxidative stability of heat-stabilised polyamide 66 was evaluated by DSC. Calorimetric analysis was performed on both unreinforced and glass fibre reinforced material, as well as on reprocessed material.

The oxidative stability of the polyamide decreased as a result of repeated injection moulding. The reduced stability suggests that, unless restabilised, reprocessed material will degrade at a higher rate during subsequent service. The results indicated also a negative influence on the oxidative stability by the presence of glass fibres in the polyamide. This may be explained as being due to the higher processing temperature used for reinforced material, but may also be due to the surface coating of the fibres.

Both isothermal and dynamic measurements seemed to be useful for assessment of the polyamide stability. There was a relationship between data determined using both procedures. Isothermal measurements, however, are either more time-consuming or less reliable to perform compared to, for example, the oxidation peak temperature determined using dynamic conditions. The latter technique has the advantage of providing repeatable results and short analysis time.

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