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ORIGINAL ARTICLE

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An experimental set-up to analyse the oxygen consumption of elastomers during ageing by using a differential oxygen analyser

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Abstract Ageing of polymers becomes more and more important. This can be seen by the increasing number of research projects dealing with this topic. However, the influence of oxygen on changes in the mechanical performance is undisputable and important with respect to the lifetime of polymer products. Therefore, a respirometer offers the potential to detect the smallest amounts of oxygen changes in the polymers' ambient air. It will be used to analyse the oxygen consumption of rubber which is exposed for different times to elevated temperatures. In this contribution, virgin rubber samples are aged for various times in a sealed chamber at temperatures of 60, 80 and 100 °C. The decline of the oxygen concentration in the ambient air is measured by flushing the chamber with dried and cleaned air which is conducted into the respirometer. The oxygen concentration is compared with that in a reference chamber, which is exposed to the same ageing conditions as the sample under investigation. The absorbed oxygen is relevant for ageing and a considerable factor for further investigations. For this reason, an experimental set-up using a differential oxygen analyser is developed, which allows for ageing several samples simultaneously in external climate chambers. The comparison of the change in the mechanical material behaviour after ageing can provide an important contribution for improving constitutive models or ongoing researches on the fatigue strength of polymers. This work shows the development of an improved method for combining mechanical testing and the measurement of oxygen consumption.

Keywords Thermo-oxidative ageing · Experimental set-up · Oxygen consumption · Ageing performance · Differential fuel cell analyser

1 Introduction and state of the art

Nowadays, polymers are very important because of their diversity of technical applications. For example, they are deployed as anti-vibration devices in vehicle suspensions and bearings or as seals to tighten connections. They convince with plasticity, flexibility and good adherence. These benefits go along with disadvantages, especially the degradation of the mechanical properties during ageing. This process depends at least in part on the widely varying conditions the material is exposed to during its lifetime. A profound knowledge of the ageing behaviour and the changes during the lifetime is essential for the responsible use. Ageing depends on the environmental conditions which result for example from the contact with gases or fluids as well as mechanical or thermal loads. Especially, oxygen-containing environments have huge influence on polymers as well as elevated temperatures. A combination of different effects can amplify them and change the material properties up to the failure [1]. Several publications [1–4] describe the influence of oxygen on the mechanical properties

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and try to make a prediction on the change in the behaviour. In this context, it is important to distinguish between the consumption of oxygen by the material and the chemical reaction which takes place as a result of this oxygen consumption after an initial time. Usually, chemical reactions in polymers start after a time shift which is caused by diffusion-limiting oxidation phenomena [5]. This means that the oxygen is absorbed by the rubber first without any immediate consequences for the properties of the material. After some time, the changes in the material, which are caused by chemical reactions, extend from the surface to the interior of the sample. Oxidation of polymers affects the elastic modulus, mostly via oxidative crosslinking. For example, correlation between localised oxidation levels and modulus changes during ageing was shown by Celina [1]. Concerning the development of a material model which considers ageing phenomena, the knowledge of the underlying chemical processes plays an essential role. Repeated chemical reactions on the molecular level like chain scission or network reformation are the driving processes for the change in the material properties [6]. In general, the conventional Arrhenius relation is not able to express the real oxygen consumption and diffusion, as well as the changes in the mechanical material properties. This is due to the diffusion-limiting effects, which prevent or decelerate the incident [1,5]. The time shift is called “oxidation induction time” [4]. The oxygen rate significantly depends on the temperature and the time of exposure. Therefore, the oxidation will continue until a saturation is attained. In addition, the rate of oxidation depends among others on the oxygen partial pressure in the ambient environment [4].

Polymer oxidation is a function of simultaneously elapsing chemical and physical phenomena [1] which could be accelerated by increasing temperature. Physical ageing of polymers, which becomes remarkable with approaching the glass transition temperature, leads to a decrease in the free volume as well as to thermoreversible changes in the material properties. This process usually takes place below the glass transition temperature. Raising the temperature above the glass transition will increase the molecular mobility and the free volume such that the material can reach its original state in a short time. Several possibilities exist to test physical ageing separated from other effects that should not be discussed in this contribution [6].

