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SPECIAL

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Experimental investigation of the dynamic mechanical behaviour of chemically aged elastomers

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Abstract In recent years, the application of elastomer components has surprisingly increased in a large number of technical areas. Therefore, these materials have gained in significance in many fields of research. The possible applications of elastomer components range over a wide scale and naturally include areas as automotive, mechanical, plant, marine and civil engineering. Because of the characteristics of elastomers regarding ductility, processability, flexibility and adhesiveness, it is impossible to abstain from the application of this material. Although elastomers are used in different fields, only little basic research has been practiced in the area of ageing. Hence, it is necessary to conduct more research within this area in the future. Also relating to ageing behaviour, little experimental research on elastomers is known. From earlier research experiences with rubber, it is known that these materials can change their characteristics over time. These findings make intensive research activities on the long-term behaviour of elastomers indispensable. In the area of chemical ageing, detailed examinations are important since the molecular structure as well as the integrity of the material can alter. Based on these changes, different properties such as weight, tensile and flexural strength as well as the thermal and dynamic material properties can change. In order to be able to predict the lifetime of elastomer components such as automotive tires or suspension bushings, all environmental influences have to be explored intensely. In the area of chemical ageing, diverse experimental methods are necessary. Contemporary research work shows that the dynamic mechanical properties of chemically aged elastomers do not alter with increasing age. Currently, it is monitored whether these statements apply to all elastomers. The ageing behaviour of natural rubber is examined and evaluated in media such as air, sea water, distilled water, freshwater as well as different salt solutions. In this article, DMA, DSC and TMA tests are carried out to investigate the chemically aged specimens. Since ageing tests are very time-consuming, repetitions are not made. In the DMA tests, small strains are applied.

Keywords Dynamic mechanical behaviour · Chemically aged elastomers · Thermal oxidation

1 Introduction

The majority of the world's natural resources are only available to a limited extent and non-renewable. Recent years have brought an increase in environmental awareness worldwide. This has consequences on market economies and the related product research and manufacturing. Furthermore, these changes have a strong influence on the costs of the raw materials, which are needed to produce elastomers with special properties. Since the application of elastomer components has increased in many areas, this material gained also significance in research. In the modern industrial area, elastomers find usage in manifold fields such as auto-

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motive, mechanical, plant, marine and civil engineering, hygiene and environmental conservation. Thus, many areas of life would be unthinkable without this material [13]. In addition, elastomers possess appropriate properties concerning ductility, processability, flexibility and adhesiveness and therefore make this material indispensable. First of all, elastomers are used in automotive engineering due to their elasticity and viscoelasticity for tires, door seals and sealing components in fuel systems. Concerning the increasing interest to apply this material intensive examinations are necessary. When comparing elastomers to metallic materials, which are very well researched, there is an urgent need to investigate and to model the short- and long-term behaviour of elastomers. Expertise in the field of ageing is still insufficient. In this context, two types of ageing are differentiated: physical and chemical ageing. The former describes property changes in relatively short amounts of time, which are completely reversible by an increase in temperature. It is caused by an alteration in the materials morphology or the configuration of the molecules. Physical ageing takes place below the glass transition temperature and results from the macromolecules attempt to reach a thermodynamic equilibrium state and hence a rather densely packed structure. If a polymer is quenched from above to below the glass transition temperature, a thermodynamic state of non-equilibrium, i.e. a relative large free volume, is frozen. In the course of physical ageing, the free volume relaxes to smaller values or even to zero. During reheating to a temperature level above the glass transition, the equilibrium configuration of the macromolecules is disturbed and the free volume increases again [9]. Therefore, physical ageing is a thermoreversible effect. In contrast to physical ageing, chemical ageing is caused by chemical changes in the macromolecular network. In consequence of heat, radiation or oxidation, chain scission and chain recombination as well as cross-link formation and chain degradation, different material properties are modified. Generally, chemical ageing is irreversible and takes place on a longer amount of time than physical changes [4]. These processes influence the properties of this material. In order to understand these effects and to model them in the context of continuum mechanics comprehensive experimental research is necessary, in which all environmental influences are explored thoroughly. To this, different experimental methods are required. The following experimental investigation is a fundamental basis for the development of constitutive models to represent chemical ageing under environmental influences.

Existing research results from the literature demonstrate that dynamic mechanical properties such as the storage and the loss moduli of chemically aged elastomers do not change significantly due to increasing degrees of ageing. In other research works, e.g. Johlitz et al. [8] investigated the mechanical properties of aged elastomer samples with respect to their stress–strain properties, thereby continuous and intermittent relaxation tests were performed. In 1944, Tobolsky et al. [17] study the thermo-oxidative ageing. In the case of long-term relaxation tests, the influences of oxygen and temperature have been studied. A summary can be found in [16]. Furthermore, studies have been made in terms of the influence of temperature profiles, as well as of oxygen (see, e.g. Blum et al. [1], Shaw et al. [14] and Duarte and Achenbach [3]). Steinke [15] inspected also the thermo-oxidative ageing of elastomers and focussed on temperature and oxygen. Furthermore, Johlitz [7] dealt with general ageing phenomena. Naumann et al. [10] deal with the simulation of chemical ageing in the field of mechanical material properties. Colin et al. [2] also studied the thermal oxidation of the kinetic parameters for post-cross-linking and reversion of torsional measurements.

2 Experimental investigations

In the scope of this research work, chemically aged elastomer samples are subjected to dynamic mechanical excitations. The ageing process of materials made from natural rubber is investigated in air, distilled water, freshwater, sea water, as well as in different salt solutions. The specimens are stored in the media for 14 weeks under isothermal temperature conditions at 80 °C. The influence of the media to the specimens is explained in the context of diffusion and osmotic effects, which occur due to differences in concentration. The specimens are removed from the respective media and temperatures in intervals of 2 weeks and are investigated with regard to their dynamic mechanical properties.

2.1 Material

Natural rubber used for the experimentation. It was delivered in the form of mats (20 cm × 20 cm) with the hardness of 55 Shore-A.

