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Oxidation of Polymers Studied by Microcalorimetry

Introduction

The deterioration of polymeric materials is often caused by oxidation and typically manifested by gradually increasing yellowing and embrittlement. Accelerated tests such as oven ageing at increased temperatures using mechanical and chemical characterisation at regular intervals have routinely been used to assess the oxidative stability and useful life of polymers. However, although conventional characterisation techniques such as FTIR, LC, DSC and chemical analysis have been successfully used to characterise the oxidation products formed, the sensitivity of such techniques is usually not sufficient to monitor oxidation in its initial stage.

Rate sensitive techniques such as oxygen absorption, chemiluminescence techniques (CL) and microcalorimetry offer a possibility to study stability and degradation of polymers during *in situ* conditions. Oxygen absorption measures the amount of oxygen absorbed by a sample whereas the chemiluminescence techniques measures the intensity of the weak light emission associated with oxidation of organic molecules. Oxygen absorption and chemi-

luminescence are both directly related to oxidation whereas microcalorimetry is a *non-specific* technique, sensitive to all physical and chemical processes occurring in a sample. For this reason microcalorimetry has found applications in a variety of areas, *e.g.* stability studies of drugs, polymers and explosives, efficiency of stabilisers, water vapour permeability, polymorphism and compatibility.

This application note demonstrates the applicability of TAM (Thermal Activity Monitor) – a multichannel microcalorimetric system to study oxidation of polyamide 6 film.

Experimental

Blow moulded unstabilised 40 μm thick polyamide 6 film was aged in ambient atmosphere in the temperature range of 100-140°C and characterised by various mechanical and chemical techniques such as tensile testing, FTIR and DSC. In addition, the oxygen absorption, the light emission as well as the heatflow was monitored during *in situ* oxidation. The CL measurements were performed using a CLD 100 instrument from Tohoku and the heatflow measurements by the use of a TAM microcalorimeter, model TAM 150 from Thermometric. The *in situ* oxidation

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Fields of application

Material science – Stabilisation and Degradation of Polymers

Instrument configuration

2277 -051/052	Thermal Activity Monitor - TAM 150
2277-201	4 ml Ampoule Microcalorimetric Unit
2250-040	4 ml Stainless Steel Perfusion Ampoule
2277-301	Stainless Steel Ampoule - as reference
640-1/2	Mass Flow Controller
2277-131	Digitam Software

References

1. Forsström, D., Thesis "Novel Techniques for Characterisation of the Oxidative Stability of Polyamides", KTH, Stockholm, Sweden (1999).
2. Gijsman, P., Tummers, D., and Janssen, K., *Polym. Deg. and Stab.* **49**(1) (1995) 121.

measurements were performed under an atmosphere of dry air using a flow rate of 3 ml min⁻¹. Thin film samples having a mass of 0.2-0.4 g were used in order to avoid influence of diffusion.

Results

Figure 1 shows the strain at break versus time for the polyamide film at different ageing temperatures. The time where a drop in strain at break occurs may be defined as the useful lifetime of the film. The oxidation of the film is accompanied by an autoretardant increase in the carbonyl index as measured by FTIR, see Figure 2. It is interesting to note that the oxidative behaviour of polyamides is rather different from polyolefins that generally show an induction period of low rate of oxidation before a pronounced increase in rate occurs.

Figure 3 shows the CL intensity time curve and the time integral *i.e.* the total luminous intensity (TLI) for polyamide 6 in ambient atmosphere at 110°C. The corresponding heatflow time curve and the time integral, *i.e.* the heat energy are shown in Figure 4.

It is obvious that the CL intensity time curves and the heatflow time curves of polyamide 6 shows individual characteristics. The CL curve shows an apparent 'induction period' of high intensity followed by a sigmoidal increase through a maximum, which is related to the drop in strain at break. The corresponding heatflow time curves shows a maximum, which is related to the end of the induction

period of the CL curve. The TLI time curve shows an auto-accelerated shape whereas the Energy time curve essentially shows an autoretardant shape similar to the accumulation of carbonyl groups shown in Figure 2 and to oxygen absorption data published in the literature².

The different shapes of the CL time and the heatflow time curves, also observed in the corresponding time integral curves, reflect a different sensitivity of the two techniques to oxidation of polyamides. Although both the microcalorimetric and the CL techniques reflects the same oxidation process, the results show that the monitored quantities, *i.e.* the CL emission and the heatflow, are sensitive to different *sub processes* of the overall oxidation process. The results suggest that microcalorimetry

might become a new complementary tool in studying oxidation and stabilisation mechanisms of polymers.

Conclusions

Two rate sensitive and continuous techniques, *i.e.* microcalorimetry and a chemiluminescence technique, proved to be sensitive to oxidation of polyamide 6 film, however exhibiting individual characteristics. The techniques were found to relate to each other and to a drop in strain at break. Microcalorimetry was specifically found sensitive to monitor oxidation during the initial stage of oxidation. Both techniques offer convenient tools in elucidating the mechanism of stabilisation and degradation of polymers and should be regarded as complements to other techniques giving new information on the oxidation process.