The omnipresence of ambient oxygen plays an essential role in the evolution of chemical ageing. The chemical reactions can lead to chain scission as well as to crosslinking processes in the polymer network. Naturally, both mechanisms are coexistent though one of them may dominate and will affect the material behaviour more significantly. In polymers, ageing may be also based upon a chemical radical reaction, which is known as basic autoxidation scheme (BAS) [4]. Ageing inhibition is either based on the isolation of the polymer from the environment for instance by means of waxes or it focused on stopping the radical reaction. These methods are limited to the direct vicinity of the polymer [4].

Scheirs et al. [7] provided an excellent overview of various methods for measuring the oxygen consumption of polymers. They range from pressure measurements over gravimetric methods up to gas chromatographic techniques to measure oxygen partial pressures as, e.g. reported by Assink et al. [2].

This article describes the experimental set-up for measuring the oxygen consumption of elastomeric materials using a commercial fuel cell respirometer. This instrument has been used successfully for measuring the respiratory cycles of small animals and insects [2] or for high-precision atmospheric oxygen measurements [8]. The current work focusses on designing a set-up to accomplish measurements with standard polymer samples. It offers the possibility to combine the experimental testing of the oxidation rate with mechanical investigations. The figured set-up provides the basis for future investigations of elastomers in the context of ageing phenomena. Therefore, the attention will be turned to the interaction of the amount of absorbed oxygen and the corresponding change of the mechanical parameters. The delivered results should serve as an input for prospective material models and improve the lifetime prediction of polymers.

2 Experimental set-up

The main device of the experimental set-up is the respirometer, an Oxzilla II Differential Oxygen Analyser from Sable Systems International (Las Vegas, NV). It consists of two sensitive fuel cell detectors which can detect minor changes in the oxygen partial pressure. The testing set-up should be as flexible as possible without limiting the accuracy. It permits continuous and intermittent measurements. An intermittent measurement consists of the external ageing of the sample in an oven. After several periods of time, the chamber with the aged specimen is fixed into the device, and an intermittent test is performed. In contrast, a continuous measurement means testing the amount of absorbed oxygen during the whole time of ageing. Therefore, the chambers have to be linked with the device all the time, and external ageing is not possible.

The fuel cells lead to a voltage which is proportional to the present oxygen partial pressure in the analysed airstreams. A weak acid electrolyte within the cells is separated from the air current by a gas-permeable

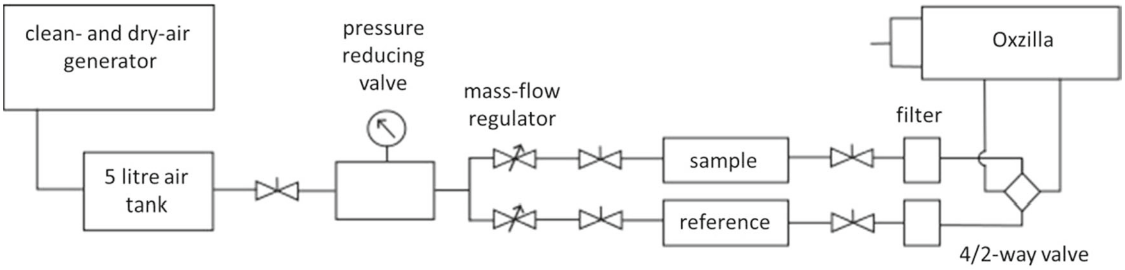

Fig. 1 Schematic structure showing the measurement set-up

membrane [2]. It is important for the measurement to subtract the output of the fuel cell connected to the sample from the output of the other cell which is connected to the reference. This process is necessary because several effects may disturb the measurement, like changing pressure or temperature. A simplified scheme of the set-up is shown in Fig. 1.