2.2 Experimental methods

2.2.1 Dynamic mechanical analysis

Various mechanical properties of materials can be determined by dynamic mechanical analysis (DMA). With this technique, it is possible to draw conclusions to the dynamic mechanical behaviour during ageing processes of materials. The DMA is based on a sinusoidal mechanical deformation of the specimen. The temperature T, the static predeformation $\varepsilon_{\text{stat}}$, the strain amplitude $\Delta\varepsilon$ and the frequency f can be varied as parameters:

$$\varepsilon(t) = \varepsilon_{\text{stat}} + \Delta\varepsilon \sin(2\pi f t) \tag{1}$$

When the strain amplitudes are not too large, i.e. less than about 5 %, this excitation leads to a phase-shifted stress response, which oscillates with the same frequency. In general, the phase shift φ, the static stress σ_{stat} and stress amplitude $\Delta\sigma$ depend on all parameters of the mechanical excitation (1) and on the temperature of the specimen.

$$\sigma(t) = \sigma_{\text{stat}} + \Delta\sigma \sin(2\pi f t + \varphi) \tag{2}$$

The DMA device measures the time-dependent strain excitation (1) and the resulting stress response (2). The phase shift φ between stress and strain as well as the storage and the loss modulus E' and E'' are determined by standard methods:

$$E' = \frac{\Delta\sigma}{\Delta\varepsilon}\cos(\varphi), \quad E'' = \frac{\Delta\sigma}{\Delta\varepsilon}\sin(\varphi) \tag{3}$$

In this paper, the storage and the loss modulus are measured as functions of the frequency for the differently aged elastomer specimens.

The dynamic mechanical tests were driven with a device developed by the company GABO. It is a system which belongs to the model series EPLEXOR −500 N. In the scope of this work, the specimens are harmonically strained at a constant temperature of 23 °C with a predeformation of 5 %. The frequency is varied between 0.1 and 80 Hz, and the strain amplitude is 0.5 %. The storage and the loss modulus (3) are determined according to DIN standard 53513. Flat specimen with a cross section of approximately 40 mm × 5 mm and a thickness of 2 mm are used. Previously, the specimens are stored at a temperature of 80 °C in air, distilled water, freshwater, sea water as well as in different salt solutions.

2.2.2 Differential scanning calorimetry

One of the most significant methods in the analysis of plastics is the Differential Scanning Calorimetry (DSC). This technique originates from the area of thermal analysis. It is used to determine conversion temperatures and changes in enthalpy of solids and liquids under controlled changes in temperature. The amount of gathered or emitted heat under isobaric conditions is determined by changes in the physical or chemical properties of the specimen. Thus, it is possible to determine the heat capacity of a material in dependence on the temperature process. To this end, the thermal behaviour of the material to be examined will be compared with that of a reference sample. The behaviour of the reference sample is known and will not change during the test phase. Eventually, the DSC measurement will specify the specimens gathered and emitted heat flow as a function of the temperature or time. It is vital that the specimen as well as the reference sample is subjected to a controlled temperature programme during the DSC method [5].

The DSC experiments take place in a device developed by the company Netzsch. It is a system of the model series DSC 204 F1. Within this work, the specimens are quenched down to a temperature of −100 °C and afterwards heated to a temperature of 120 °C with a heating rate of 10 °C per minute and then to a temperature of −100 °C with the same cooling rate [6]. With the DSC technique, the dependence of the glass transition on ageing is studied.

2.2.3 Thermomechanical analysis

After ageing, elastomers exhibit significant changes in their thermomechanical properties. During the experimental technique of Thermomechanical Analysis (TMA), the materials changes in dimension depending on temperature and time will be measured by means of a piezoelectric sensor with a selected load. Softening, stiffening, phase changes or sintering stages can occur adjacent to the thermal expansion. Hence, the TMA technique is a fundamental method for the indirect investigation of the materials composition, its structure or the manufacturing conditions. The process-dependent thermal expansion behaviour is determined to evaluate the changes in property of chemically aged elastomers. The glass transition temperature of the polymer can be determined by the change in the thermal expansion coefficient within the glass transition range. Below the glass transition temperature, the thermal expansion coefficient of many polymers is about one-third of that in the high-temperature range. The Thermomechanical Analysis is carried out using the device TMA/SDTA841 developed by the company Mettler Toledo. Within this study, which provides the glass transition temperature as well as the thermal expansion coefficient, the specimens are firstly cooled to a temperature of −100 °C. Afterwards, they are heated to a temperature of 120 °C with a heating rate of 10 °C per minute, and finally, they are quenched to a temperature of −100 °C with the same cooling rate.

3 Results and discussion

In this work, the examinations of the mechanical behaviour during chemical ageing take place in a period of 14 weeks. Here, the specimens are removed from the ageing media in week 1, 2, 4, 6, 8, 10, 12 and 14 and afterwards subjected to the previously described research methods DMA, DSC and TMA. Since the measuring expenditure is very high, it was only possible to monitor one specimen per medium and testing method. The media used for this investigation include distilled water, freshwater, sea water from the island Borkum and 6, 12 and 24 % salt solutions. The results of the DMA tests are presented in terms of the storage and the loss modulus according to their dependence on both the frequency and the ageing time. They also depend on the ageing medium (Fig. 1).

Figure 2 depicts the overall results of the storage modulus over a period of 14 weeks ageing in air. The red curve in the middle is the reference curve of the unaged material. It increases with a nearly constant slope with increasing frequency. This increase is caused by the flexibility of the segments. A segment is that part of a molecular chain which is forced to vibrate with the excitation. Vibrations of the constant segments are increasingly hindered due to rises in frequency, which leads to an increase of the modulus. Furthermore, it can be observed that the storage modulus increases primarily with increasing ageing time. Its maximum value is reached after 6 weeks of ageing. The storage modulus decreases after 8 weeks of ageing and reaches nearly the same level as after 2 weeks ageing. The modulus of the specimen with an ageing time of 10 weeks shows a level between those which were aged over 1 and 2 weeks. The starting value of the storage modulus is approximately 6 MPa. It can clearly be seen that an ageing period of 12 weeks leads to the same level as 10 weeks. Figure 2 also demonstrates that 14 weeks of ageing features a starting value of the storage modulus of approximately 1.27 MPa. The fact that the storage modulus firstly increases with the ageing time and then decreases is caused by the interaction between two different chemical reactions: one leads to the degeneration of the original network and the other to the creation of new bonds. In the first part of the ageing process, the creation of new bonds is dominant where as after 6 weeks the degeneration is more pronounced.

