

INFLUENCE OF HFO REFRIGERANTS ON THE VISCOELASTIC BEHAVIOR OF ELASTOMERS

Sebastian Eyerer ^{(a),(b)}, **Peter Eyerer** ^(c), **Christoph Wieland** ^{(a),(b)},
Hartmut Spliethoff ^{(a),(b),(d)}

^(a) Technical University of Munich, Institute for Energy Systems,
85748 Garching, Germany, sebastian.eyerer@tum.de

^(b) Technical University of Munich, Munich School of Engineering, Geothermal Alliance Bavaria,
85748 Garching, Germany

^(c) Fraunhofer Institute for Chemical Technology, 76327 Pfinztal, Germany

^(d) Bavarian Center for Applied Energy Research, 85748 Garching, Germany

ABSTRACT

The hydrofluoroolefines (HFO) have been introduced within the last years as new generation of refrigerants having a significantly lower Global Warming Potential. Compared to the state-of-the-art fluids within the class of hydrofluorocarbons (HFC), the HFO molecules are unsaturated, consisting of double bonded carbon atoms. The difference in the chemical structure may cause different interaction with polymers, especially elastomers, which tend to swell when exposed to certain refrigerants. In this study, the influence of modern refrigerants on the viscoelastic behavior of elastomers is analyzed. The investigated refrigerants are two state-of-the-art fluids, namely R245fa and R134A, as well as three next-generation refrigerants R1233zd-E, R1234yf and R1234ze-E. The investigated polymers comprise ethylene-propylene-diene rubber, fluororubber, chlorobutadiene rubber and nitrile butadiene rubber. From this analysis it can be concluded, that the investigation of the viscoelastic behavior gives meaningful insights to better understand the fluid-polymer interaction and thus helps to evaluate the material compatibility.

Keywords: Low-GWP Working Fluids, Polymers, Chemical Stability, Swelling Test, Creep Behavior, Refrigeration, Elastomers, Viscoelastic Behavior

1. INTRODUCTION

The transformation of the global energy supply is a major challenge of the 21st century in order to become more sustainable and independent from fossil sources. To meet this challenge there are three main approaches: expansion of the use of renewable energy sources, increase in efficiency on the demand side and enhancement of waste-heat recovery. The Organic Rankine Cycle (ORC) technology focuses on the first and the latter approach in terms of electrical power generation from low temperature heat sources such as solar, geothermal brine or industrial waste heat (Vélez et al., 2012). However, the currently dominating working fluids for ORC systems have significant environmental impact due to their extremely high Global Warming Potential (GWP) (Macchi and Astolfi, 2017). The most widespread refrigerants in ORC applications are hydrofluorocarbons (HFC) such as R134A, which is often used in geothermal power plants and low-temperature heat utilization, and R245fa, whose main application is waste heat recovery of low to medium temperature heat (Quoilin et al., 2013).

To overcome this environmental impact of the ORC working fluids, a new generation of refrigerants, the hydrofluoroolefines (HFO), has been introduced within the last years. These fluids have a significantly smaller Global Warming Potential (GWP), compared to the state-of-the-art working fluids. Especially, due

to legislative acts such as the F-Gas regulation (The European Parliament and the Council of the European Union, 2014), the application of these working fluids is highly encouraged.

From a thermodynamic point of view, these fluids can possibly be applied to existing systems as a drop-in replacement (Eyerer et al., 2016). However, the material compatibility of the fluid and the system materials must be ensured. HFO refrigerants are unsaturated molecules, meaning that they have a double bond joining two carbon atoms together. Especially, compared to the HFC refrigerants, which are saturated molecules consisting of single bonded carbon atoms, the interaction with polymers might differ. Special focus should be put on elastomers because they tend to swell and thus significantly change their mechanical properties when they are exposed to certain refrigerants. Within ORC plants and refrigeration units, elastomers are applied i.e. as sealing materials or as construction materials in components. A prominent example is the diaphragm in positive displacement pumps, which are often applied to experimental ORC test rigs (Quoilin et al., 2013).