Standard compressed air is used to flow both chambers and to press the air into the fuel cells of the respirometer. This is provided by a clean- and dry-air generator; the air has to be dry and clean to avoid damaging the respirometer and perturbing the measurements. The fuel cells react very sensitive to alternating air moisture; thus, the air has to have constant moisture. Absorption dryers guarantee a dew point of about −73 °C. The installed clean-air generator is optimised for minor volumes of compressed air and is able to pre-dry it roughly by a coalescing filter used to separate humidity from the air current. For reaching better dryness, the air has to pass two chambers filled with an active granulate. One is absorbing water from the humid air; the other one is simultaneously dried by a second stream of air. A valve switches between the two drying chambers in a constant period of time.

Although the compressor includes an air reservoir, an additional 5 l vessel for compressed air is connected downstream to increase the intervals the clean-air generator has to run especially during long-term experiments. A barometer shows the current pressure, which is about 5–6 bar in order to check the devices during the measurements and for the online control of the running experiment. A pressure regulator is installed next in line, which reduces the pressure for the subsequent devices before splitting the air leading pipe into two parallel lines. One is used for the sample, and the other serves for the reference stream. The pressure is reduced further down to a value of about three bar by a pressure reducing valve which is adjacent to the branch pipe tee. This step is necessary to protect the mass flow controllers described next.

Both lines are regulated by a Natec Senors® mass flow controller. They are calibrated for a gas flow up to 100 sccm/min. This set-up guarantees exactly the same mass flux of oxygen for each flow line. The accuracy of the mass flow controllers presented is ±0.6 sccm/min for an air flux of 100 sccm/min. All lines are as short as possible in order to minimise the time required to flush the chambers and to avoid pressure losses as far as possible. Only an identical mass flow in both lines can yield a meaningful result. If there is not exactly the same amount of oxygen molecules in the sample and the reference stream, the determination of the oxygen consumption of the investigated polymers will be impossible.

Most commercial mass flow controllers allow only temperatures up to 50 °C. But for the presented experimental set-up, higher temperatures are required to provide the opportunity of measurements with heated air. Therefore, mass flow controllers which are based on the thermal principle cannot be used. The selected ones are a special fabrication and allow for the decrease in pressure at a laminar fluid element. They are working at temperatures up to 100 °C. Generally, the set-up is designed to be used for continuous and intermittent measurements. The former means that the ageing process occurs during the chambers are flushed by air and connected to the respirometer. Therefore, it is beneficial to keep the option open doing this with heated air to accelerate the ageing process. In the case of intermittent measurements, the chambers are not connected to the respirometer all the time. The ageing is also done in the tightened chambers but in an external oven. After this, both the sample and the reference chamber are attached to the set-up and the oxygen content of the contained air is tested once.

Four magnetic block valves enable a monitored process of the experiment. They are closed without any voltage applied (standard mode) and allow air flow when energised. The valves open at a definite moment, and the measurement starts by pressing the remaining air out of the chambers into the respirometer. All pipes are made of high-quality stainless steel to avoid an adulteration of the oxygen content by corrosion. Pipes with 8 mm aperture are used upstream of the mass flow controllers to provide a sufficient amount of air. The same

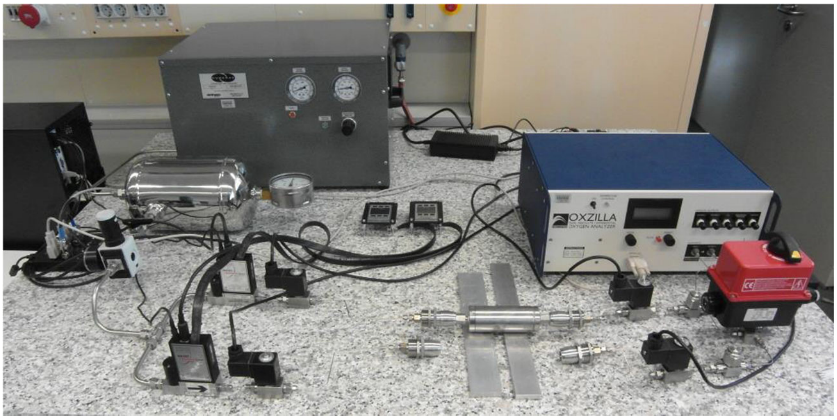

Fig. 2 Experimental set-up

tubes that are inside the respirometer are used downstream with a diameter of 1/16 in. These very slim tubes should reduce the clearance volume of the design and accelerate the air current. All devices are connected by Swagelok® couplings and cutting rings; self-sealing NPT threads are used. Thus, any contact at the fittings between the tested polymer material and the cleaned air reference is avoided. Cutting rings are also without sealing.

