Heat ageing

Test methods, precision and a new range of ovens

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Investigations over the past few years have shown that polymer heat ageing tests give poor reproducibility rates. To discover the reasons, studies have been made of various oven designs and their influence on the process. The outcome is a new generation of ageing ovens.

Introduction

Several investigations during the past years have shown the poor reproducibility when doing heat ageing tests of polymer materials. This paper reviews the test methods, the ovens used for heat ageing tests and gives examples of the poor reproducibility. Results from a project to investigate the factors influencing heat ageing results are presented together with the latest developments of heat ageing ovens.

Test methods

The most used test methods for ageing of polymers are ISO 188 - ”Rubber vulcanised and thermoplastic - heat ageing tests” and IEC 811 for testing of cable materials.

Types of ageing ovens used

Three types of equipment have been used for the ageing of polymers; cell ovens, cabinet ovens and oxygen or air bombs. The ageing of polymers in oxygen bombs at high pressure will not be discussed, as with this type of ageing it is not possible to do any correlation with natural ageing.

Cell ovens

Cell ovens have been used for a long time for the ageing of polymers. The idea is to achieve a steady temperature by using a large block of aluminium and to separate the samples by using one cell for each material.

The first type of cell oven had a large aluminium block with a lot of holes in the block. In the holes were glass test tubes placed for the samples. To get an exchange of the air two small glass tubes were placed in the cork of the test tube. One of the glass tubes went down to the bottom of the test tube and the other glass tube ended just below the cork. The idea was to achieve an air circulation caused by the temperature gradient in the test tube.

No one have, to my knowledge, however been able to measure the air exchange rate in such an oven, even if attempts have been made.

A later type of cell oven had larger cells in the aluminium block and forced air exchange by using an air pump with a flow meter. This type of oven was a great improvement over the first type. The preheating of the the air was however not always satisfactory, as the air in the cells could be up to several degrees Celcius lower than the temperature of the aluminium block.

Cabinet ovens

Until a few years ago, there were not any cabinet ovens designed especially for the ageing of polymers available on the market. So the laboratories have purchased standard drying ovens.

The standard ovens on the market can be divided in two categories, with or without a fan.

The ovens without a fan normally have very large variations of the temperature in space, up to 10 °C is not unusual, especially when the throttle is open to get an air exchange. This type of oven is often used by the cable industry, as the standard they are using, IEC 811, states that no fan is allowed in the oven. To get an acceptable temperature tolerance of ±1°C the ovens are measured to find a usable area with this tolerance. Normally an area of a few liters is found in the middle of the ovens where the samples can be placed.

The ovens with a fan is normally used in the rubber industry, as companies have been more concerned of a uniform temperature than to have a low air speed, which is required in ISO 188. The detrimental effect on the test result of a high air speed has alsonot been known until recently, see ref 1.

Reproducibility in heat ageing tests

At the beginning of the 1980s it was decided to include within ISO TC 45, Rubber and Rubber Products, a precision clause in all test method standards. The precision clauses were established by carrying out Interlaboratory Test Programmes, ITPs, to establish the repeatability (within laboratory) and the reproducibility (between laboratories) for the test methods.

This work inspired us in Sweden to start an interlaboratory test program, organised by the Swedish National Testing Institute. During the years 1982 - 1988, 14 interlaboratory tests were carried out.

All these interlaboratory tests within ISO and in Sweden have shown that the spread in the test results is worse than anyone could have expected.

Table 1 shows the result from an ITP for heat ageing done in Sweden 1988, (ref 2)

Table 1 Ageing test reproducibility

12 different labs, ITP 1988	mean	s	R
Change in tensile strength (%)	-18	5,3	15
Change in elongation at break (%)	-40	5,8	16
Change in microhardness, IRHD	-13	3,8	10

s = std deviation

R = Reproducibility in actual units of measurements

”Until a few years ago, there were no cabinet ovens available on the market which had been designed especially for ageing polymers”

Investigation of factors influencing heat ageing test results

The problem of obtaining reproducible test results when doing heat ageing tests have been shown in several Interlaboratory Test Programs (ITP) carried out in Sweden and within ISO TC 45 during the last ten years. To improve the situation a project within the Swedish Plastic and Rubber Institute, has studied thedifferent factors influencing ageing results. (ref 1)

