



Efficiency of stabilisers in polymers measured by microcalorimetry

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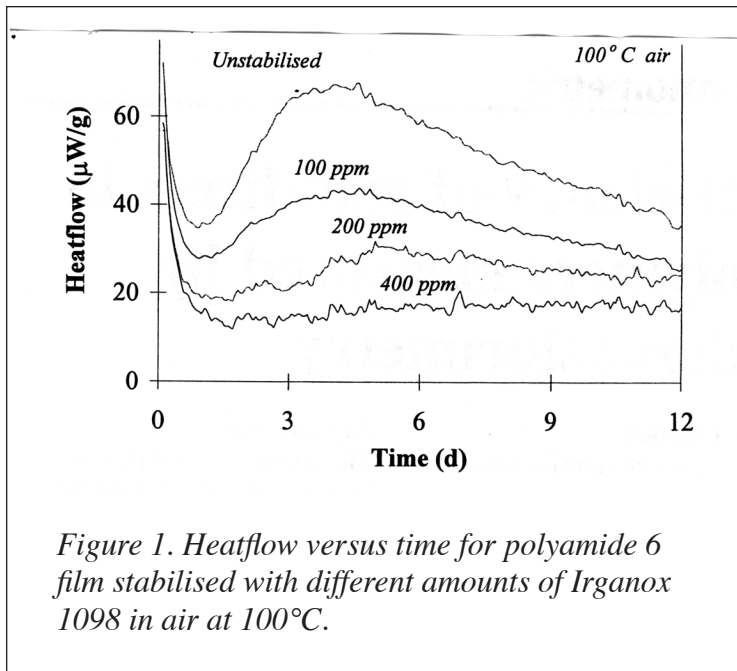
INTRODUCTION

During recent years rate sensitive techniques such as chemiluminescence and microcalorimetry have gained increasing interest in the field of oxidative stability of polymers. This application note demonstrates the usefulness of the Thermal Activity Monitor - TAM - a multichannel microcalorimetric system, for studying the efficiency of stabilisers in polymers.

Oxidation of polymers proceeds via a chain radical mechanism. The main features of this degradation mechanism are the regeneration of reactive alkyl radicals and the formation of hydroperoxides. To prevent oxidation certain types of stabilisers, e.g. radical scavengers such as phenolic antioxidants and hydroperoxide decomposers are commonly added to the polymer in small amounts. A classical way to evaluate the stability of a polymer material is to use high temperature DSC, i.e. above the melting point of common semi-crystalline polymers such as polyamides and polypropylene. The sensitivity of the TAM system enables oxidation studies far below the melting point and in this respect cancels out some disadvantages associated with high temperature measurements.

EXPERIMENTAL

The oxidative stability of unstabilised and stabilised 40 μm thick polyamide 6 film was studied by means of microcalorimetry. Irganox 1098, which is a hindered phenolic anti-oxidant, was used as a stabiliser. The oxidation studies were performed in air in the temperature range of 100 - 120°C. A Thermal Activity Monitor, model TAM 150, intended for use in the temperature range of 20 - 150°C was used with 4 ml Stainless Steel Perfusion Ampoules. Air was flushed through the ampoules



by means of a peristaltic pump using a flow rate of 3 ml min⁻¹. Typically, 0.2 - 0.4 gram of film was used. Since the films were sufficiently thin to ascertain no influence of diffusion the heatflow was normalised to the mass of the sample.

RESULTS

Figures 1 and 2 show the heat-flow versus time curves in air at 100 and 120°C respectively. It was shown by mechanical and chemical characterisation that the polyamide 6 films oxidise directly on heating showing embrittlement after 1.5 and 8 days at 100°C and 120°C, respectively. From Figures 1 and 2 it is concluded that the heatflow versus time curves varies throughout the useful lifetime of the material. The heatflow versus time curve is characterised by an initial peak followed by a second peak after which the heatflow is continuously declining. In the presence of the phenolic antioxidant the curves are shifted towards lower heat-

flow levels and longer times. However, the efficiency of this type of antioxidant in polyamide 6 is rather poor, e.g. the time to a drop in strain at break is extended only by a factor two. Figure 3 shows the data of Figure 2 plotted as heatflow versus energy evolved. It is observed that the maximum of the curves appear in the range of 18 J g⁻¹ for all films. The similar shape of the heatflow versus heat energy curves indicates that the oxidation mechanism remains unchanged in the studied temperature interval. Furthermore, since it was found that a drop in strain at break corresponds to an energy of roughly 50 J g⁻¹, microcalorimetry appears to be a highly sensitive technique to detect oxidation, also during the initial stages of oxidation.

CONCLUSIONS

Microcalorimetry proved to be very sensitive to oxidation. The high sensitivity of the TAM system enables oxidation studies to be performed in the low temperature range. The efficiency of a phenolic antioxidant (Irganox 1098) in polyamide 6 could readily be estimated.

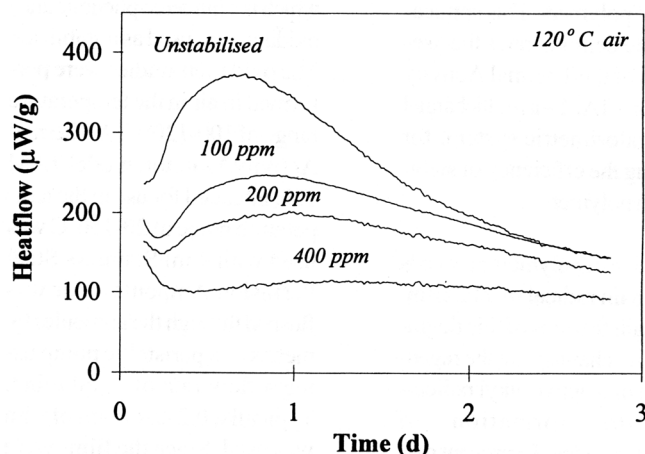


Figure 2. Heatflow versus time for polyamide 6 film stabilised with different amounts of Irganox 1098 in air at 120°C.

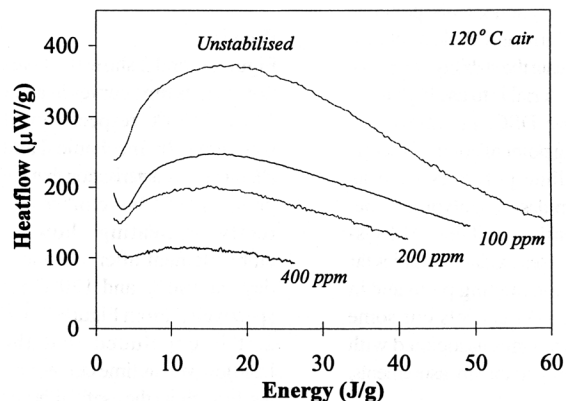


Figure 3. Heatflow versus energy evolved for polyamide 6 film stabilised with different amounts of Irganox 1098 in air at 120°C.

REFERENCES:

1. Forsstrom, D., Thesis, *Novel Techniques for Characterisation of the Oxidative Stability of Polyamides*, KTH (1999)