In recent years, some studies focusing on thermal and chemical stability of refrigerants have been published. However, investigations in the material compatibility of polymers and refrigerants are rare. For example, the refrigerant manufacturers Honeywell Inc. (2015) and Chemours (Leck, 2009) published compatibility tests of their refrigerants with some construction materials. However, according to their own reports, this information can rather serve as guides to identify suitable combination, than as a proof of compatibility. Majurin et al. (2015) put special focus on the HFO refrigerants R1234yf and R1234ze-E and investigated the compatibility with elastomers such as chloroprene (CR), ethylene-propylene-diene rubber (EPDM), fluoric rubber (FKM) and silicone rubber as well as thermoplastics such as polyethylene (PE), polyamide (PA) and PTFE. In previous studies (Eyerer et al., 2018; Eyerer et al., 2017), the authors of this publication provided an in-depth analysis of the material compatibility of several HFO and HFC refrigerants with EPDM, FKM and PTFE. They evaluated the change in weight, volume and hardness of polymer samples due to the exposure to the refrigerants and explained the relevant mechanisms for the fluid-polymer interaction.

However, the viscoelastic behavior of elastomers and the influence of the exposure to refrigerants has not yet been studied and thus is the purpose of this publication. The viscoelasticity is thereby a material property describing both viscous and elastic characteristics when a stress is applied. Thus, a viscoelastic material exhibit time-dependent strain. The influence of refrigerants on this time-dependent behavior of the materials is important in order to ensure a sufficient functionality and lifetime of the polymer components within ORC systems or refrigeration units. The focus of this study is now on the investigation of the viscoelastic behavior of elastomers and the possible change of this property due to the exposure to refrigerants. In order to present a critical analysis, several fluids from the groups of HFO and HFC are considered. By that means, the difference of HFO and HFC refrigerants can be analyzed. The analyzed fluids are R245fa, R134A, R1233zd-E, R1234yf and R1234ze-E. The investigated elastomers comprise ethylene-propylene-diene rubber (EPDM), fluororubber (FKM), chlorobutadiene rubber (CR) and nitrile butadiene rubber (NBR).

The structure of the study comprises a brief explanation of the relevant fundamentals of the viscoelastic behavior. Then, the experimental methodology and the data evaluation procedure is described. Finally, the results are presented and discussed as well as relevant conclusions are drawn.

2. FUNDAMENTALS OF VISCOELASTIC BEHAVIOR

In this section, some fundamentals and relevant models for viscoelastic materials are presented. Typically, the viscoelastic behavior of materials can be described by mechanical models using elastic springs and viscous dashpots. There are two basic models which can be found in literature (Elsner et al., 2012): the Maxwell model, which consists of a spring and a dashpot connected in series and the Voigt-Kelvin Model, which is a parallel connection of a spring and a dashpot. A combination of these two models is the Burgers Model (or 4-parameter Model), which is depicted in Fig. 1. Using this Burgers Model, the material behavior in terms of stress σ and strain ε can be described by the differential equation:

$$\ddot{\sigma} + \left(\frac{c_1}{d_1} + \frac{c_1 + c_2}{d_2} \right) * \dot{\sigma} + \frac{c_1 * c_2}{d_1 * d_2} * \sigma = c_1 * \dot{\varepsilon} + \frac{c_1 * c_2}{d_2} * \varepsilon \quad (1)$$

where c_1 , c_2 are the respective spring coefficients and d_1 , d_2 are the respective damping coefficients, as

depicted in Fig. 1. Solving this equation for a constant stress σ_0 , the time-dependent strain during loading can be obtained:

$$\varepsilon_{load}(t) = \frac{\sigma_0}{c_1} + \frac{\sigma_0}{d_1} * t + \frac{\sigma_0}{c_2} * \left(1 - e^{-\frac{t}{\tau}}\right) \quad (2)$$

where $\tau = d_2/c_2$ is the retardation time. If the constant stress σ_0 is released after the time t_1 , the solution of Eq. (1) describes the development of the strain during unloading:

$$\varepsilon_{unload}(t > t_1) = \varepsilon_{load}(t_1) - \frac{\sigma_0}{c_1} - \frac{\sigma_0}{c_2} * \left(1 - e^{-\frac{t_1}{\tau}}\right) * e^{-\frac{t-t_1}{\tau}} \quad (3)$$