The experimental curves from ageing in distilled water in Fig. 3 show that the basic elasticities, i.e. the starting values of the storage modulus at the smallest frequency, change significantly over the ageing time. The values are the following ones: after week 1: 7.7 MPa, after week 2: 8.6 MPa, after week 8: 1.10 MPa, after week 10: 2.9 MPa, after week 12: 1.97 MPa and after week 14: 2.5 MPa. The results which belong to ageing in freshwater in Fig. 1 show that the starting value of storage modulus increases after 1 and 2 weeks of ageing. Afterwards, the starting values of the storage moduli decrease from week to week just until 12 weeks of ageing are reached. After an ageing time of 14 weeks, the starting value of the storage moduli rises extremely to 8.8 MPa. The increase of the aged specimens' storage modulus after 1 and 2 weeks is coherent with that of the specimen aged in distilled water. Assuming that the specimen which was used for the 2 weeks ageing test is an exception (due to scattering), one observes an obvious trend towards lower storage moduli, while the decrease of the basic elasticity of 10 MPa has been halved. The reason for the basic elasticities decreases the dominant effect of chain degradation, which is caused by the chemical ageing. A change in the frequency-dependent part of the storage modulus can be anticipated on the basis of the reference sample, which intersects the curves of the specimens after 1 and 2 weeks of ageing. The experimentally determined values of the basic elasticity for the medium sea water in Fig. 4 increase during the first 2 weeks of ageing. Then, they decrease from week to week under a value of 0.09 MPa after reaching the peak value of approximately 6 MPa. Hence, the elastomer firstly becomes more stiff in the sea water with prevailing network building. The diffusion of the sea water into the material leads to less cross-linking reactions within the material and consequently to a more dominant chain degradation after 4 weeks of ageing such that the elastomer becomes softer. These findings are coherent with the results of Retka, who determined that the chemical ageing in sea water leads to

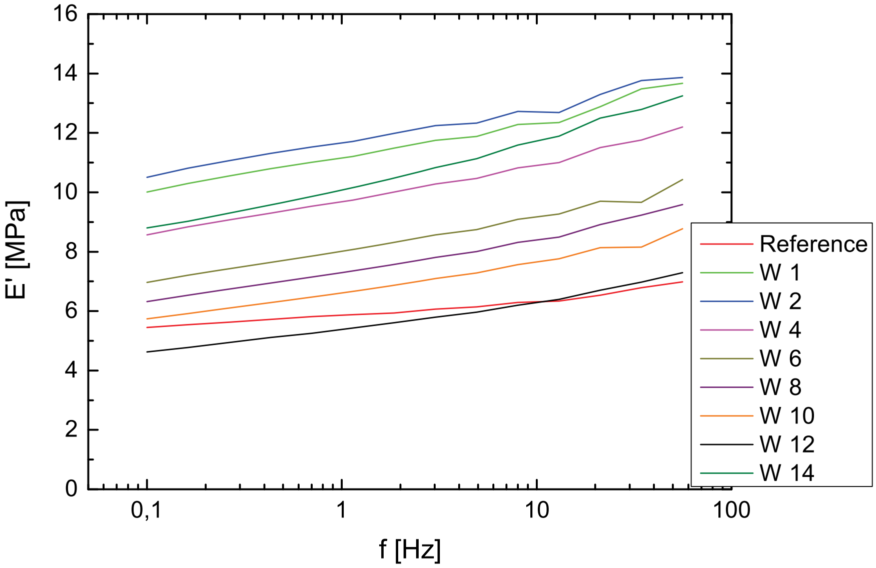

Fig. 1 Storage moduli of specimens that are aged in freshwater

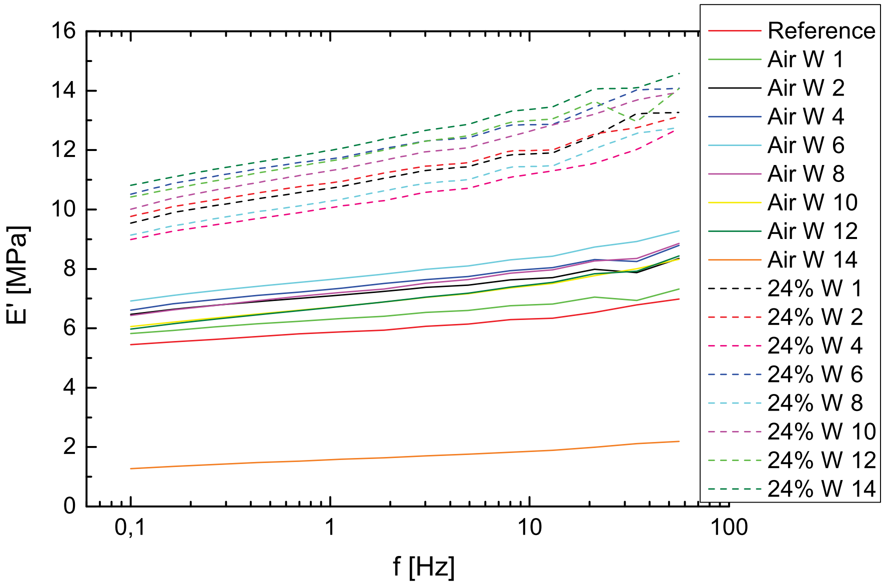

Fig. 2 Storage moduli of specimens that are aged in air and 24 % salt solutions

fast and prevailing chain scission [12]. Regarding the 6 % salt solution in Fig. 3, the basic elasticities decrease after the first 2 weeks of ageing. Subsequently, they increase to a higher value of about 11 MPa after reaching the minimum of 9 MPa after an ageing period of 6 weeks. Eight weeks of ageing lead to a softening of the material due to the decrease of the basic elasticity, respectively, and the decrease of the storage modulus. This observation indicates a dominant chain degradation. Over the course of ageing, the basic elasticity rises to approximately 13 MPa after 14 weeks of ageing, which corresponds with the so far measured starting value of the storage modulus. Furthermore, a predominant formation of new cross-links can be observed between the ageing weeks 8, 10 and 12. At this point of time, there is no obvious trend towards a softening of the material. In Fig. 4, the experimentally measured values of the storage moduli of all specimens that were aged in 12 % salt solutions are displayed. In comparison with the virgin specimen, the basic elasticity of the specimen after 1 week of ageing increases significantly from 5 MPa to 11 MPa. The following measurements demonstrate a reduction in the basic elasticity until 10 weeks of ageing are reached. Since after 10 weeks of ageing the basic elasticity increases, a starting value of the storage modulus of 12.7 MPa is reached in week 14. The data of