The project started with an inventory of the ovens used for ageing tests among the 12 participating Swedish rubber companies. Based on this inventory four of the ovens and a new designed oven were chosen for a closer study. The ovens were investigated for the following:

- temperature uniformity in time
- temperature uniformity in space
- set, shown and actual temperature
- air speeds
- air exchange rates
- ageing results in different ovens

The following factors influencing the ageing were then further investigated in different ways:

- temperature
- air speed

Measurements of the ageing ovens

Based on the inventory the following ovens were measured in one laboratory.

- Heraeus UT 5042
- Heraeus UT 5060E
- Salvis TSW 60
- Elastocon EB 01
- Elastocon EB 04

Temperature variations in time

A PT 100 sensor was placed in the centre of each oven. The sensors were connected to a data logging system connected to a PC-computer, with a resolution of ±0,1°C. The temperature was adjusted as close as possible to 100°C. The ovens were run for 5 days to see temperature variations in time. The results are shown in table 2.

Table 2 Temperature variations in time

5042	5060E	TSW 60	EB 01	EB 04
°C	°C	°C	°C	°C
13,8	0,1	0,2	0,1	0,1

The UT 5042 oven had a mechanical controller, the other ovens had electronic controllers. With a modern electronic controller temperature variations in time seems to be no problem.

Temperature variations in space

A frame with five PT 100 sensors located in each corner and in the centre, connected to a data logging system, was placed inside each cabinet and was moved between three positions. The outer sensors were placed about 50 mm from the walls. the results are shown in table 3 and fig 1 to 3.