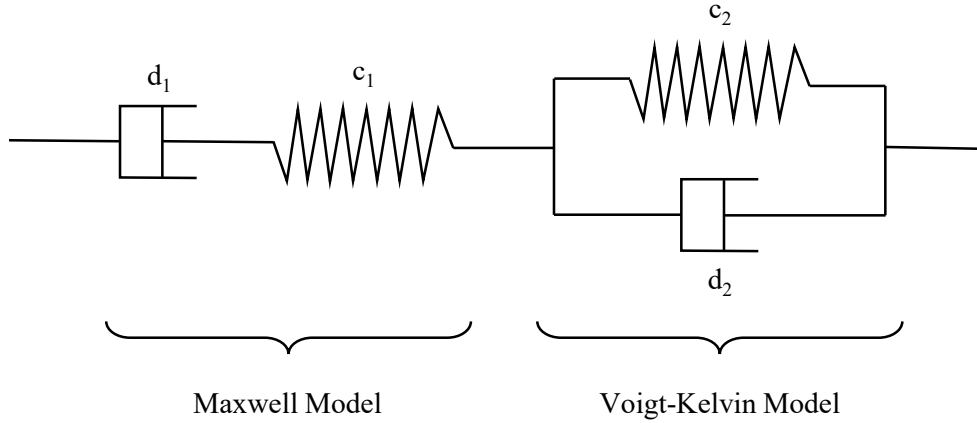


Figure 1: Burgers model – a spring-dashpot model for viscoelastic material

This viscoelastic behavior is exemplarily depicted in Fig. 2 for a constant stress σ_0 , which is released after the time t_1 . At the time t_0 , the constant stress is applied. The material responds to that stress with an instantaneous strain ε_{ela} and a further time-dependent strain. The instantaneous strain ε_{ela} is reversible, after unloading the material at time t_1 . In the above-described model, the spring in the Maxwell model with the spring constant c_1 is responsible for that elastic strain. Thus, the elastic strain is:

$$\varepsilon_{ela} = \frac{\sigma_0}{c_1} \quad (4)$$

The time-dependent behavior from state ② to state ③ in Fig. 2 is described by the Voigt-Kelvin Model and the dashpot in the Maxwell model. There, the Voigt-Kelvin model describes a fully reversible creep, which can be expressed with the retardation time:

$$\tau = \frac{d_2}{c_2} \quad (5)$$

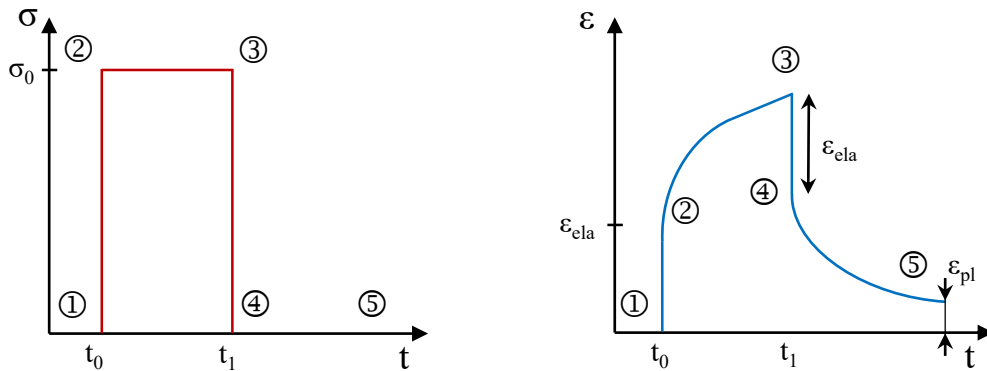


Figure 2: Stress and time-dependent induced strain for a viscoelastic material

Furthermore, the dashpot in the Maxwell model describes the time-dependent linear creep between states ② and ③, which is irreversible. Thus, this dashpot is responsible for the plastic deformation of the material after the time t_1 and, thus, can be expressed by:

$$\varepsilon_{pl} = \frac{\sigma_0}{d_1} * t_1 \quad (6)$$

Concluding from this fundamental model, the viscoelastic behavior of polymers can be expressed by the elastic and plastic strain as well as the retardation time as defined in Eq. 4 – 6.