Both the sample and reference chambers are made of stainless steel (V4A) which does not react with the oxygen. The challenge was to construct chambers with the possibility to open and close them several times without losing air tightness. The chamber openings need to be big enough to fill them with different test pieces. Viton sealings are used for the chamber's secondary tightening, and the primary caulking is provided by the threads. All chambers are equipped with sealing express couplings allowing external ageing in a commercial oven.

Filters are installed behind the chambers to capture any dirt or loose particulates of more than 0.5 µm in order to shield the respirometer. One inevitable problem of the respirometer is its drift. In order to prevent this drift, a frequent switching between both inlets is necessary [9]. A 4/2-way cross-connected valve enables this function. It switches the lines after a constant period of time. The necessary period is determined to 100–120 s in test measurements. Both lines are brought together downstream the respirometer in order to avoid pressure differences and to reach a common pressure level at the outlet. Consequently, variations in ambient pressure are prevented because they could influence the signal of the two fuel cells differently [10]. The experimental testing set-up is shown in Fig. 2.

Data storage is managed by a serial interface (RS 232) and controlled by a program implemented in LabView, National Instruments. The respirometer has a digital output and exports permanently the oxygen content of both lines plus their difference. These data are plotted over time and saved in a table. The program could also regulate the mass flow controllers and the airflow at the given value. The valves are switched by a relay board, which converts the digital signal into 24 V direct-current voltage. Only the clean- and dry-air generator is not controlled by LabView. It is adjusted manually, and a pressure sensor switches to on and off automatically.

3 Potential experimental investigations

The elastomer samples are stored in vacuum to avoid any uncontrolled oxygen-induced ageing before starting the experiments. They are shrink-packed immediately after being produced to prevent any contact with oxygen. The rubber is also kept free from exposure to UV-radiation. After that, the material is unpacked and the desired specimen geometry is die-cut directly before starting the oven-ageing. In the experiments, S2-test pieces are used to perform relaxation tests after measuring the oxygen consumption. Subsequently, the samples are placed in the chambers. It is important to check the correct placing of the samples in the chamber in order to guarantee a well-defined contact surface with the surrounding air because the magnitude of the contact area has a significant influence on the ageing process [1,6]. The chambers were locked and sealed by a Viton ring. The samples are placed inside the chamber on a kind of grillage to minimise, as far as possible, the contact to

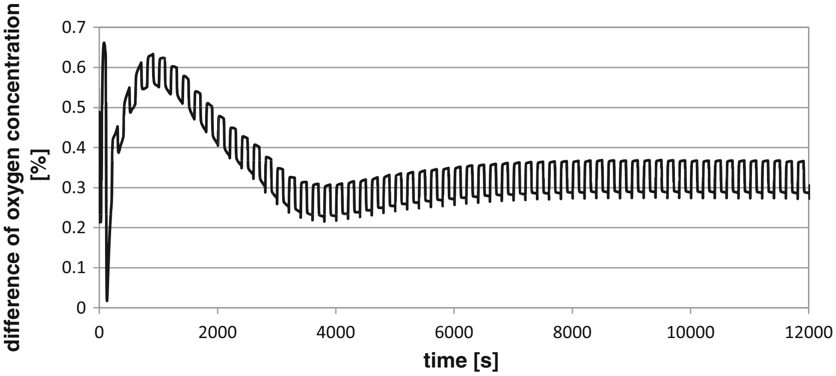

Fig. 3 Stabilisation phase of the respirometer and offset effect between fuel cells