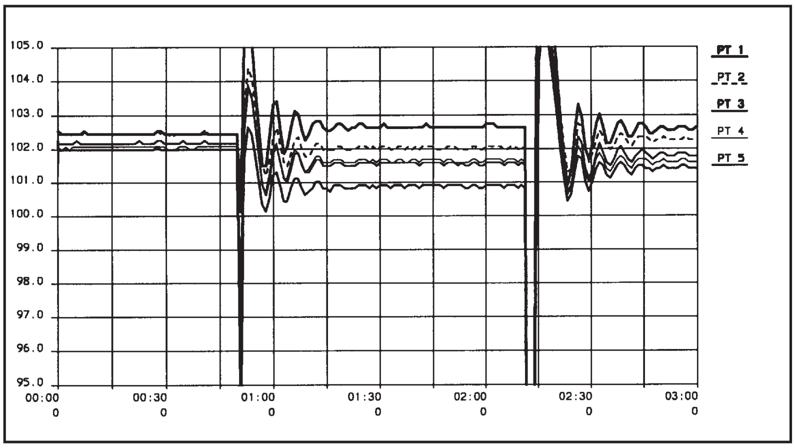

Figure 1 *Temperature variations in space, UT 5060E*

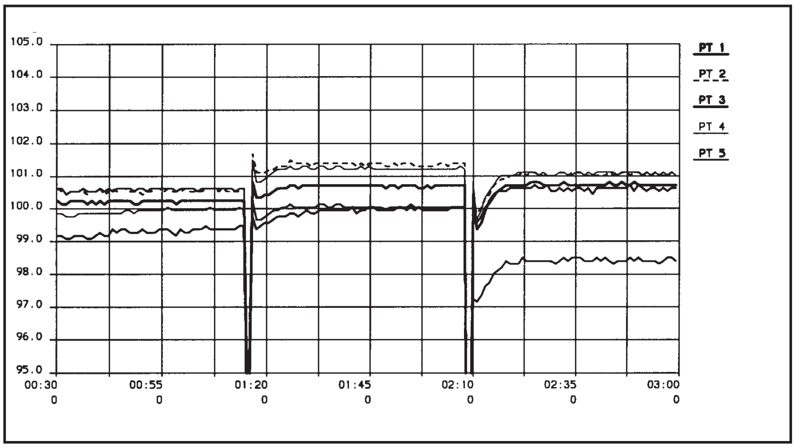

Figure 2 *Temperature variations in space, TSW 60*

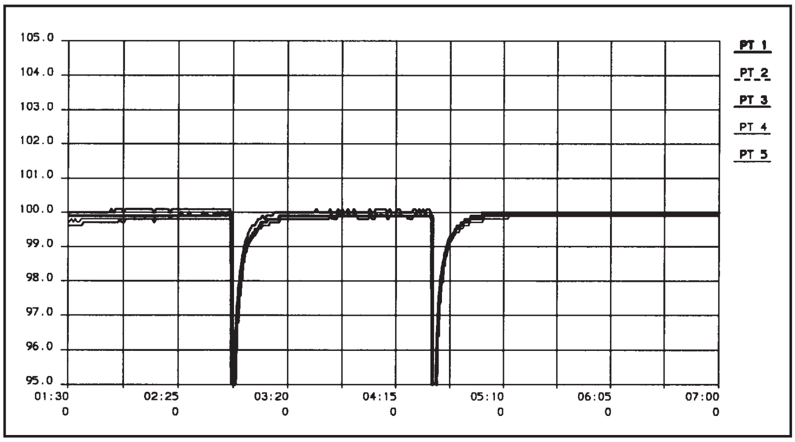

Figure 3 *Temperature variations in space, EB 04*

Table 3 Temperature variations in space

Location	5042	5060E	TSW 60	EB 01	EB 04
	°C	°C	°C	°C	°C
Inner	0,9	0,5	1,3	N/A	0,4
Centre	0,7	1,7	1,3	N/A	0,3
Outer	0,7	1,1	2,7	N/A	0,2
Total	1,2	1,7	3,1	0,5	0,4

NA = not applicable

The table shows the difference between five points in each location and the total difference (all points all locations)

Air speeds

The air speeds have been measured in 27 points in the ovens and the results are shown in table 4.

The air speeds of the ovens EB 01 and EB 04 are dependent of the air exchange rate only and have not been possible to measure. The value is calculated from the air exchange rate.

The traditional heating cabinets show great variations in air speed from almost 0 up to 5 m/s. The flow is rotating and turbulent. The air movement is created by a fan behind a baffle, either in the back or in one side of the cabinet.

In EB 01 and EB 04 the air is passed through a flowmeter with a control valve, going from the bottom to the top of the cabinet more as a laminar flow.

In the former version of ISO 188 Rubber - Accelerated ageing test, the standard stateted that ”provision shall be made for a slow circulation of air through the oven of not less than three and not more than ten changes per hour.” In the latest version of ISO 188 is added ”the air speed shall be dependant of the air exchange rate only”.This means that no fans are allowed inside the testing cabinet and then the three standard ovens tested do not meet the requirements for low air speed.

Air exchange rates

The air exchange rates have been determined both by calculating the air volume by measuring the air speed and area in the exhaust hole and by measuring the time needed to fill a 125 l plastic bag attached to the exhaust hole. The results are shown in table 5.

The air exchange rate in EB 01 and EB 04 is set by a flow meter and a control valve.

In ISO 188 Rubber - Accelerated ageing test, the requirement for air exchange is 3 - 10 exchanges per hour, while the IEC 811 requires 8 - 20 exchanges per hour.

Table 4 Air speeds

Speed	5042	5060E	TSW 60	EB 01	EB04
	m/s	m/s	m/s	m/s	m/s
min speed	0,5	0,0	0,4	<0,001	<0,001
max speed	2,6	4,5	3,0	<0,001	<0,001

Table 5 Air exchange rates

Oven	5042	5060E	TSW60	EB 01	EB 04
Exhaust	Air changes per hour				
Open	~160	~40	~300	20	16
Closed	0	0	~20	0	0

Long term ageing, two ovens

One rubber compound of a NBR/PVC blend was aged in two of the ovens during 1 000 h at 100°C. One Salvis TSW 60 and one Elastocon EB 01 cell oven were used.

The micro hardness and tensile test were performed after 72, 336 and 1 000 h. The temperature in the ovens were adjusted to be 100°C in the centre of each oven. The results are shown in figure 4.