3. EXPERIMENTAL METHODOLOGY

In this section, the experimental procedure, the investigated refrigerants and polymers as well as the measuring devices are described. In order to analyze the influence of HFO refrigerants on the viscoelastic behavior of elastomers, material samples are exposed to three different HFO, namely R1233zd-E, R1234yf and R1234ze-E as well as two HFC refrigerants, namely R245fa and R134A as a reference. The investigated polymers comprises EPDM, FKM, CR, and NBR such that 20 fluid-polymer combination have been analyzed. To evaluate the influence of the refrigerants, the time-dependent strain is measured for a constant stress. These measurements are taken at the three states before the exposure, directly after the exposure and after a subsequent drying period. The values after the drying period are quite interesting because they allow analyzing irreversible changes in the material properties due to the exposure with the refrigerants. In order to have a consistent experimental procedure, the same conditions as in a predecessor study of the authors (Eyerer et al., 2018) have been ensured before, during and after the exposure. First, the polymer samples have been stored before the exposure, following the recommendations of ISO 175:2011-03 and without further cleaning in order not to have any influence of the cleaning substances and to represent real application. Then, the samples are exposed to each refrigerants for 28 days. The exposure temperature has been set to 75 °C, in order to represent typical operation temperatures of a heat pump or an ORC plant. During the exposure period, the samples are stored in non-alloyed steel (material number: 1.0254) pressure vessels, to ensure the refrigerants to be liquid at the exposure temperature. The subsequent drying period of the samples is set to 21 days. There, the polymer samples dry at 25 °C in a 0.01 bar vacuum atmosphere also representing real application conditions because ORC or refrigeration systems are evacuated for example for maintenance or to change the refrigerant. The duration of 21 days of drying procedures ensures that the refrigerant can completely desorb from the polymer samples.

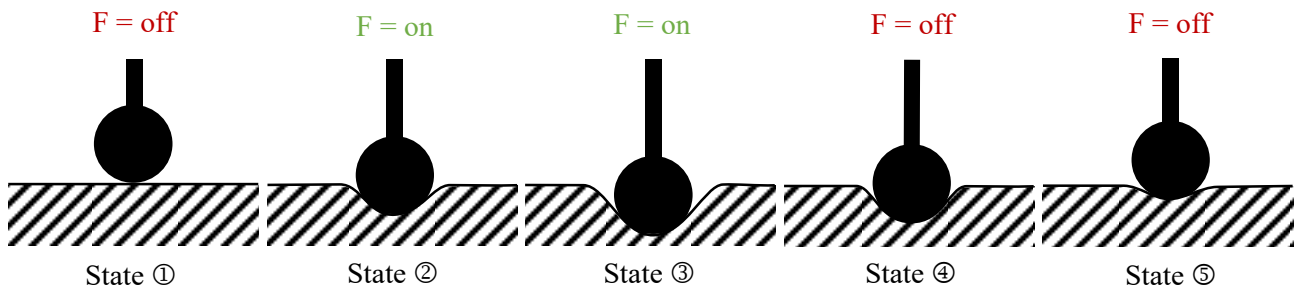


Figure 3: Sketch of the measuring procedure

To analyze the change of the viscoelastic behavior, the time-dependent strain is measured with a durometer for small load hardness according to IRHD (International Rubber Hardness Degree). The measurement procedure in this study follows the DIN ISO 48:2010. Therefore, an indenter with a spherical diameter of 1.5 mm is used together with a small preload of 1 g and a main load of 15 g. The resulting depth of indentation is in the range of 1 to 60 μm depending on the polymer. Due to this small indentation depth of the small load hardness measurement, the exposure time of the material samples inside the refrigerants can be much shorter than for macroscopic measurements such as the change in mass, volume or Shore hardness. Thus, the total experimental procedure for material compatibility evaluation can be significantly shortened with the approach described in this study. In Fig. 3, the measuring procedure is illustrated. The indication of the states ① to ⑤