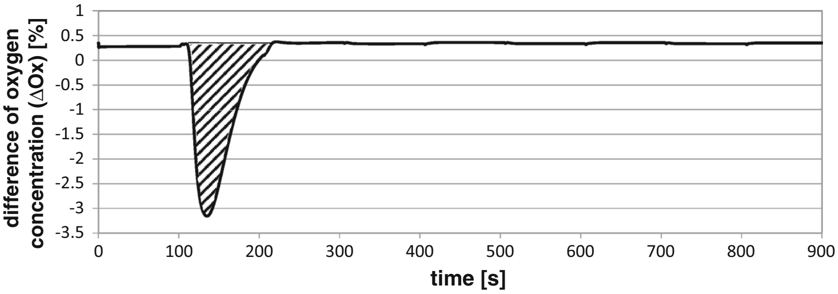

Fig. 4 Difference in oxygen concentration of an elastomer aged over 89 h at 60 °C

the chambers and to ensure an ideal air flux. Therefore, it is important that the samples do not block the inlet and outlet of the chamber. The ageing is carried out in air-circulating ovens at elevated temperatures of 60, 80 and 100 °C.

The chambers are preheated before being assembled. Ageing starts when the samples are in the oven and ends when they are removed. Special attention is paid to maintain ambient pressure in the chambers during the time of increasing temperatures to avoid any manipulation of the experiment. After a fixed time, the chambers are taken out of the oven and permit to cool down at room temperature. This cooling is necessary to have a definite base of temperature before starting the measurement, because the respirometer is very sensitive to variations in temperature.

It takes some time for stabilisation in order to avoid the drifting of the respirometer mentioned above. The respirometer has to be started 4 h before starting any measurement. During this time, two empty chambers were connected to the experimental set-up and a constant mass flux of air was flowing through the respirometer. Figure 3 visualises such a stabilisation process in which the difference in the oxygen concentration between both fuel cells is built up. The switching of the crossover valve every 100 s is clearly visible. There is always an offset between the fuel cells, which can be eliminated easily by calibrating the respirometer. This is not realised in Fig. 3 yet.

After the oscillation is faded away the levelling process, signal recording is stopped for a short time to change the connected chambers with the chambers containing the aged specimens. All magnetic block valves are closed and will be opened at once. Cleaned and dried air flows into the sample and reference chambers, where it is mixed with the consumed air and then pressed out of the chambers straight into the respirometer. The measured signal represents the oxygen consumption of the material and is a measure for the progress of ageing. Figure 4 shows the difference of oxygen concentration (ΔOx) between both fuel cells for a typical elastomeric material which was aged for 89 h at 60 °C. The valves are opened 100 s after starting the recording. One fuel cell detects a decreasing concentration of oxygen according to the readings. Since the mass flow of the experimental set-up of 100 sccm/min is known, it becomes possible to quantify the absorbed oxygen. The hatched area in Fig. 4 is a measure for the amount of absorbed oxygen during the period of ageing. The signal after 300 s obviously shows that there is now noticeable sensitivity in the oxygen concentration to the mass flow regulation or the drift of the respirometer.

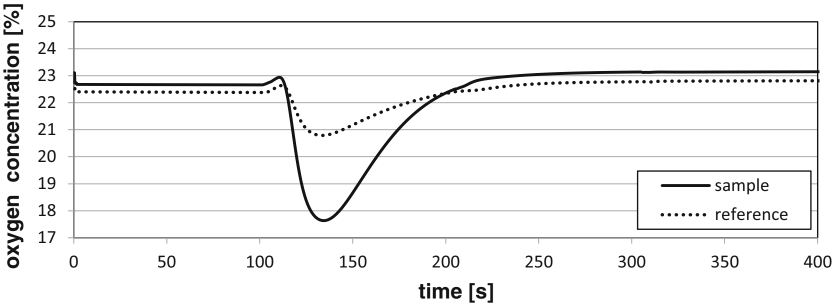

Fig. 5 Oxygen concentration drop for an elastomer aged over 89 h at 60 °C

Hoffman et al. [3] explained the interpretation of such a signal. The quantity used is called "oxygen consumption rate" and has the unit (mol/g/s). It arises by multiplying the gas flow rate, $\dot{m}$, by the integral of the oxygen concentration versus flow time. The volume of oxygen is measured in moles. The value obtained is divided by the sample weight, m_{sample}, and the ageing time, t_{ageing}, and will result in a normalised oxidation rate.