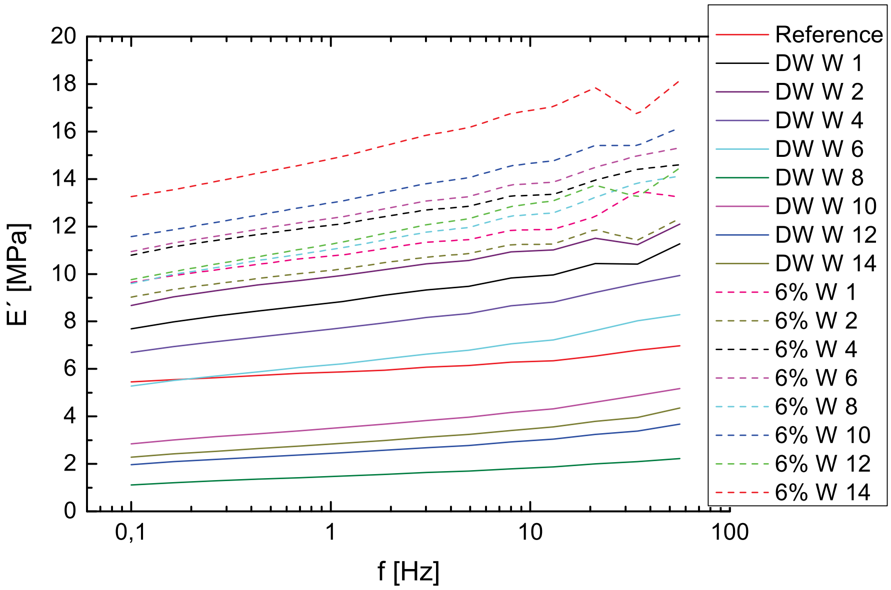

Fig. 3 Storage moduli of specimens that are aged in distilled water and 6 % salt solutions

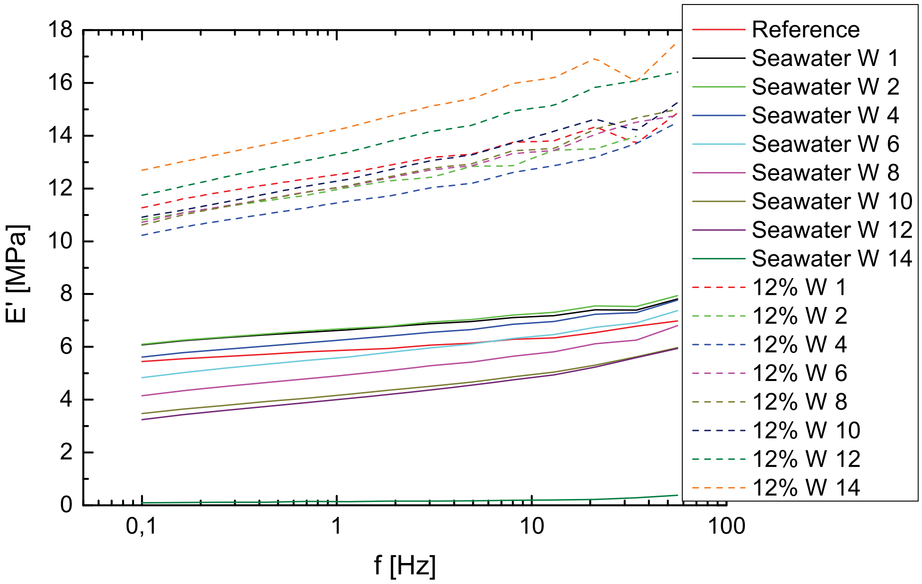

Fig. 4 Storage moduli of specimens that are aged in sea water and 12 % salt solutions

the specimens that were aged in the 24 % salt solution in Fig. 2 show that after 1 week of ageing the basic elasticity drops from 10.5 to 9.5 MPa. No obvious trend is observed during the following ageing weeks. It can only be observed that the storage moduli increase and decrease discontinuously. From week 10 to week 14, a continuous increase of the basic elasticity until approximately 10.8 MPa can be recognised (Fig. 5).

The following section presents the experimental results of the frequency-dependent loss modulus in dependence on the ageing process. Figure 6 depicts the results of the specimens' loss modulus in air. The red reference curve with a mean loss modulus of approximately 0.5 MPa lies underneath all other progressive graphs. It can clearly be seen that all specimens feature an identical course. Further, a slight increase of the loss modulus is observed between 1 and 10 Hz in all specimens aged over periods between 1 and 14 weeks. A pronounced increase in the loss modulus is observed above 10 Hz dependent on the amount of ageing. The exception is the loss modulus curve of about 0.2 MPa, which belongs to the specimen aged for 14 weeks. The frequency dependence of the loss modulus depends hardly on the duration of ageing but its mean value rises. This becomes clear