also corresponds with Fig. 2. In state ①, the position of the surface area is detected and the indenter is placed directly on the surface but without a load. State ② corresponds with the time t_0 , where the main load is activated leading to the instantaneous strain ε_{ela} . Until state ③, the depth of indentation increases due to the time-dependent creep, described above. In state ④ and ⑤, the indenter is unloaded which leads to an immediate as well as a time-dependent reduction of indentation depth by the recovery behavior of the material. In state ⑤, there is a constant indentation depth observed, which is no more time dependent. This is caused by plastic deformation of the material and corresponds to the plastic strain ε_{pl} . Due to the time-dependency of that measurement, it is important to ensure a constant measuring period for each sample. In this study, a loading and unloading time of 300 sec has been used, respectively.

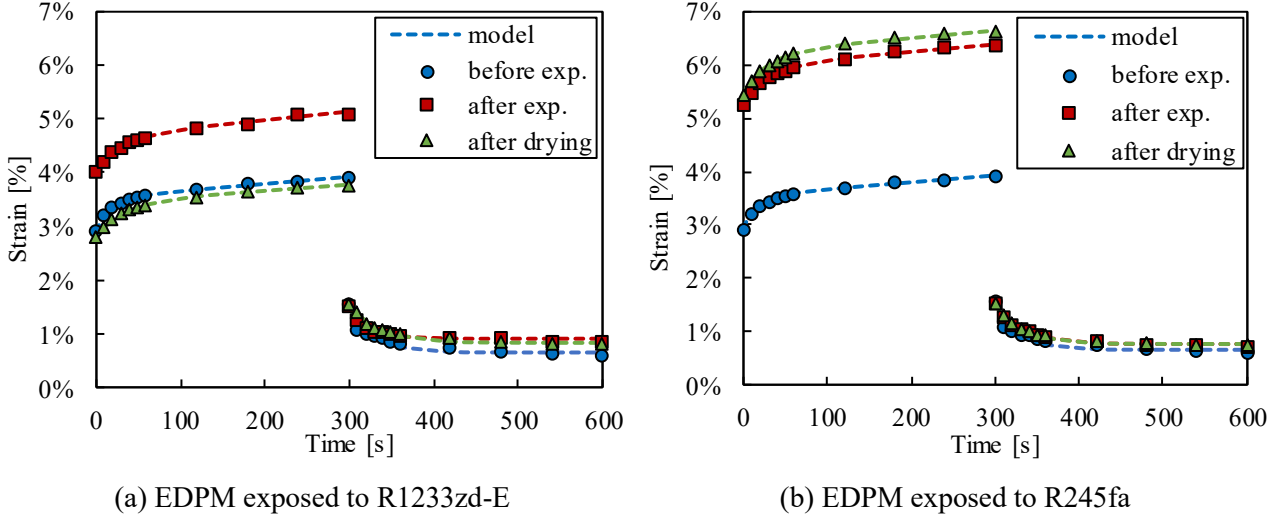


Figure 4: Time-dependent strain of EDPM samples exposed to R1233zd-E and R245fa

Fig. 4 shows exemplarily the measured values of the time-dependent strain of the EPDM samples before and after the exposure as well as after the drying procedure. In order to be able to evaluate the influence of the exposure to the refrigerants, the measured values are fitted to the above described model equations (cf. Eq. 2 and 3) for the viscoelastic behavior. By that means, the three characteristic values, namely the elastic and the plastic strain as well as the retardation time can be calculated. The change of these values due to the exposure to the refrigerants finally can be used to interpret the influence of the fluids on the viscoelastic behavior of the investigated elastomers.