$$\text{Oxygen consumption rate}\left[\frac{\text{mol}}{g * s}\right] = \frac{\dot{m} * \int \Delta\text{Ox}(t)\text{d}t}{m_{\text{sample}} * t_{\text{ageing}}}$$

The integration limits have to be adapted to the measurement and cannot be trivialised. They depend on the time span in which the valves are opened and how fast the amplitude is fading out. A typical result of oxygen consumption is shown in Fig. 5 for a standard elastomer aged for 96 h at 60 °C. Both fuel cells detect a decrease in the oxygen concentration when the chambers are flushed. All valves are closed during 100 s. The remaining differences between the two readings are due to an offset that does not disturb the measurement. In the moment where the chambers are opened, the oxygen concentrations rise shortly before falling. This short rising is caused by the respirometer, which is drifting while the valves are closed. After opening the valves, the graph declines because a depression is induced in the chambers due to the cooling after ageing. The difference between sample and reference represents the absorbed amount of oxygen. The air in the chambers was mixed with the produced air coming from the generator and is slowly deflated to the respirometer. The oxygen concentration is increasing again as soon as there is no more old air left in the chambers and level of at the value of the generator air.

4 Validation of the experimental results and discussion

In order to validate the experimental set-up and to get some first impressions of the magnitude, some measurements were performed. A standard elastomer which is used in the automotive industry is taken but without ageing inhibitor. The rubber mats are die-cut into S2-samples for tensile tests and put into the chambers. Three samples are always placed in one chamber at the same time in order to increase the contact surface and to get a higher signal level. Of course, this has to be considered in the interpretation. The samples are aged for a period of 24 and 96 h, allowed to cool down up to room temperature (approximately 23 °C) and are then connected to the respirometer. The results are illustrated in Fig. 6. The scale of the graph coincides with that which was used by Steinke [4]. The polymer absorbs more oxygen during a longer time of ageing. The results prove the expected higher oxygen consumption at a higher temperature during ageing. Although there are very few measurements, it is possible to distinguish that there is a nonlinear relationship between oxygen consumption and temperature. It is necessary to act with caution and distinguish between the oxygen consumption (mol/g) and the oxygen consumption rate (mol/g/s).

The mechanical properties of the specimens can be tested right after these preceding measurements on the oxygen consumption. The samples are clamped into a tension testing machine, and relaxation tests are started. These tests are conducted with a preload of 0.3 N (0.033 N/mm^2) to straighten the specimens. Then, a tensile strain of 20 % was applied. After these, the stress is recorded for a period of 1 h. Figure 7 shows the results after an ageing time of 24 h at three different temperature levels. There is hardly a change visible due to the temperature level for the exposure period used.

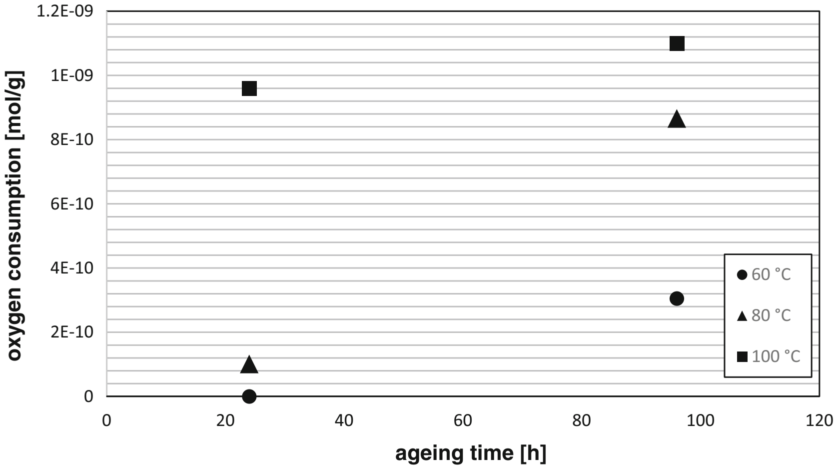

Fig. 6 Oxygen consumption rate of an elastomeric material without ageing inhibition