The results in the figure shows that the ageing does not follow the same reaction in the two ovens. The surface of the tested rubber was aged much more in the heating cabinet than in the cell oven. The main difference between the ovens were the air speed. The micro hardness test is mainly measuring surface effects. The tensile test however did not show the same big differences. The air speed seems to be of greater importance for heat ageing than is presently recognised.

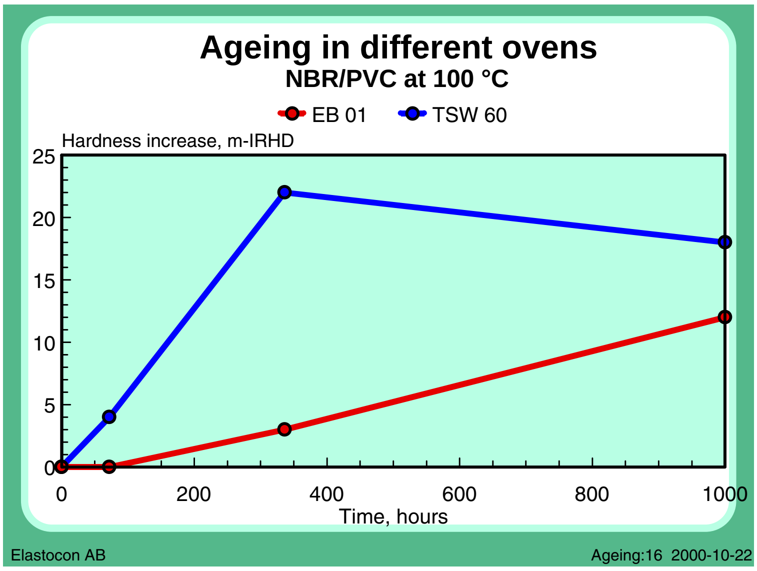

Figure 4 *Long term ageing, different ovens, micro IRHD*

Temperature influence on ageing

Four rubber compounds, NR, SBR, NBR and EPDM, were aged at three temperatures, 95, 100 and 105°C, in a cell oven during 168 h. Before and after the ageing, micro hardness and tensile test were performed.

The results shows a clear influence of the temperature, even in the limited range of ±5 °C. The NR compound shows a dramatic reduction in properties in the temperature range of 100 °C and the temperature seems to be too high for ageing of NR. Figure 5. To keep the temperature variations within close limits seems to be an important factor in reducing variations in ageing of polymers. Calculations have shown that a temperature offset of 1 °C during an ageing test, corresponds to about 10 % testing time, and we don't allow so much variation in the time.

Air speed influence on ageing

To make a closer investigation of the influence of air speed on heat ageing results, two special ovens were developed. One oven with an air speed of about 0,3 m/s and one with about 3 m/s. Four rubber materials, NR, SBR, NBR and EPDM, were then aged at 70°C (NR, SBR) and 100°C (NBR, EPDM) for 1 000 h in these ovens plus in a cell oven with an air speed of about 0,001 m/s. Weight loss, micro hardness and tensile tests were performed on the four materials after one, three and six weeks of ageing. Some of the results are shown i figures 6 and 7.

The figures show a great difference in the weight loss at different air speeds and analysis shows that softening oils and antioxidants have evaporated. This loss of softener will of course effect most of the other properties as well.

