Thermochimica Acta, 214 (1993) 141–144
Elsevier Science Publishers B V , Amsterdam

Oxidation of polyethylene monitored by microcalorimetry at 70°C.

Lars-Erik Paulsson

FFV Materialteknik i Karlskoga
S-691 80 Karlskoga, Sweden

Abstract

Sensitive calorimeters has become very useful at many laboratories for material sciences. Based on heat measurments these instruments can be used to monitor heat generated or consumed by chemical reactions or physical processes The sensitivity of modern microcalorimeters makes it possible to study slow processes which makes the method suitable to study ageing processes close to room temperature.

In our laboratories TAM microcalorimeters has been used for many years for a varity of studies:

-Compatibility of explosives with other materials (1)
-Stability of energetic materials
-Metall corrosion at different RH (2)
-Diffusion of gases through rubbers/polymers (3)
-Oxidative and hydrolytic reactions in polymers.

In this report we want to show the behaviour of polyethylene when tested in a microcalorimeter and the suitability of the instrument for studies of oxidation of aged polyethylene.

1. METHODS

0,5 -1 g of polyethylene samples in the shape of rods or sheets are weighed into 3 ml glass ampoules. The ampoule is closed and introduced into an isothermal microcalorimeter (TAM,-calorimeter, Thermometric AB, Järfälla,Sweden)) . After 30 minutes in order to reach temperature equilibrium the measurements are started and the heat generated from the sample is continously registered giving curves with µW/g vs time.

This paper was presented at the 13th Nordic Symposium on Thermal Analysis and Calorimetry, Stockholm, Sweden, 9–11 June 1992

2. NORMAL POLYETHYLENE

During the years we have tested many different samples of polyethylene in our microcalorimeters when performing compatibility tests.

Most samples of polyethylene tested in our calorimeters at 70°C show an initial exotherm that gradually goes down to zero. The shape of the curves are normally very similar for polyethylene in air, in nitrogen and immersed in water

We have no explanation of this initial exotherm that is common for many thermoplastic materials.

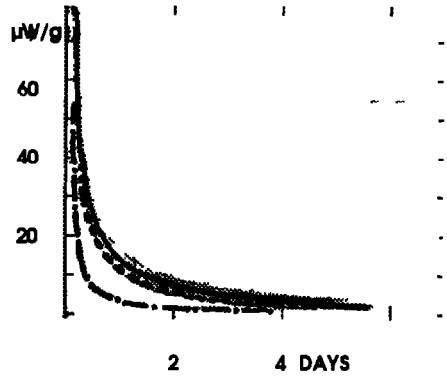


Fig 1 Microcalorimetry at 70°C
Normal polyethylenes

3. UNSTABLE POLYETHYLENE "VIT"

A particular polyethylene sample "VIT" behaved in a different way.

With this particulare polyethylene we found a somewhat higher heatflow value and a deviation from the normal curves when tested in air.(Fig 2 "AIR") By testing this sample in an atmosphere of 100% oxygen we found still higher heat flow values - 75µW/g.(Fig 2 -"O2") In nitrogen we found a curve more like the curves for normal polyethylene (Fig 2 "N2") indicating that this polyethylene can be degraded by oxygen at 70°C and that the process can be monitored by the microcalorimeter.

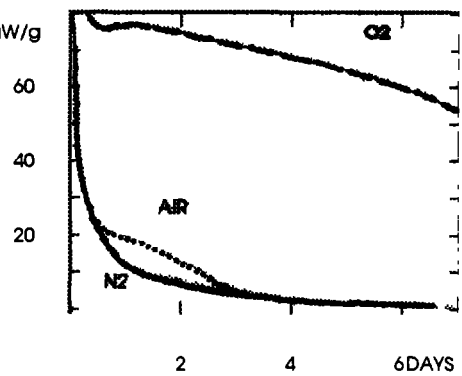


Fig 2 Microcalorimetry at 70°C
Unstable polyethylene "VIT"

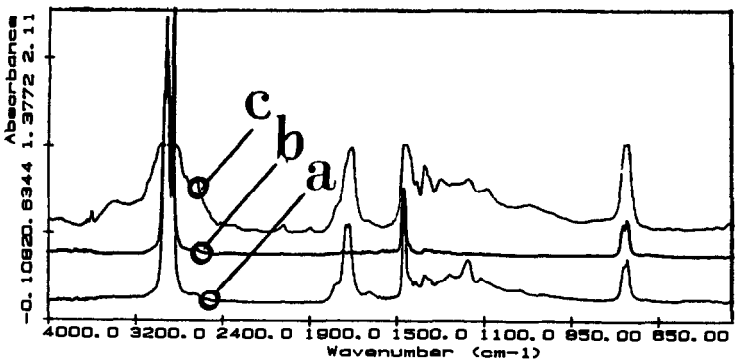
The sample "VIT" is a HDPE from a 3,5 mm thick commercial available polyethylene bottle with an unknown prehistory.