4. RESULTS AND DISCUSSION

In this section, the change of the viscoelastic behavior of the investigated polymer samples due to the exposure to five different refrigerants is presented. Fig. 5 depicts the relative change of the elastic strain ε_{ela} directly after the exposure to the refrigerants (cf. Fig. 5 (a)) and after the subsequent drying period (cf. Fig. 5 (b)).

In order to focus on the difference of HFO and HFC refrigerants, the results for R1233zd-E and R245fa are exemplarily analyzed. The refrigerants R1233zd-E is considered to be a low-GWP alternative for R245fa and possibly being applicable as drop-in replacement (Eyerer et al., 2016). Looking at the EPDM samples, it can be observed in Fig. 4 and Fig. 5 that the elastic strain increases directly after the exposure to R1233zd-E. In case of the exposure to R245fa, the increase of the elastic strain is even higher. The increase of the elastic strain represents a decrease in hardness of the material and can be explained by the absorption of refrigerant molecules inside the polymer matrix (Eyerer et al., 2018). Such a behavior can also be found for NBR and FKM being exposed to all of the investigated fluids. Due to the fact, that the relative change of the elastic strain of EPDM being exposed to R245fa is higher than after the exposure to R1233zd-E, it can be concluded, that the R245fa molecules can better be absorbed by the elastomers. Looking at the state after the drying procedure, an interesting finding is that the elastic strain of the samples being exposed to R1233zd-E almost has the same value as before the exposure. In contrast to that, the samples being exposed

to R245fa almost keeps the same elastic strain as directly after the exposure (cf. Fig. 4 and Fig. 5). Since the refrigerant molecules are desorbed after the drying period, the corresponding change of the elastic strain is supposed to be caused by changes of the polymer properties. The spring with the coefficient c_1 in Fig. 1 is responsible for the elastic strain. Thus, it can be concluded, that the interaction of EPDM with R245fa causes a decrease of that spring coefficient c_1 . A reduction of the degree of crystallization and thus higher entropy-elasticity might be an explanation for that. In contrast to that, a very slight reduction of the elastic strain of the EPDM samples being exposed to R1233zd-E can be observed in Fig. 5 (b). This, in turn, might be explained by a slight dissolution of the plasticizers in the EPDM material.

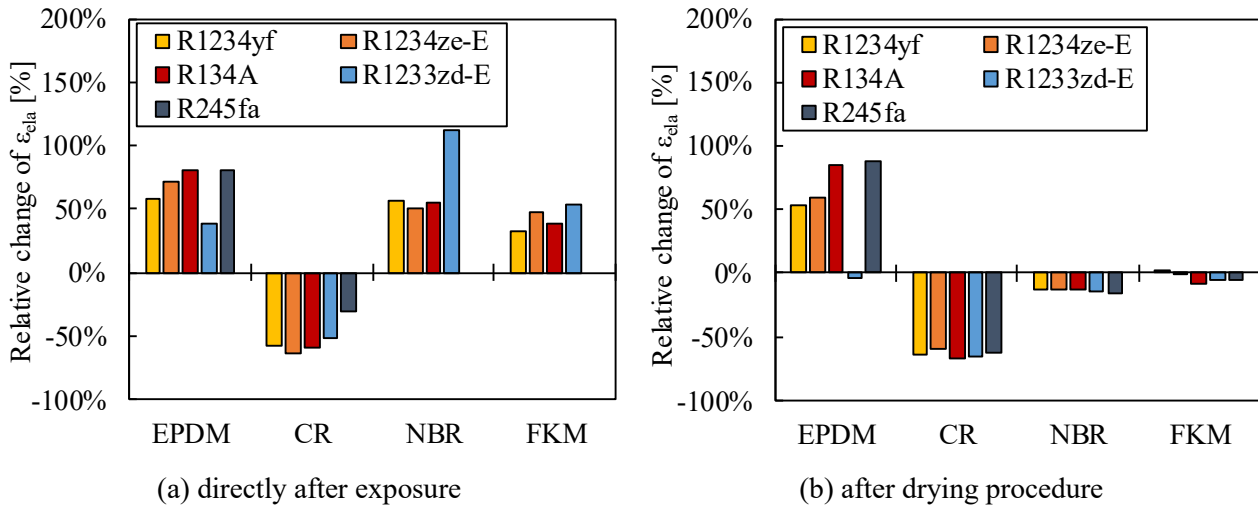


Figure 5: Relative change of the elastic strain ϵ_{ela} of the elastomers due to the exposure to the refrigerants