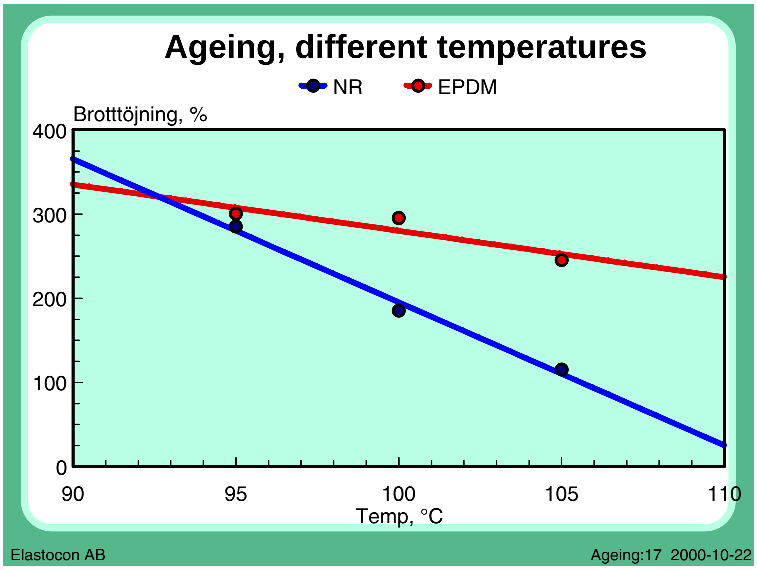

Figure 5 Temperature influence

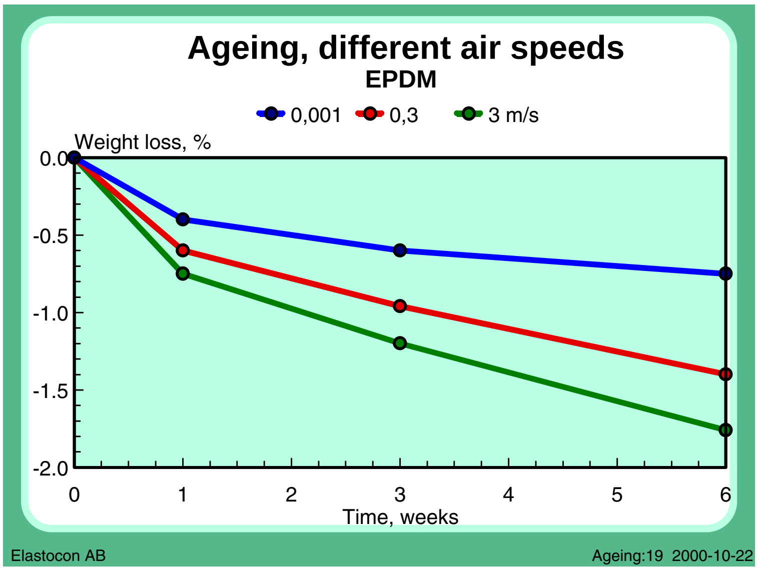

Figure 6 EPDM, weight loss at different air speeds

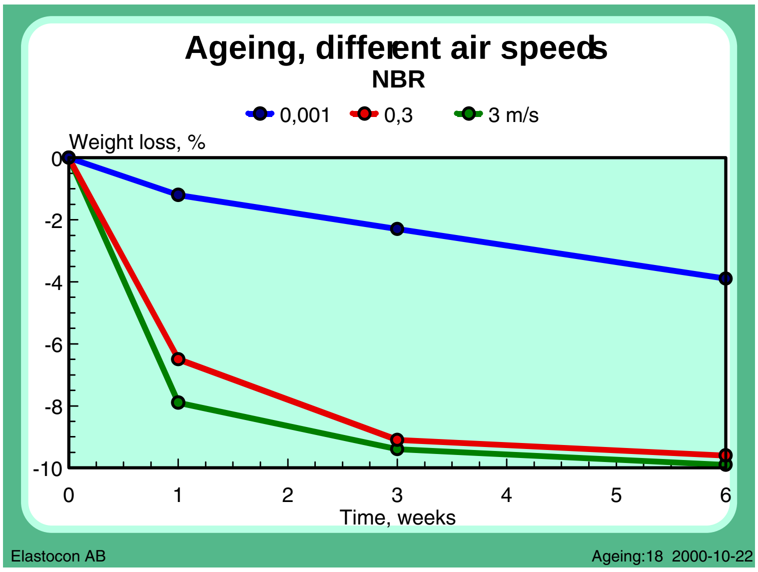

Figure 7 NBR, weight loss at different air speeds

Summary

This project has shown that the main factors contributing to poor reproducibility between laboratories when doing heat ageing tests are air speed and temperature. The results have been presented to ISO TC 45 and have been taken into consideration during in revision of ISO 188 ”Rubber vulcanised and thermoplastic - heat ageing tests”. Sweden had suggested that the new version of ISO 188 (published 1998) should include more clearly defined testing conditions for the ageing test especially regarding air speed. No fans are allowed in the test space and the air speed shall be dependant of the air exchange rate only. Besides the ageing in still air Sweden suggested the addition of an ageing test at high air speed (1 m/s), for the study of air speed influence.

