Available online at www.sciencedirect.com

ScienceDirect

Energy Procedia 129 (2017) 137–144

Energy Procedia

www.elsevier.com/locate/procedia

IV International Seminar on ORC Power Systems, ORC2017
13-15 September 2017, Milano, Italy

Material compatibility of ORC working fluids with polymers

Sebastian Eyerer [a,b,*], *Peter Eyerer* [c], *Markus Eicheldinger* [a], *Sebastian Sax* [a], *Christoph Wieland* [a,b], *Hartmut Spliethoff* [a,b,d]

[a] *Technical University of Munich, Institute for Energy Systems*
Boltzmannstr. 15, 85748 Garching, Germany
[b] *Technical University of Munich, Munich School of Engineering, Goethermal Alliance Bavaria*
Boltzmannstr. 17, 85748 Garching, Germany
[c] *Fraunhofer Institute for Chemical Technology*
Joseph-von-Fraunhofer Str. 7, 76327 Pfinztal, Germany
[d] *Bavarian Center for Applied Energy Research*
Walter-Meißner-Str. 6, 85748 Garching, Germany

Abstract

In this study, the material compatibility of refrigerants focusing on hydrofluoroolefines (HFO) with typical polymers in ORC plants and refrigeration units is analyzed with consistent testing conditions and a complete uncertainty analysis of the results. One state-of-the-art refrigerant, namely R245fa, as well as the low-GWP fluids R1233zd-E and R1234yf are taken into account. The investigated polymers are ethylene-propylene-diene rubber (EPDM), fluoric rubber (FKM) and polytetrafluoroethylene (PTFE). In the case of EPDM, two different compositions are analyzed. To complement the study the material compatibility with a polyolester (POE) lubricant is also investigated. The material compatibility is evaluated by changes in volume, weight, Shore A as well as in small load hardness. With the small load hardness measurements, the hardness directly at the samples surface can be determined and thus important information on chemical interaction is provided. This study points out the importance of material compatibility testing especially investigating the difference between hydrofluorocarbons (HFC) and HFO, because the unsaturated characteristic of the HFO may lead to considerable changes in material compatibility compared to HFC refrigerants.

Peer-review under responsibility of the scientific committee of the IV International Seminar on ORC Power Systems.

Keywords: Organic Rankine Cycle, low-GWP working fluids, elastomeres, chemical stability, material compatibility, hydrofluoroolefines

---

* Corresponding author. Tel.: +49 89 289 16264; fax.: +49 89 289 16271; E-mail address: *Sebastian.Eyerer@tum.de*

Peer-review under responsibility of the scientific committee of the IV International Seminar on ORC Power Systems.
10.1016/j.egypro.2017.09.189

1. Introduction

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, which are within the class of hydrofluorocarbons (HFC). Especially, due to legislative acts such as the F-Gas regulation, 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 [1]. However, the material compatibility of the fluid and the system materials must be ensured. Special focus should be put on polymers because they tend to swell when exposed to certain refrigerants. Within ORC plants and refrigeration units, polymers 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 [2].

In recent years, some studies focusing on thermal and chemical stability of refrigerants have been published [3]. However, investigations in the material compatibility of polymers and refrigerants are rare. For example, Han et al. [4] analyzed the refrigerant R161 with thermoplastics such as polytetrafluoroethylene (PTFE), polypropylene (PP), and polyvinyl chloride (PVC) as well as elastomers such as natural rubber, silicone rubber and neoprene. In addition, the refrigerant manufacturers Honeywell [5,6] and Chemours [7] 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. [8] put special focus on the HFO refrigerants R1234yf and R1234ze-E and investigated the compatibility with elastomers such as neoprene, ethylene-propylene-diene rubber (EPDM), fluoric rubber (FKM) and silicone rubber as well as thermoplastics such as polyethylene (PE), polyamide (PA) and PTFE.