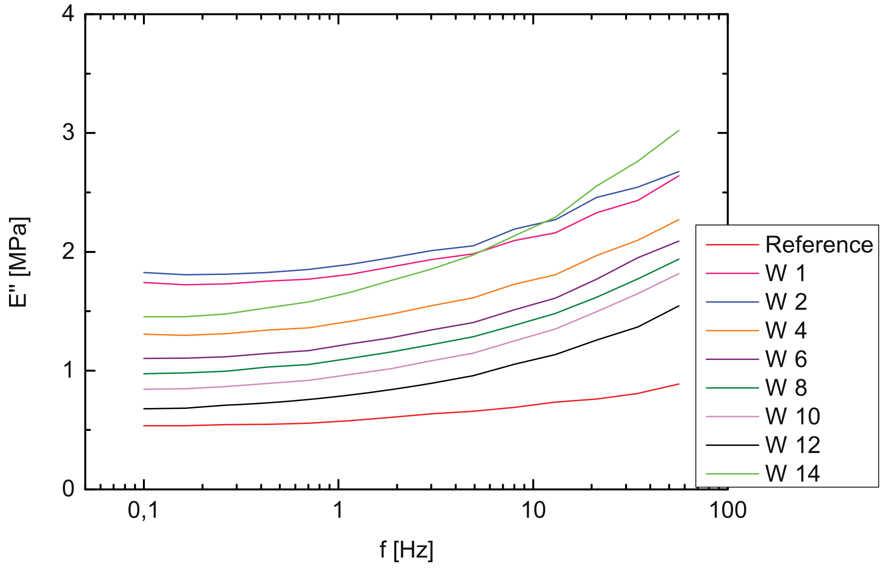

Fig. 5 Loss moduli of specimens that are aged in freshwater

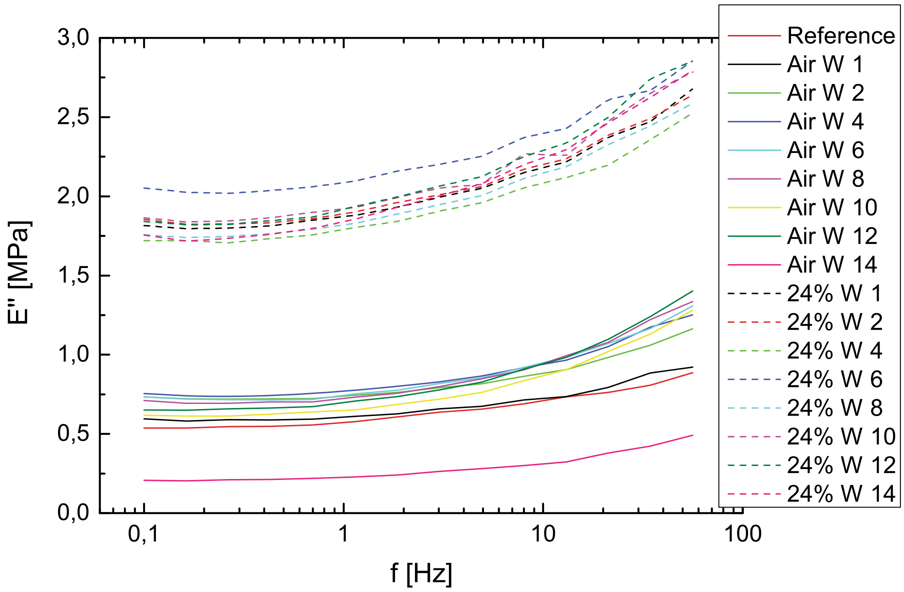

Fig. 6 Loss moduli of specimens that are aged in air and 24 % salt solutions

after ageing of 4 weeks, respectively, at higher frequencies. After the fourth ageing week, the loss modulus drops from week to week until it reaches a value of about 0.2 MPa in week 14. On the first glimpse, it is obvious that the changes in the loss modulus with increasing ageing time in distilled water are not significant in Fig. 7. The loss modulus increases during the first two ageing weeks in comparison with the reference sample. The figure shows that ageing leads to a drastic decrease of the modulus from week 4 on. A pronounced increase of the loss modulus of about 1.7 MPa is observed during the first 2 weeks of ageing in freshwater in Fig. 5. After the fourth week of ageing, the curves demonstrate a continuous reduction of the loss modulus. However, it increases enormously in week 14, approximately in the same scope as during the first two ageing weeks. The measurements of the loss modulus in sea water in Fig. 8 are nearly identical with the results from distilled and freshwater. A pronounced increase takes place during the first 2 weeks of ageing. Starting from week 2, a continuous decrease of the loss modulus can be observed with exception of week 12, which exhibits a slight increase in comparison with week 10. The samples that were aged in the 6 % (Fig. 7), 12 % (Fig. 8) and 24 % (Fig. 6) salt solutions do not show a clear trend. Figure 9 depicts the results of the storage moduli of sea water

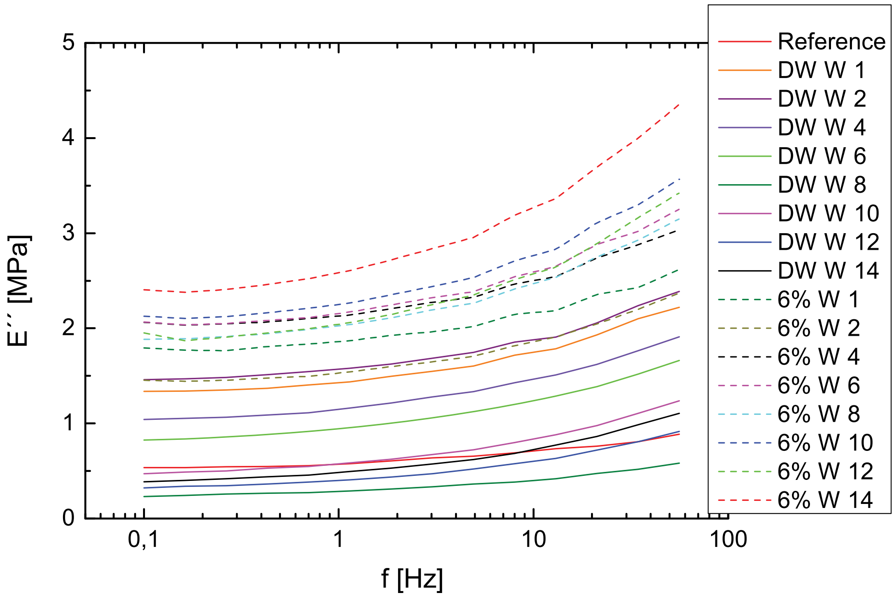

Fig. 7 Loss moduli of specimens that are aged in distilled water and 6 % salt solutions