In order to follow the exemplarily discussion of the EPDM samples being exposed to R1233zd-E and R245fa, Fig. 6 shows the relative change of the plastic strain ϵ_{pl} . It can be observed, that R1233zd-E causes a significantly higher increase of the plastic strain of the EPDM samples than R245fa. This fact can be observed for the state directly after the exposure and for the state after the drying period. Thus, both refrigerants cause an irreversible change in the damping coefficient d_1 of the material; however, R1233zd-E has greater impact. The above-mentioned dissolution of plasticizers out of the polymer matrix due to the interaction with R1233zd-E might be the explanation for higher plastic deformation. The dissolution of plasticizer molecules out of the polymer matrix leads to smaller distances between the polymer chains and thus to higher intermolecular binding forces between the chains. This effect leads to increasing damping properties of the material.

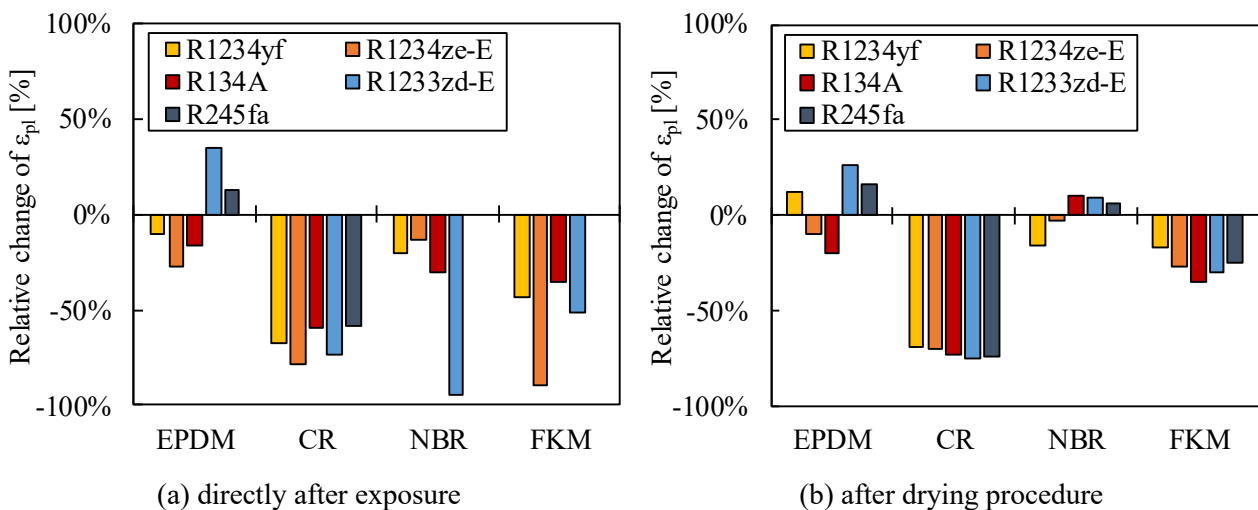


Figure 6: Relative change of the plastic strain ϵ_{pl} of the elastomers due to the exposure to the refrigerants

The last parameter to be discussed, is the retardation time τ . The respective changes due to the interaction

with the investigated refrigerants are depicted in Fig. 7. Looking again at the EPDM samples and the two refrigerants R1233zd-E and R245fa, an increase of the retardation time can be observe for both fluids and both states (after exposure and after drying period). The increase of the retardation time can be caused either by a higher damping coefficient d_2 or by a lower spring coefficient c_2 of the Voigt-Kelvin model. An interesting finding is that the influence of both refrigerants on the retardation time of the EPDM samples is almost equal. Combining the above discussion with this finding, it can be concluded, that the R245fa mainly causes a decrease of both spring coefficients c_1 and c_2 , while R1233zd-E mainly causes an increase of the damping coefficients d_1 and d_2 . Both explanations of a reduced degree of crystallization caused by the interaction with R245fa and the dissolution of external plasticizers caused by the interaction with R1233zd-E can thus be confirmed.