The focus of this study is now put on the HFO refrigerants R1233zd-E and R1234yf, which 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. Therefore, the material compatibility of the refrigerants with typical polymers in ORC plants and refrigeration units is analyzed. For good comparability of the results, a set of consistent testing conditions with an exposure temperature of 23 °C has been defined and an uncertainty analysis of the results is provided. In this study, R245fa, which is a state-of-the-art refrigerant, is compared with the low-GWP fluids R1233zd-E and R1234yf. The investigated polymers are the two elastomers ethylene-propylene-diene rubber (EPDM) and fluoric rubber (FKM) as well as polytetrafluoroethylene (PTFE) which is classified as a thermoplastic material. In the case of EPDM, two different compositions with different amounts of carbon black and plasticizers are analyzed. To complement the study, also the material compatibility with a polyolester (POE) refrigeration oil, namely Reniso Triton SE170, is investigated. In plants using a volumetric expander, such POE oils are typically used to ensure sufficient sealing and lubrication of the rotor flanks and the bearings [1]. Thus, the construction materials also need to be compatible with POE.

2. Methodology

In order to meet this purpose, at first the experimental program of the compatibility tests is described, followed by an explanation of the applied method of uncertainty analysis. Afterwards, different assessment criteria to evaluate the compatibility are summarized. Finally, the results are presented and discussed and conclusions are drawn.

2.1. Experimental program

A typical measure to determine the material compatibility is the change in volume and weight after the exposure of a polymer sample in the corresponding refrigerant. These changes in the physical properties indicate possible swelling of a sample and thus chemical interaction between polymer and refrigerant. Furthermore, the change in Shore A hardness indicates a possible incompatibility due to a change in mechanical properties. To determine the Shore A hardness an indenter with a truncated cone is used to define the depth of indentation at a defined load. Typically, the depth of indentation of a Shore A Durometer is in the range of 1 to 2.5 mm and thus gives a mean value of the hardness along the polymer samples thickness. However, a possible chemical interaction between polymer and fluid starts at the surface of the sample and propagates towards the center due to mass transfer mechanisms. Therefore, the change in hardness directly at the samples surface can provide important information on chemical interaction and thus gives a deeper understanding of material compatibility. To analyze this change in surface hardness, the small load hardness according to IRDH (International Rubber Hardness Degree) is measured in this study following ISO 48. Therefore, an indenter with a spherical diameter of 1.55 mm is used together with a minor preload of 1 g and a main load of 14.786 g. The resulting depth of indentation is in the range of 1 to 60 µm depending on the material. Thus, the small load hardness represents the properties directly at the samples surface and provides the possibility to detect local changes in properties [9,10]. The material samples in this study are cylindrical with a height of approx. 5 mm, a diameter in the range of 3 - 5 cm and an initial weight in the range of 8 - 17 g. All samples of one material have the same initial dimensions and weight. To summarize the experimental procedure of this study, the material compatibility is evaluated by changes in volume, weight, Shore A as well as in small load hardness according to IRHD. Therefore, these values are measured before the exposure, directly after the exposure and after a drying period. For each polymer-refrigerant combination, one sample is used. The conditions for the exposure as well as for the drying period are not standardized and are dependent on the future intended operation condition of the materials. Thus, also the test conditions such as exposure period or temperature differs in literature. Table 1 provides an overview of the test conditions found in literature.

Table 1: Overview of test conditions for material compatibility found in literature

Test conditions according to ref.	Majurin et al. [8]	Han et al. [4]	Honeywell [5]	EN ISO 175	present study
Conditioning before exposure	No conditioning	Cleaning with acetone and deionized water; Drying at 125°C	Nothing reported	Storage at 23 °C and 50 % rel. humidity	Storage at 23 °C and 50 % rel. humidity, no further cleaning
Exposure period and temperature	21 – 28 d 85 °C – 127 °C	14 d 60 °C	24 h -	24 h, 7 d or 16 w 23 °C or 70 °C or depending on appl.	28 d 23 °C
Drying period and temperature	24 h 85 °C – 127 °C	no drying	no drying	50 °C or depending on appl.	8 w 23 °C and 50 % rel. humidity

Based on the overview in table 1 the test conditions of this study are defined. Before the exposure, the polymer samples are stored following EN ISO 175 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 the refrigerants for 28 days at 23 °C. The subsequent drying period of the samples is set to 2 months at 23 °C and 50 % rel. humidity, equal to the conditioning before the exposure. 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. Before and after the exposure period, the samples are stored unsealed in a temperature and humidity controlled atmosphere. With the exposure temperature of 23 °C, the results are directly valid for the low-pressure part of an ORC where typical condensation temperatures are between 20 °C and 30 °C. A relevant component in this part of an ORC is for example the feed pump.

