



Thermo-oxidative ageing of elastomers: A modelling approach based on a finite strain theory



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ABSTRACT

Polymers are highly important in industrial applications such as bearings, seals, bonds and coatings. Since these components are used in various areas of engineering, it is obvious that they are exposed to different environmental influences such as mechanical stresses, temperature profiles and chemical or biological substances. Therefore, their properties change over time which leads to limited operating times.

In this contribution, the chemical ageing of elastomers within air is examined. A representative example for this phenomenon is the thermo-oxidative ageing of elastomeric bearings in automobiles. After the state of the art is presented and highlighted by scientific data, the experimental equipment necessary for the thermo-oxidative ageing studies is introduced. According to that, experimental data are shown and analysed. From the theoretical point of view, a constitutive approach is formulated by evaluating the Clausius–Planck inequality. The model exhibits a physically-based structure such that a clear identification of all material parameters is possible and meaningful numerical simulations can be shown. The contribution is closed by a summary and outlooks to future trends and objectives.

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1. Introduction

The application range of polymeric materials covers almost all areas of industrial engineering. Examples for components made out of these materials are bridge bearings, engine gaskets, coatings or the use as an adhesive for bondings in lightweight constructions. Polymers are characterised by their excellent workability, formability and versatility.

The manifold application of these materials attracts a worldwide interest in the study of their mechanical and thermal properties. Thus, e.g. [Bouvard et al. \(2013\)](#) propose a viscoplastic model that both describes the time-, temperature- and stress-dependent material behaviour. [Laiarinandrasana et al. \(2009\)](#) investigate the temperature-dependent material behaviour of Polyvinylidene Fluoride and develop interesting constitutive equations based on the mechanics of porous media. As more high ranking activities in the field of polymer research the group of Anand and co-authors should be mentioned. In the paper of [Anand et al. \(2009\)](#) a thermo-mechanically coupled theory for the modelling of polymers under finite deformations is developed, which is applied to various materials in the work of [Ames et al. \(2009\)](#). An extension of this contributions on coupled problems in the glass transition region as well as an adaptation of the model parameters and meaningful simulations can be found in [Srivastava et al. \(2010a,b\)](#). [Ayoub et al. \(2012\)](#) developed a damage model which considers the high-cyclic fatigue of elastomers with respect to multiaxial loading conditions and in [Ayoub et al. \(2013\)](#) stress-softening,

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hysteresis and permanent set of rubber-like materials were investigated and modelled by using a finite time-dependent constitutive approach. As one can see, in the area of the thermomechanical behaviour of unaged polymers and fatigue, there is a huge amount of interesting literature. But from the industrial point of view, the mechanical behaviour of aged polymers is also of great interest and an increasing area of research. The current article will focus on this.

During their use polymers are exposed to various environmental influences which may affect their mechanical properties. These mainly include climatic factors such as temperature, UV radiation, oxygen, ozone moisture and the interaction with media like e.g. fuels, oils or chemicals. These mentioned influences are some of the so-called outer ageing criteria and their interactions with the solid lead to measurable changes in the mechanical properties of the material so that the operation time is limited. In contrast to this, inner criteria are for example the incomplete polycondensation or vulcanisation, unstable crystallisation or internal stresses. Ageing processes are usually thermally activated, i.e. an elevated temperature may accelerate the ageing process, cf. [Becker and Braun \(1996\)](#).

Following the contributions of [Ehrenstein and Pongratz \(2007\)](#), ageing is defined as an ensemble of all physical and chemical changes of a material over a period of time which influences the mechanical material behaviour in such a way that the durability is limited. Besides the notation physical and chemical ageing also the items short-term and long-term behaviour are used. This contribution is focussed on chemical ageing.

Chemical ageing is an irreversible process that changes the chemical structure of the molecules in the polymer network. It cannot be reversed by heating, see for example [Hutchinson \(1995\)](#) and [Ehrenstein and Pongratz \(2007\)](#). Rather this process is rooted in the macromolecular structure of the polymers and the associated bonding forces. Therefore, the macromolecules are degenerated or rebuilt due to diffusion-controlled or reaction-driven processes. Such processes can be for example induced by exposure, biological or chemical environmental conditions or the reaction with oxygen. In this case, the solid is penetrated by the substance (fluid, gas) through its surface and after a so-called initial time, the irreversible changes of the mechanical properties are triggered by chemical reactions between substance and solid. In general, several substances can simultaneously diffuse into the solid and not only react with the solid, but also among themselves.