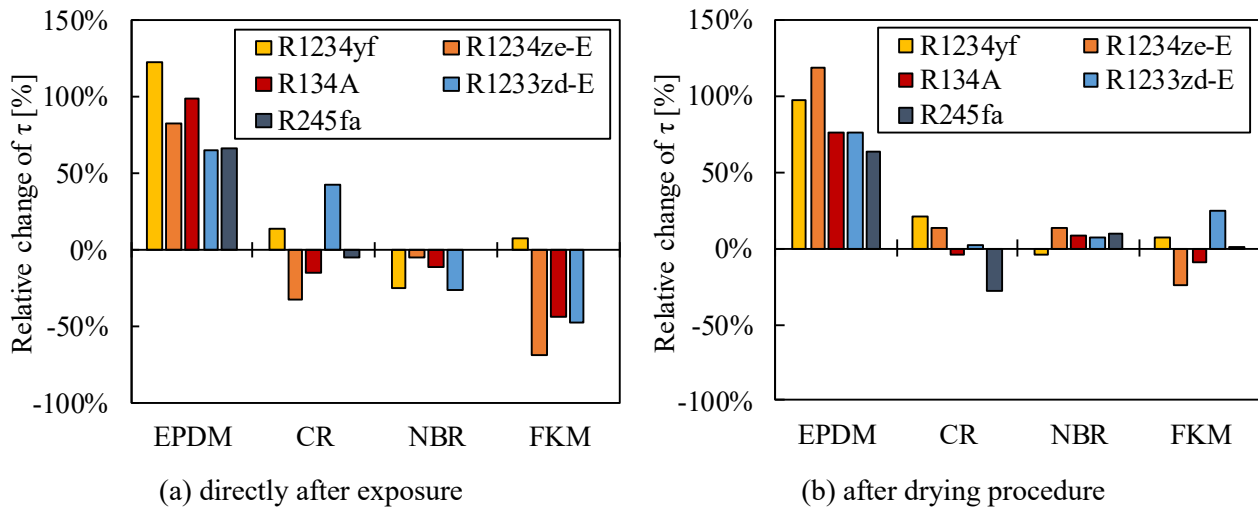


Figure 7: Relative change of the retardation time τ of the elastomers due to the exposure to the refrigerants

Due to a lack of space, only the discussion of the interaction of EPDM material with R1233zd-E and R245fa has been presented. However, the discussion and interpretation of the fluid- polymer interaction for all other refrigerants and polymers can be done analogously.

5. CONCLUSION

In this study, the influence of HFO and HFC refrigerants on the viscoelastic behavior of polymers have been analyzed. Therefore, five different refrigerants, namely R1233zd-E, R245fa, R1234yf, R1234ze-E and R134A have been used to expose four different types of elastomers comprising EPDM, CR, NBR, and FKM. In order to interpret the viscoelastic behavior, three characteristic parameter, namely the elastic and plastic strain as well as the retardation time, have been investigated. From this analysis, it can be concluded that the investigation of the viscoelastic behavior gives meaningful insights to better understand the fluid-polymer interaction and thus helps to evaluate the material compatibility. From the exemplarily presented discussion of EPDM exposed to R1233zd-E and R245fa, it can be concluded that the interaction of EPDM with R245fa cause a decrease of the spring coefficient within the Maxwell model. This might be caused by a reduction of the degree of crystallization and thus a higher entropy-elasticity of the material. In contrast to that, the exposure of EPDM to R1233zd-E cause a higher damping coefficient of the dashpot within the Maxwell model. This effect can be explained by a dissolution of external plasticizers of the material due to the interaction with R1233zd-E.

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