2.2. Data evaluation and uncertainty analysis

The quantity of interest is the change in the above-mentioned properties due to the exposure and the subsequent drying. Therefore, the relative change of an arbitrary property x is defined. For a series of measurements, the respective arithmetic average $\bar{x}$ is applied:

$$\frac{\Delta\bar{x}_1}{\bar{x}_0} = \frac{\bar{x}_1 - \bar{x}_0}{\bar{x}_0}; \qquad \frac{\Delta\bar{x}_2}{\bar{x}_0} = \frac{\bar{x}_2 - \bar{x}_0}{\bar{x}_0}. \tag{1}$$

The state before the exposure is indexed with 0 and the state directly after the exposure has the index 1. The evaluation of the state after the drying period has the index 2. In order to be able to interpret the results correctly, an uncertainty analysis of the measuring chain is provided. In table 2 the measuring range and the accuracy of the applied equipment is specified. Since the quantity of interest is derived from these measured values, the Gaussian law of error propagation is applied, to quantify the uncertainty of this derived quantity. Generally speaking, when the quantity of interest y can be obtained by independent measured quantities x_j with a physical correlation in the form of $y = f(x_1, x_2, \dots, x_k)$, the standard deviation of the derived quantity σ_y is described by:

$$\sigma_y = \sqrt{\sum_{j=1}^{k} \left(\frac{\partial f}{\partial x_j}\sigma_{x_j}\right)^2}. \tag{2}$$

Describing this quantity of interest by its arithmetic average $\bar{y}$ and its empirical standard deviation σ_y means that the next measured value lies within the range of $\bar{y} \pm \sigma_y$ with a probability of 68.3 %. Other typical confidence intervals are 95.5 % and 99.7 % with a range of $\pm 2\sigma_y$ and $\pm 3\sigma_y$, respectively. However, the desired value is a range, in which the true value can be found. This is described by the standard deviation of the mean value $\sigma_{\bar{y}} = \frac{\sigma_y}{\sqrt{n}}t$. Here, the factor t considers the uncertainty of the empirical standard deviation of the measurement series. This quantity is student-t-distributed and varies depending on the number of measurements n within a sample and the considered confidence level. In this study, a confidence level of 68.3 % is used and at least three measurements are made. For further information on the applied methodology, reference is made to another publication of the authors [11].

Table 2: Measuring range and accuracy of applied equipment

Measuring instrument	Measured quantity	Measuring range	Accuracy of measurement
High accuracy caliper	length	0 to 15 cm	0.01 mm
Analytical balance	weight	0 to 220 g	0.1 mg
Shore A Durometer	Shore A hardness	0 to 100 °	1 °
Micro IRHD instrument	Depth of indentation or IRHD	0 to 0.5 mm	0.1 µm

Applying the Gaussian law of error propagation (cf. equation (2)) to the problem at hand, equation (3) can be derived. For the change in weight, in Shore A as well as in small load hardness this equation can directly be applied to calculate the empirical standard deviation of the change in the respective property. However, the volume change requires a further step, because only the diameter and the height is measured to calculate the volume. In order to ensure sufficient accuracy of the measurements, the diameter is determined at five different positions.

$$\sigma_{\frac{\Delta\bar{x}_1}{\bar{x}_0}} = \sqrt{\left(\frac{1}{\bar{x}_0}\sigma_{\bar{x}_1}\right)^2 + \left(-\frac{\bar{x}_1}{\bar{x}_0^{\,2}}\sigma_{\bar{x}_0}\right)^2} \tag{3}$$

2.3. Assessment criteria

Table 3: Overview of assessment criteria of material compatibility found in literature