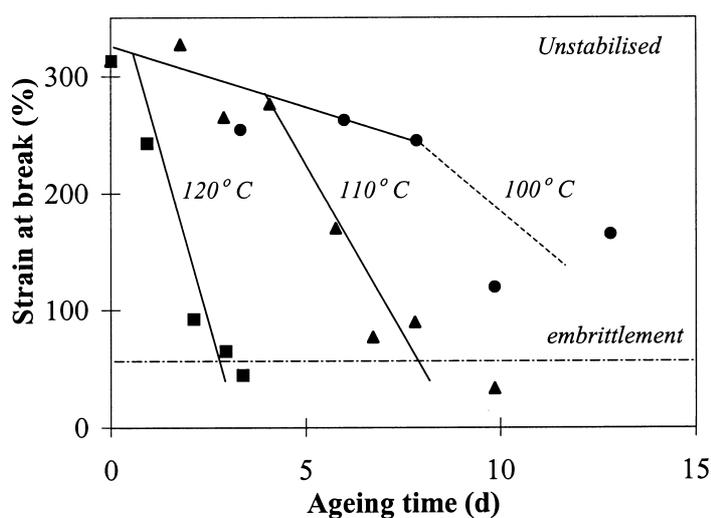


Figure 1.

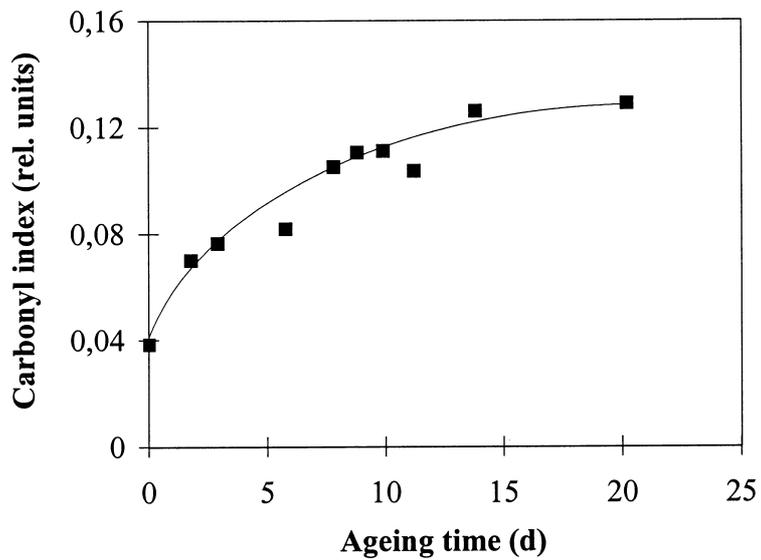


Figure 2.

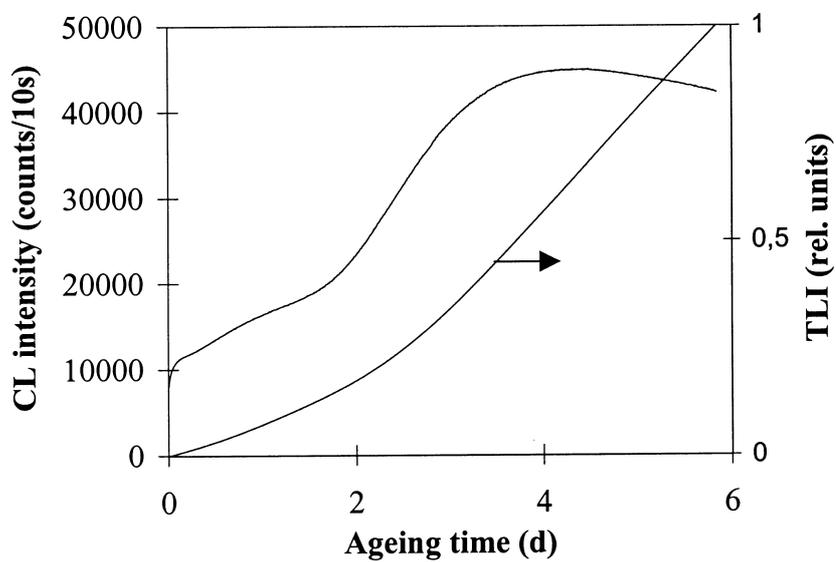


Figure 3.

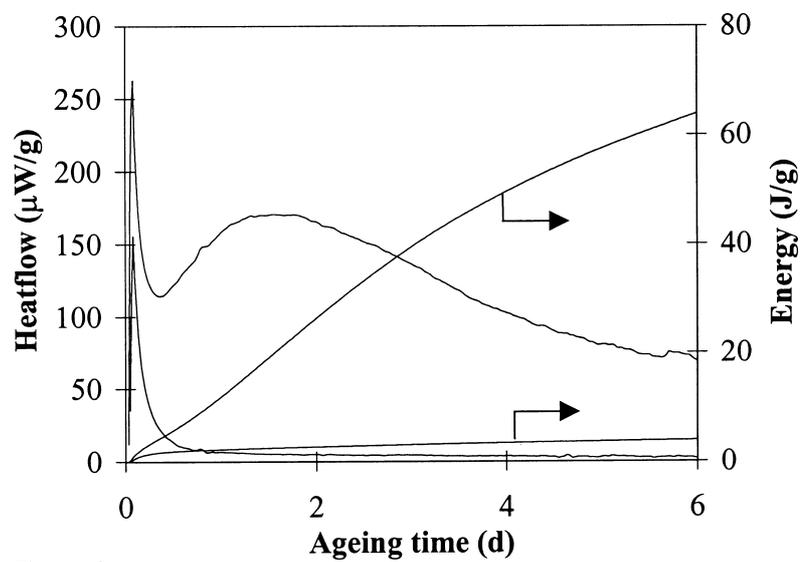


Figure 4.