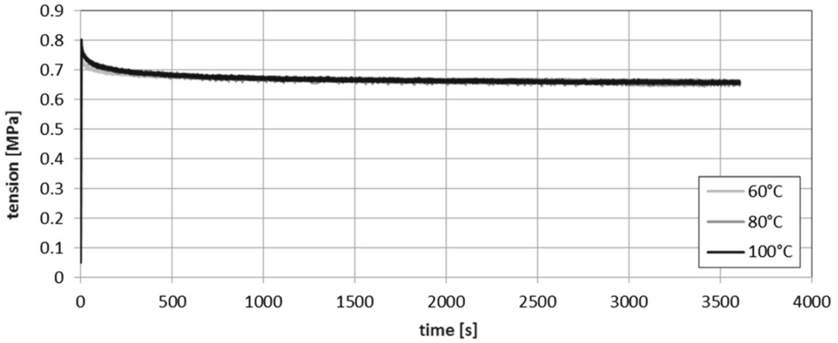

Fig. 7 Relaxation test after a 24 h ageing period

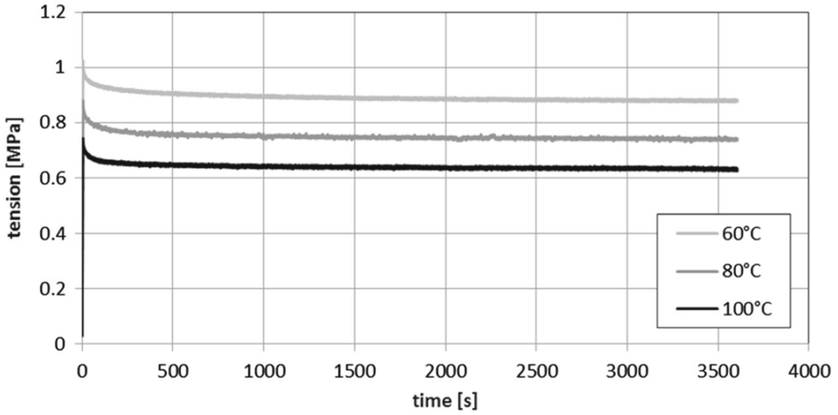

Fig. 8 Relaxation test after 96 h ageing

Figure 8 shows the corresponding results after 96 h of ageing. Some changes occur referring to Fig. 7. Ageing phenomena effect changings in the molecular structure and influence the mechanical properties which can be seen in the graph. As mentioned before, the material absorbs oxygen from the ambient air during ageing. The amount of consumption depends on the duration of ageing and the temperature (Fig. 6). Oxygen molecules infiltrate into the microstructure of the polymer, which starts at the surface and expands into the depth with ongoing time. The rate of this process depends on several factors, like the structure of the polymer itself, the concentration of the ambient oxygen, the temperature or the ageing inhibitor. After entering the polymer, the actual process of chemical ageing starts with changing the molecular structure, mostly via oxidative crosslinking or chain scission [1]. Longer ageing at elevated temperatures entails an increased consumption of oxygen and consequently major changes of the mechanical behaviour.