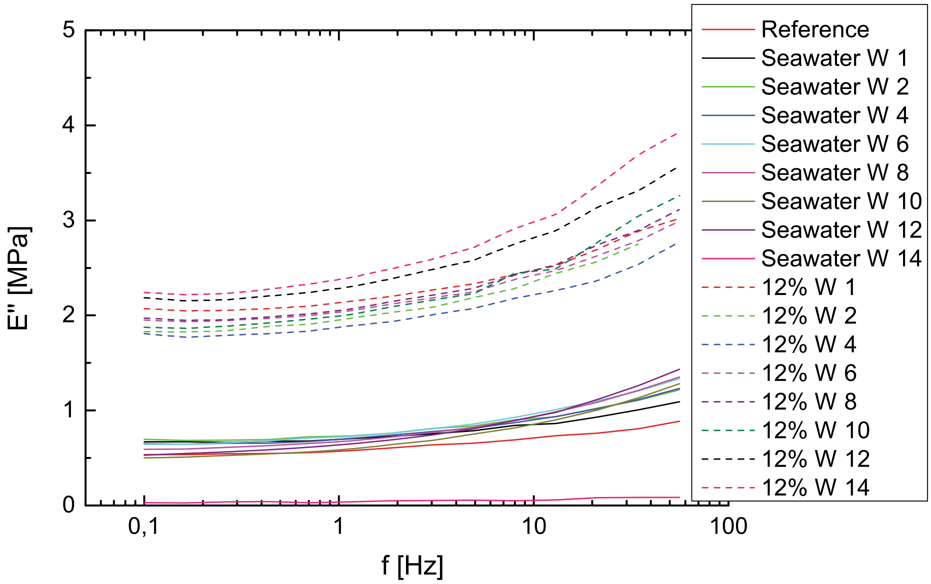

Fig. 8 Loss moduli of specimens that are aged in sea water and 12 % salt solutions

and 12 % salt measured throughout an ageing period at a frequency of 13 Hz. Figure 10 shows the results of the loss moduli for 13 Hz. The results for 12 % salt display the highest values, and, in contrast, those for sea water the lowest measured for all batches.

In order to analyse the influence of ageing on the glass transition, DSC and TMA experiments are carried out. Since thermal expansion and specific heat are influenced by different polymerphysical mechanisms, both tests are carried out and compared.

The experimental results of the glass transition temperature in dependence on the ageing time, which are determined by means of the DSC technique, are depicted in Fig. 11. The values vary between −62 and −54 °C and are wide-ranging. The curves which belong to the media air and sea water exhibit the lowest glass transition temperatures, whereas the specimens aged in the 24 % salt solution exhibits the highest value. The maximum difference between the glass transition temperature of the virgin material and those of the samples which are aged over 16 weeks in sea water is about 1.5 °C. Therefore, the overall differences belonging to the other ageing

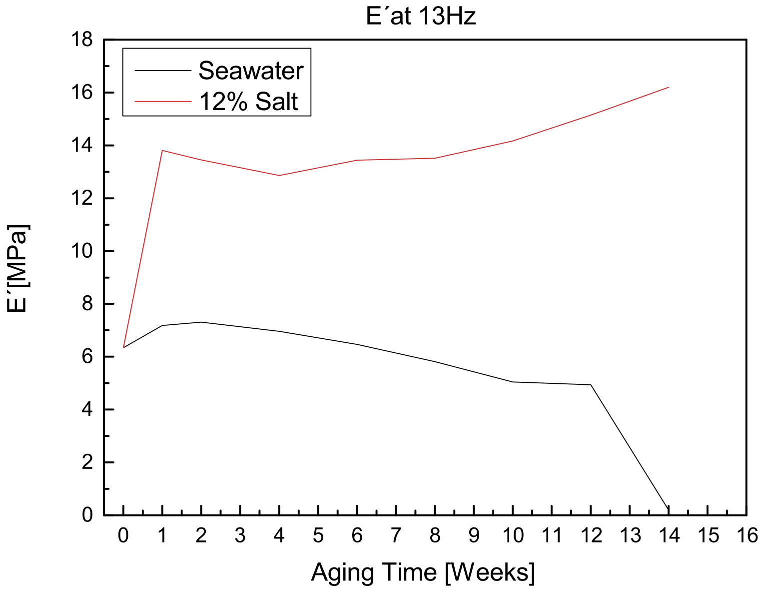

Fig. 9 Storage moduli of specimens that are aged in sea water and 12 % salt solutions

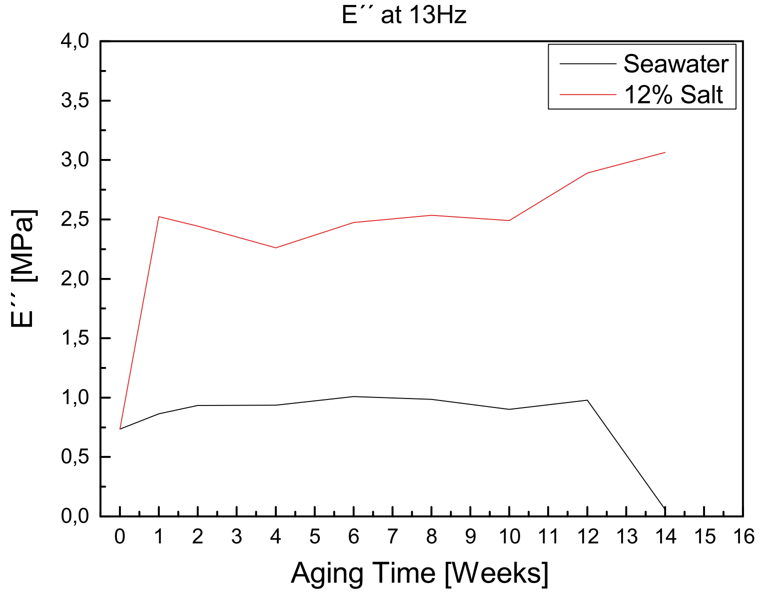

Fig. 10 Loss moduli of specimens that are aged in sea water and 12 % salt solutions

media are below 1.5 °C. Applying the common interpretation of the glass transition temperature, nearly no changes in the molecular mobility of the macromolecules are observed after an ageing time of 16 weeks. This observation corresponds to the observation that the frequency dependence of storage and loss modulus is also independent on the ageing process.