Design of new ovens for heat ageing tests

Elastocon has during the last decade been involved in the development and design of new ageing ovens for achieving better reproducibility and repeatability when doing heat ageing tests of polymers. The work has been done in parallel with the research project reported above. We have developed a series of both cell ovens and cabinet ovens for the ageing of polymers.

Cell ageing ovens

Elastocon designed the first cell oven EB 01. 1987, a four cell oven with large cells with a diameter of 100 mm. The oven is now improved and the third generation is on the market, see figure 8.

The temperature system in the oven uses two digital PID controllers with 0,1 °C resolution. One of the controllers is used to control the temperature in the aluminium block. The other controller is used to measure and display the air temperature in one of the cells, close to the samples.

The temperature alarm system is also connected to this controller. The temperature variation in time and space can be kept to half of what is required in the ISO 188 heat ageing standard, or ±0,5 up to 100 °C and ±1 up to 200°C.

The exchange of air is made using an air pump, which pumps the filtered air through a separate flow meter into the bottom of each cell. Before the air enters the cell, it is preheated to the test temperature by passing through channels in the aluminium block. The air pressure is monitored by a piezoelectric pressure sensor, connected to the alarm system. The air exchange rate can be set with the flowmeter to 3-20 exchanges per hour. The air speed is dependent of the air exchange rate only and is calculated to be below 0,001 m/s.

Figure 8 *Cell oven EB 01-II with four cells*

Figure 9 *Cell oven with 6 cells and individual temperature EB 20*

1995 Elastocon made the first triple temperature celloven, EB 07. The triple oven has the same specification as the EB 01 cell oven, but the temperature can be set individually in each cell. This allows for a very flexible use of the oven. Later also a cell oven with 6 cells and individual temperature control was developed, see figure 9.

Cabinet ageing ovens

1992 Elastocon presented it's first cabinet oven for ageing with the same specification as the cell oven, see figure 10.

The basic temperature system is the same as in the cell ovens, but to achieve a uniform temperature in space is more difficult in a cabinet oven. The normal way of achieving a uniform temperature in space in a cabinet oven is to use a fan and have a high air speed stirring the air. A high air speed is however not suitable for ageing tests and the only way to get a uniform temperature in still air, is to have all sides of the cabinet at the same temperature. In the cell oven this is achieved by keeping the aluminium block at correct temperature. In the cabinet oven we get the same results by using an inner chamber and having a fan blowing the air with high air speed around the inner chamber.

To exchange the air, fresh air is pumped through a flowmeter into the air stream around the inner chamber, close to the heating elements. The preheated air enters the testing space though a distribution chamber in the bottom of the inner chamber and moves slowly (<0,001 m/s) up to the top, where it is evacuated through a small chimney.

We have also designed a budget priced version of our cabinet ageing oven. To reduce the price we excluded the air pump, flowmeter and window. To still get an air exchange rate within the specification, we use the fan to get fresh air into the system and we set the air exchange rate by adjusting a throttle in the air inlet, see figure 11.

”Temperature variation in time and space can be kept to half of what is required in the ISO 188 heat ageing standard”

Figure 10 *Cabinet ageing oven EB 04-II*

Figure 11 *Cabinet ageing oven EB 10*

Additional information in the third edition Nov 2010

During 2009 Elastocon developed a new improved range of ageing ovens using a PLC with a colour touch screen for control of the ovens. By using a PLC it is also possible to design a cell oven with 6 cells with individual temperature control.

The new range of ageing ovens have the following improvements:

Cell ovens

- Improved insulation for lower energy consumption
- Lower surface temperature
- Settings are done on a colour touch creen
- Micro PLC control
- Resetable countdown timer for each cell
- Individual cell identifier - "Test name"
- Alarm history

Cabinet ovens

- Improved insulation
- Lower surface temperature
- New touch screen control utilising a micro PLC
- Countdown timers.
- Alarm history.
- Test names can be given.
- Improved door with new hinges and two point locking.
- Improved door sealing.
- Easier shelf installation and removal.
- New four glass window

Oven for stress relaxation tests

References

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