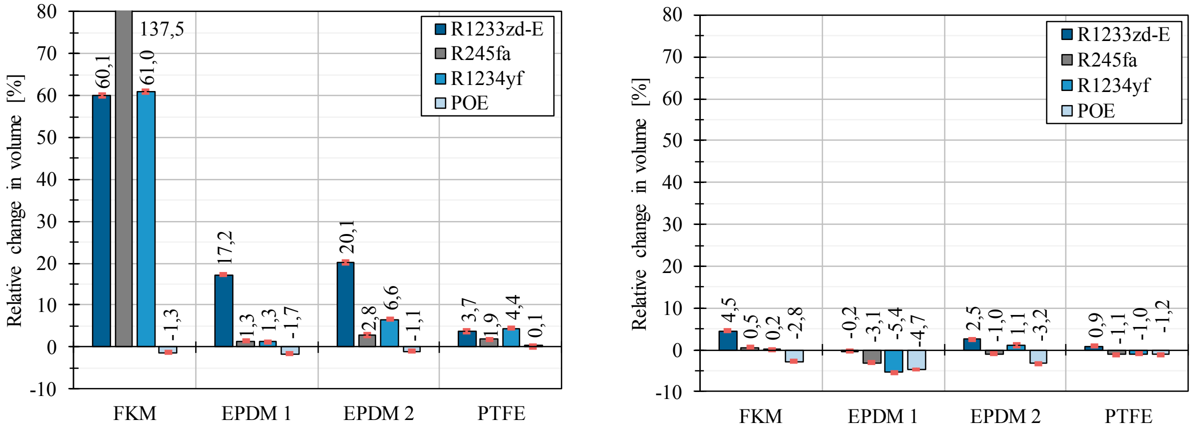
Assessment criteria	Majurin et al. [8]		Han et al. [4]	Honeywell [5]	ISO 175 [12]
Type of polymer group	Elastomers	Thermoplastics	Elastomers	Elastomers	Polymers
Weight $\frac{\Delta m_1}{m_0}$ and volume $\frac{\Delta V_1}{V_0}$ changes	(1): > 0 % and < +20 % (2): > +20 % and < +30 % (3): > +30 % or < 0 %	(1): > -2 % and < +10 % (2): > +10 % and < +20 % (3): > +20 % or < -2 %	(1): < ±10 % (2): < ±20 % (3): > ±20 %	(1): > 0 % and < +10 % (2): > +10 % (only one quantity) (3): > +10 % (for all quantities)	no definite values (depending on application)
Hardness changes $\frac{\Delta H_1}{H_0}$ (Shore A)	(1): < ±10 % (2): < ±15 % (3): > ±15 %	-	-	(1): < ±10 % (2): > +10 % (only one quantity) (3): > +10 % (for all quantities)	no definite values (depending on application)
Legend:	(1) = good compatibility; (2) = limited compatibility; (3) = poor compatibility				

In the end, the aim is to evaluate the material compatibility and identify suitable refrigerant and polymer combination. Therefore, it is necessary to define criteria for this assessment. However, similar to the wide range of test conditions in literature (cf. table 1) the assessment criteria also vary with the different studies. Table 3 provides an overview of the assessment criteria found in literature. These criteria refer to the state directly after the exposure.

In this study, no assessment criteria are defined because of the strong dependence on the future intended application of the materials. When the elastomers for example are used as a seal, a decrease in volume is unacceptable. Using the elastomer as a diaphragm in positive displacement pump, however, a decrease in volume might be permissible. Therefore, this study focusses on a clear presentation of the measurements such that the reader can directly link these findings to the relevant application.

3. Results and discussion

In the following section the change in volume (cf. fig. 1), weight (cf. fig. 2), Shore A hardness (cf. fig. 3) and small load hardness according to IRHD (cf. fig. 4) are discussed. Therefore, each quantity (except the small load hardness) is depicted at the state directly after the exposure and after the drying period.



(a) (b)

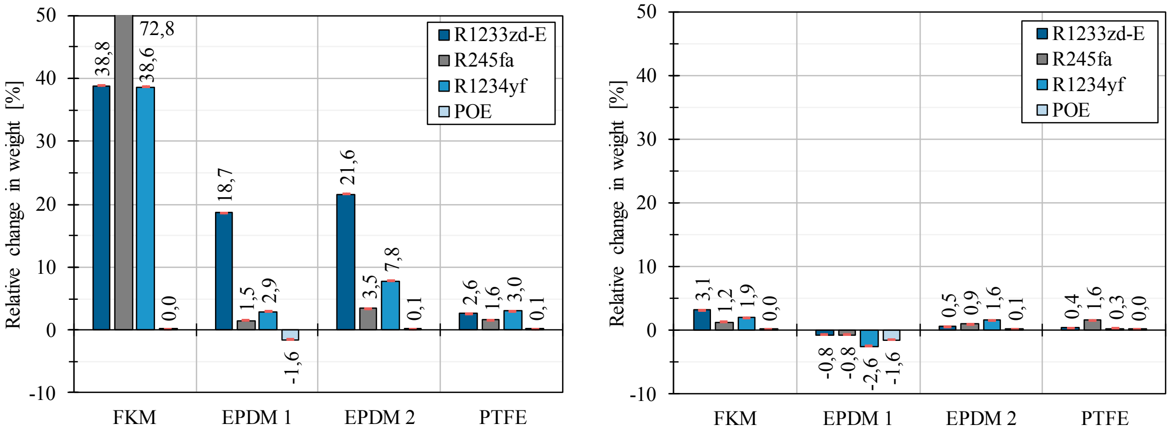
Fig. 1. Relative change in volume directly after exposure (a) and after subsequent drying (b)