The results of all changes in the glass transition temperature measured by TMA as a function of the ageing time in all media are depicted in Fig. 12. At a first glance, no clear trend is seen between the different media. Taking a closer look to the data, it is clear that the material aged in air shows a greater temperature difference than the material, which is aged in distilled water. The maximum difference between the highest and lowest change in the glass transition temperature belongs to the ageing medium air and amounts to 6.99 °C; in the case of distilled water, a value of 6.7 °C is obtained. The maximum temperature differences between ageing in freshwater and sea water are between 4.34 and 4.76 °C. The lowest temperature differences are observed for the specimens that are aged in the 6 % salt solution (3.09 °C), in the 12 % salt solution (2.65 °C) and in the

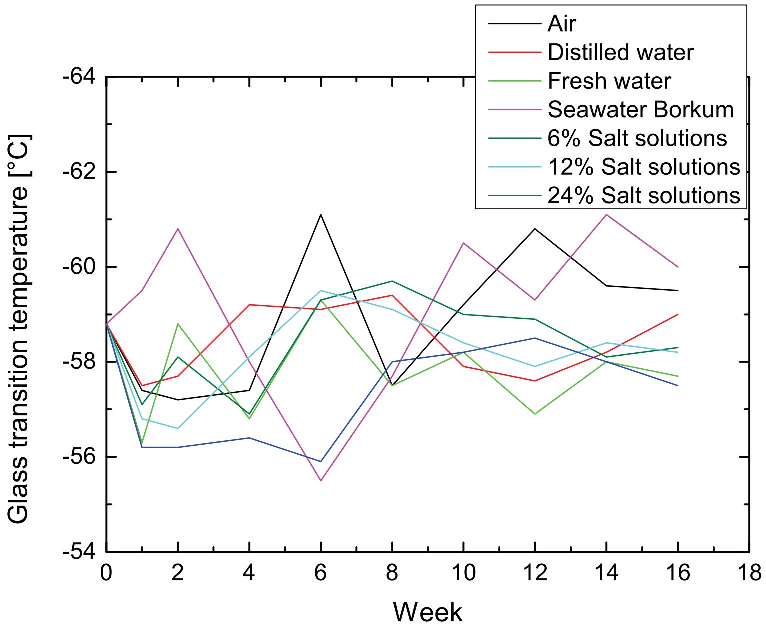

Fig. 11 DSC: glass transition temperature (Tg) specimens that are aged in different media

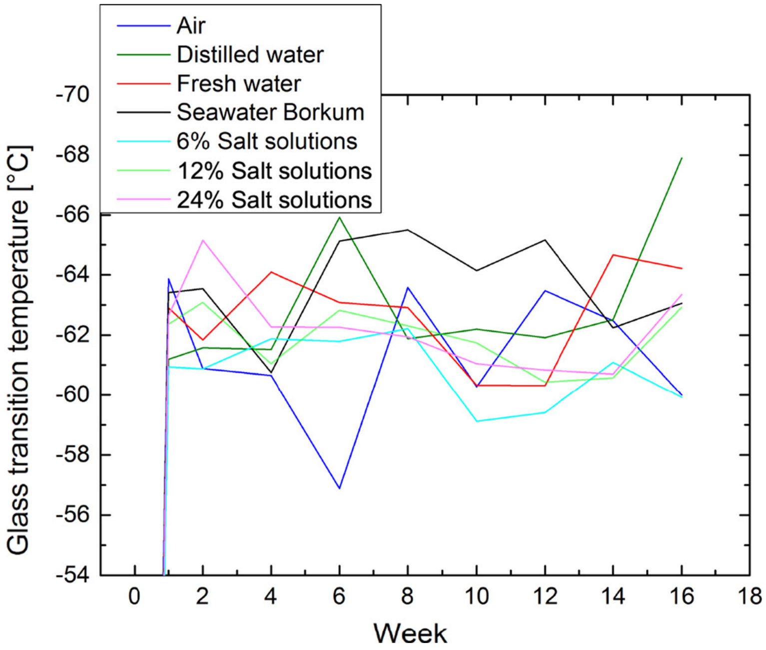

Fig. 12 TMA: glass Transition Temperature (Tg) during ageing

24 % salt solution (4.45 °C). The variations in the glass transition temperature between the reference sample of the virgin material and the samples which were aged over 16 weeks are rather low in spite of the obvious difference between the lowest and highest measured value. Consequently, the maximum difference between the glass transition temperature of the specimens aged over 16 weeks and that of the reference specimen is 5.89 °C in the ageing medium distilled water. The other differences between the virgin and the aged samples over 16 weeks lie under 3 °C. Resulting from the DSC and TMA findings, a change in the molecular mobility of the materials can be excluded during an ageing time of 16 weeks in various media at 80 °C.