One of the most important ageing processes is the reaction and interaction with oxygen, the so-called thermo-oxidative ageing, cf. [Becker and Braun \(1996\)](#). This refers to a diffusion–reaction-driven process. Regarding the ongoing chemical reactions in this case, both network degradation or chain scission as well as network reformation and reorientation processes can be observed. It has been examined by [Tobolsky \(1967\)](#) that the two effects can overlap, where, depending on the system and the ambient medium, the one or the other effect may be dominant. Already in 1944, studies on thermo-oxidative ageing were performed and published by [Tobolsky et al. \(1944\)](#). It has been worked out that the chemical degradation process depends on both, the oxygen concentration and the temperature. This property is exploited in experimental ageing studies to achieve a significant reduction in testing time. At first, the material's lifetime is examined for higher temperatures than the operating temperature. In a second step, the observed material behaviour is extrapolated to lower temperatures so that the operating time can be estimated.

From the experimental point of view, there exist established tests by means of which the chemical ageing behaviour of materials can be detected as a function of the temperature and the exposure in a variety of media. The standard experiments can be divided into continuous and intermittent investigation of the mechanical properties of aged specimen. The basic idea and the physical motivation of these tests can be found in the contributions of [Andrews et al. \(1946\)](#), [Dunn et al. \(1959\)](#), [Ore \(1959\)](#), [Scalan and Watson \(1957\)](#), [Smith \(1993\)](#) and [Tobolsky \(1967\)](#).

Continuous relaxation tests are also known as chemical stress relaxation tests. In these experiments, substance samples are stored at constant temperature and strain in an ambient medium over a period of several weeks or months and the stress behaviour is recorded over time, cf. [Tobolsky \(1967\)](#). With this test it is possible to capture the temporal behaviour of network degradation at constant temperatures and subsequently to extrapolate the results to lower temperatures by using the well-known Arrhenius function, cf. [Tobolsky \(1967\)](#), [Duarte and Achenbach \(2007\)](#) and [Shaw et al. \(2005\)](#). In general, the stress decreases monotonically during testing, unless the network reformation process causes shrinkage, [Andrews et al. \(1946\)](#). The temporal decrease in stress may reach the value zero, which is equivalent to a complete degradation of the original network of the virgin specimen with respect to the deformed configuration.

In addition to this test, the intermittent experiments have to be mentioned. In this case, substance samples are stored (usually unencumbered) under constant temperature in a selected medium. At predetermined time intervals, the aged samples are taken out from the medium and subjected to a short-term test at room temperature. This ensures that the ageing state of the sample is frozen during the short-term tests. At this point, there is a large variety of experiments that can be performed. Examples are the short-term relaxation test, the compression set test, monotonic tests or all kinds of dynamic tests.

Further studies with respect to the influence of temperature profiles, weathering, radiation and first modelling approaches have been proposed by [Blum et al. \(1951\)](#), [Duarte and Achenbach \(2007\)](#), [Ehrenstein and Pongratz \(2007\)](#) and [Shaw et al. \(2005\)](#). Compared to the problems related to the viscoelastic stress relaxation, known as a physical, reversible ageing effect, chemical ageing usually occurs on much larger time scales, cf. [Budzien et al. \(2008\)](#).

However, all experiments described have one thing in common: they all investigate substance samples with small dimensions so that any diffusion processes are negligible and a homogeneous oxygen distribution in the sample can be assumed. However, especially for components with larger dimensions, this is not the case. There, the oxygen distributions are generally inhomogeneous. Furthermore, oxidation-reaction regions can be formed, see [Pochiraju and Tandon \(2006\)](#). A review article dealing with this subject is the paper of [Audouin et al. \(1994\)](#). Based on these knowledges, it is on the one hand

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