There were no cracks observed in it and the mechanical properties were good even after forced ageing. By testing in oxygen at 180°C we found however that this polyethylene has a bad resistance to oxygen as measured by the conventional method (DSC).

Later we found bands in FT-IR indicating oxidation of the polyethylene.This was found only at the inner wall and only to a depth of 0,3 mm.(Fig 3a and 3b)

Fig 3 FT-IR::

a) VIT
Inner wall
b).VIT
Outer wall
c) OLD



4 . DIFFUSION

The curve we got when measuring in the calorimeter directly after introducing oxygen to the sample was different from the curve when we had stored the polyethylene sample in an oxygen atmosphere for 5 days at roomtemperature prior to the test in the calorimeter The heat flow curves decreased at a higher rate for the pretreated sample. This indicates that diffusion of gases into the polyethylene may be an important factor.

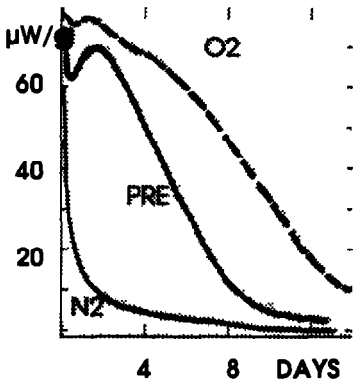


Fig 4 Microcalorimetry at 70°C
Unstable polyethylene "VIT"

5. TEMPERATUREDEPENDENCE

A parallell run was performed at 65°C of the sample pretreated in oxygen for 5 days to get an idea of the temperature dependence of the reactions. The activation energy in this very narrow temperature interval was estimated to 43 kJ/mol. If this value is correct for a wider range we would expect 5µW/g at room temperature for the sample "VIT" in oxygen. Since the calorimeter is sensitive well below 1 µW it seems possible to measure oxidation of this sample of polyethylene down to room temperature

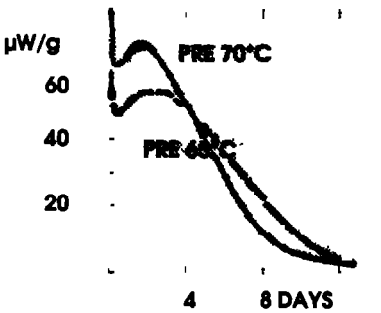


Fig 5 Microcalorimetry at 70/65°C

6. OLD DEGRADED POLYETHYLENE

We have also tested a polyethylene sample that had been used as a diffusion barrier in a building since 1969. This sample "OLD" was very brittle and its FT-IR spectra shows signs of a highly degraded polyethylene.(Fig 3c)
We found it oxygen sensitive by testing it at 70°C in the calorimeter. As can be seen from the curves the heat flow from this sample is higher in oxygen (250μW/g) than in nitrogen atmosphere.
The decrease in the curve "O2" after 4 days is assumed to be caused by lack of oxygen as we got higher heat flow values when we opened the ampoule and introduced more oxygen. The energy released was about 360 kJ/mol O_2 for both the sample "VIT" and "OLD" when calculating the energy differences between samples in oxygen and in nitrogen.

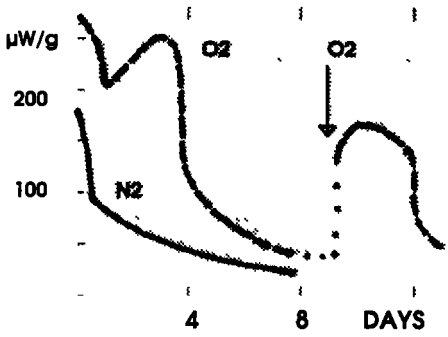


Fig 6 Microcalorimetry at 70°C
Old polyethylene

SUMMARY

When a normal stabilized polyethylene is aged there is a very little change in its mechanical and other properties for a long period of time, but then rather suddenly there will be a change leading to cracks(ref 4).This sudden change is assumed to be associated with loss of oxydation stabilizers in the polyethylene and the start of oxydative degradation of the polymeric chains.
With this report we will point out the possibility to study the oxydative degradation of old or degraded polyethylene at moderate temperatures far below its melting point with help of microcalorimetry.
We hope in the future to be able to test more well-defined polyethylenes with regard to stabilizer content/mechanical properties.

REFERENCES

1. L-G Svensson, P E Lagerkvist, N G Gellerstedt
Proc. of the ADPA Symp. on Compatibility ov Plastics and other Materials with Explosives, Propellants and Pyrotechnics, South Carolina, USA (1985) p 19

2. L-E Paulsson , L G Svensson, C K Forsgren
Microcalorimetric Methods for Corrosion Rate Measurement
Proc. Institute of Environmental Sciences Anaheim California, USA 1989, p 48

3. L G Svensson
Two applications of gas flow ampoule microcalorimtry to determine input data for the moisture penetration simulation program.
Proc. of "Pyroteknikdagen" ,Lund Sweden (1986) p 159

4. M Ifwarsson, P Eriksson
Kunststoffe, 76, 245 (1986)