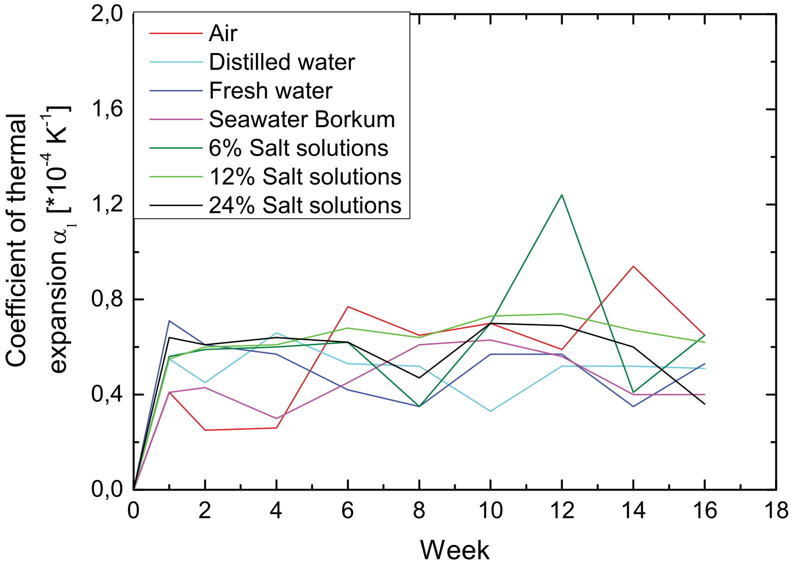

Fig. 13 Thermal expansion coefficient α_1 over ageing time t

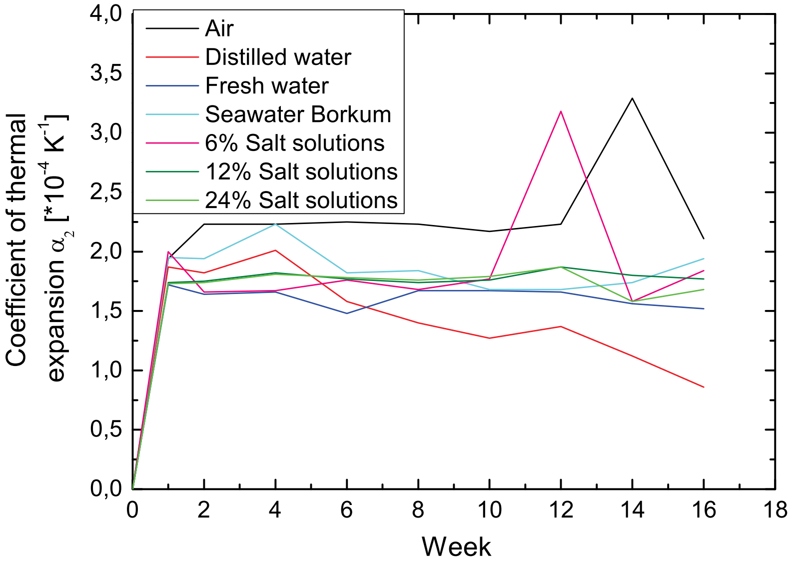

Fig. 14 Thermal expansion coefficient α_2 over ageing time t

In order to study the influence of ageing to the molecular mobility and glass transition-related phenomena in more detail, continuative measurements are necessary. Perhaps, the shape of the different DSC curves as well as the ageing-induced changes in the specific heat at the glass transition temperature should be compared. Furthermore, a slight ageing effect can be observed at increasing salinity, as in the described results of the DMA tests. Due to different experimental techniques and different physical phenomena (DSC is related to temperature-induced changes in the enthalpy of the material, and TMA is related to geometrical changes), the experimentally determined glass transition temperatures in Figs. 11 and 12 differ slightly.

The following part discusses the thermal expansion behaviour of the aged specimens. To this, thermal expansion coefficients above and below the glass transition temperature are identified. α_1 is the thermal expansion coefficient below and α_2 the coefficient above the glass transition temperature. Initially, the expansion coefficients of the virgin reference sample as well as those after ageing are determined. Figure 13 visualises the thermal expansion coefficients α_1 of the aged elastomer specimens of all media as a function of the ageing time. Comparing all thermal expansion coefficients below the glass transition temperature, it is observed that the reference samples value is located beneath the values of the aged specimens. It can be seen that the measured values fluctuate from one measurement to the other. There is no clear trend recognisable. Therefore, the greatest relative difference between the highest and the lowest value is about 376 % in the ageing medium air. Consequently, the difference between the values after 1 and 16 weeks of ageing is 158 %. Samples from the other ageing media do not show such a great difference.

In Fig. 14, one can see the changes in the thermal expansion coefficient α_2 above the glass transition belonging to all media over the entire ageing time. As seen in the previously described changes in α_1, the coefficient α_2 fluctuates in the same sense. But the percental increases and decreases are clearly lower due to higher values, whereas the absolute differences are bigger. The thermal expansion coefficients of the samples, which are aged in air and in 6 % salt solution, show great conspicuity. The sample that is aged in a 6 % salt solution reaches its peak value in week 12. But the sample that is aged in air reaches its peak value in week 14, and the curves progress from week 2 clearly over all other curves. The increase of α_2 between the virgin reference sample and the sample that is aged over 16 weeks in the 6 % salt solution is 11.5 %. The maximum difference belonging to the other media, excepting distilled water and freshwater, is located at 27.8 %. With the exception of the data which belongs to the ageing media air, distilled water, sea water and 6 % salt solution, all other data are mainly located between 1.4×10^{-4} and $1.87 \times 10^{-4}\ \mathrm{K}^{-1}$. The curves of the other media are not similar to those which are related to air and the 6 % salt solution at all. Still, none of the media showed significant changes, so that the results of all ageing media are identical.

4 Conclusion

This research work has the aim to examine changes in the dynamic mechanical behaviour of elastomers, which are chemically aged in different media. The samples are made from natural rubber with the hardness 55 Shore-A. As ageing media air, distilled water, freshwater, sea water and different solutions with salt contents of 6, 12 and 24 % are used. The temperature during the ageing process is 80 °C, and the maximum duration of ageing was 16 weeks. Samples are extracted in weeks 1, 2, 4, 6, 8, 10, 12, 14 and 16 and afterwards subjected to the classical test methods DMA, DSC and TMA. Subsequently, the experimental data are evaluated.

By means of the DMA changes in the basic elasticity are recognised. The basic elasticity is defined as the value of the storage modulus at a frequency of zero Hertz (or at the lowest frequency which was used in the tests). Here, the values which belong to the ageing media freshwater and distilled water drop significantly. This demonstrates that a pronounced softening effect takes place. Materials that are aged in air, sea water and in 6, 12 and 24 % salt solutions become more rigid with increasing ageing. In the case of freshwater and distilled water, the chain scission effects are dominant, whereas in the second case the build-up of a new network is the determining factor. In order to get more information with regard to these concurring processes, detailed chemical analyses of both the aged rubber specimens and the environmental media should be carried out. Measurements of the frequency-dependent dynamic mechanical properties of chemically aged elastomers show obvious changes in the storage and the loss modulus. The storage and loss modulus increase in dependence on the frequency and with increasing ageing time in salt water. In the case of freshwater and distilled water, at first, a stiffening occurs, and after some weeks, softening is the dominant effect. A greater increase of the storage and loss modulus dependence on the frequency with increasing ageing time is seen in sea water, air as well as in 6, 12 and 24 % salt solutions. This effect is less significant with increasing salt concentration. In coherence with the observation of smaller changes in the basic elasticities, this leads to the conclusion that the tested material, which is subjected to sea water, becomes more resistant to ageing with increasing salt concentration. From a physicochemical point of view, such behaviour is caused by osmotic effects and requires further experimental and theoretical studies. With respect to the DMA tests of the NR elastomer studied in this article, it cannot be concluded that the dynamic mechanical properties of chemically aged elastomers do not change with increasing ageing time. In [11], the authors found no influence of ageing on the storage and the loss modulus because their ageing time was too short. Petrikova et al. [11] also found few changes within their examinations. In contrast to the maximum ageing time of 16 weeks in this article, the samples of the Czech researchers were only stored for 3 weeks.

In addition to the above-mentioned mechanical tests, the material is examined with regard to changes in the molecular mobility. The configurational alterations are recognised by means of changes in the glass transition temperatures, which are determined using the common DSC and TMA techniques. An obvious change in the glass transition temperature could not be identified even in the measurements after ageing of 16 weeks, neither by means of the DSC nor by the TMA.

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