5 Summary and outlook

A testing set-up is developed, which enables accurate measurements of the oxygen consumption of elastomers due to the thermo-oxidative ageing. First experiments with subsequent mechanical loadings definitely demonstrate the interaction between absorbed oxygen and the changes in the mechanical behaviour. It is the aim of this paper to highlight the general possibility to combine mechanical tests and the measurement of the oxygen consumption by the developed testing set-up that will form a foundation within the framework of ongoing researches in this field of material science. It should be the base for both the improvement and the parameter identification of constitutive models. Experiments over short and long times of ageing at different temperatures can deliver new scientific findings. The presented work gives an instruction how the set-up is designed and provides one possibility to use it. Different materials with or without ageing inhibitor can be investigated, and the results bridge the gap between chemical and physical ageing. The combination with techniques of the analytical chemistry, for example, pyrolysis and gas chromatography–mass spectrometry [11], offers the possibility to improve existing models of polymeric materials. This widespread amount of different experimental researches is necessary to understand more and more the complex influence of interactive factors during lifetime. With help of the proposed experimental set-up, it is possible to study the oxygen consumption of polymers. In addition to this, chemical studies, which give information about the reaction of the absorbed gas and categorise the type of additives migrated out, can be made. Finally, mechanical tests complement the investigation on oxygen-induced ageing [12]. It provides an overview from the origin of oxidative ageing to the final outcome and helps to understand the interaction of the single factors like different temperatures, alternating ageing times or the ambient medium. Scientific findings about diffusion processes can be reached with the knowledge of the absorbed oxygen and its chemical reactions in the polymer. Therefore, chemiluminescence is used as a monitoring technique to assess ageing-related changes in polymers [13]. This provides the possibility to examine the degradative changes that occur in aged samples and helps to consider these facts in prospective material models. It also helps to determine the content, efficiency and nature of anti-oxidants in the polymer material. This makes it possible to control the quality of such products and their suitability to prevent or inhibit ageing [14]. There is also the change of getting new perceptions about the analyses of inhibitors in polymer materials. The testing device which has been developed and checked in this article will be used in the future to identify the material parameters of a diffusion reaction equation.

References

1. Celina, M.C.: Review of polymer oxidation and its relationship with materials performance and lifetime prediction. Polym. Degrad. Stab. **98**, 2419–2429 (2013)
2. Assink, R.A., Celina, M., Skutnik, J.M., Harris, D.J.: Use of a respirometer to measure oxidation rates of polymeric materials at ambient temperatures. Polymer **46**, 11648–11654 (2005)
3. Hoffman, E.N., Fisher, D., Daugherty, W.L., Skidmore, E.T., Dunn, K.A.: Aging Performance of Model 9975 Package Fluorelastomer O-rings. Savannah River Laboratory, Aiken (2011)
4. Steinke, L.: Ein Beitrag zur Simulation der thermo-oxidativen Alterung von Elastomeren. VDI Verlag GmbH, Düsseldorf (2013)
5. Gillen, K.T., Celina, M., Bernstein, R.: Validation of improved methods for predicting long-term elastomeric seal lifetimes from compression stress–relaxation and oxygen consumption techniques. Polym. Degrad. Stab. **82**, 25–35 (2003)
6. Johlitz, M.: On the representation of ageing phenomena. J. Adhes. **88**(7), 1–35 (2012)
7. Scheirs, J., Bigger, S.W., Billingham, N.C.: A review of oxygen uptake techniques for measuring polyolefin oxidation. Polym. Test. **14**, 211–241 (1994)
8. Thompson, R.L., Manning, A.C., Lowe, D.C., Weatherburn, D.C.: A ship-based methodology for high precision atmospheric oxygen measurements and its application in the southern ocean region. Tellus **59**, 643–653 (2007)
9. Stephens, B.B., Bakwin, P.S., Tans, P.P., Teclaw, R.M., Baumann, D.D.: Application of a differential fuel-cell analyzer for measuring atmospheric oxygen variations. J. Atoms. Ocean. Tech. **24**, 82–94 (2006)
10. Steinbach, J.: Enhancing the Usability of Atmospheric Oxygen Measurements Through Emission Source Characterization and Airborne Measurements. Max-Planck-Institut für Biochemie Jena, Jena (2010)
11. Yang, R., Zhao, J., Liu, Y.: Oxidative degradation products analysis of polymer materials by pyrolisis gas chromatography - mass spectrometry. Polym. Degrad. Stab. **98**, 2466–2472 (2013)
12. Celina, M., Minier, L., Assink, R.: Development and Application of Tools to Characterize the Oxidative Degradation of AP/HTPB/Al Propellants in a Propellant Reliability Study. THERMOCHIM ACTA, Sandia National Laboratories, Albuquerque (2002)

13. Celina, M., Trujillo, A., Gillen, K., Minier, L.: Cemiluminescence as a condition monitoring method for thermal aging and lifetime prediction of an HTPB elastomer. Polym. Degrad. Stab. **91**(10), 2365–2374 (2013)
14. Emanuel, M.: Thermo-oxidative ageing of polymers. Polym. Sci. U.S.S.R **27**, 1505–1526 (1984)