Of particular note is the significant swelling (cf. fig. 1 (a)) of FKM after being exposed to the refrigerants. This can also be confirmed by the change in weight, depicted in fig. 2 (a). FKM absorbs a significant amount of the refrigerants, also leading to a softening effect, which is much stronger compared to the other tested polymers (cf. fig. 3 (a)). The significant swelling of FKM may be explained by the chemical similarities between the structure of the refrigerants molecule and the monomers of FKM, which both consists mainly of carbon-fluorine and carbon-hydrogen bonds.

However, the retained weight gain of FKM after the drying period (cf. fig. 2 (b)), leads to the assumption, that the fluoroelastomer does not get dissolved in the refrigerants, which would lead to a weight reduction. Another interesting finding is that the swelling of FKM exposed to R245fa is more pronounced compared to R1233zd-E and R1234yf, suggesting that the double bond in the unsaturated HFOs may reduce the degree of interaction between the elastomer and the fluids.

In contrast to the investigated refrigerants, the POE lubricant causes only small changes in the investigated properties of all polymers. The reason for this might be the polarity of the POE molecules, which is much higher than the polarity of the refrigerants. In combination with the low polarity of the polymers, the interaction with the POE molecules is much less. Concerning the change in volume, the lubricant causes slight shrinking, which might be problematic for the application as sealing. However, the polymer samples are exposed to 100 % POE, which does not represent a real application where the POE is mixed with the refrigerant. Because all refrigerants lead to swelling, this negative effect of shrinking due to the exposure to POE might be overcompensated.

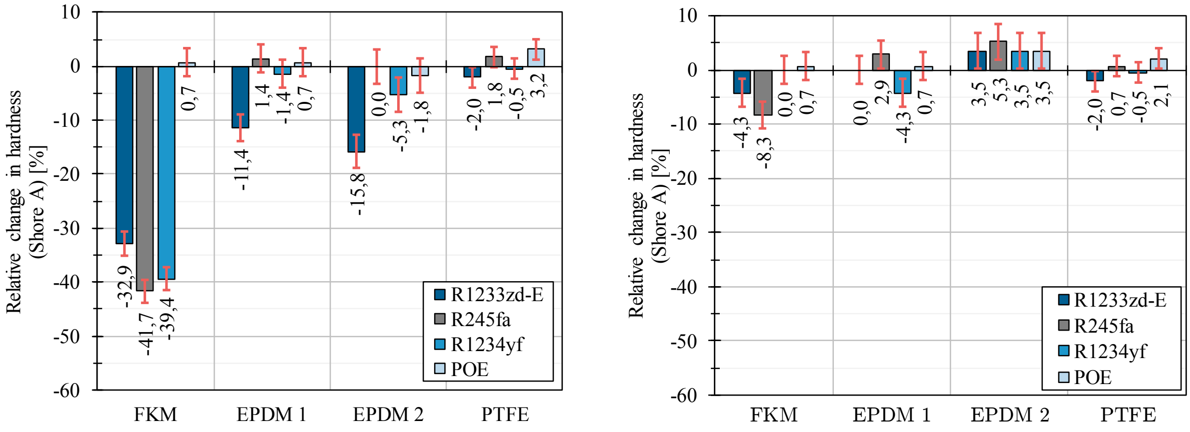
For the EPDM polymer, two different compositions are investigated, where EPDM 1 has compared to EPDM 2 a higher amount of carbon black and a lower amount of plasticizers, leading to a higher abrasion resistance and hardness. Compared to FKM, the swelling of both EPDM compositions is much less for all refrigerants. Especially, when exposed to R245fa the changes of the investigated properties are less than 3 % for both EPDM compositions. Comparing the two EPDM composition, it is striking that the change in volume and weight of EPDM 2 is larger than for EPDM 1. The plasticizers in the composition cause a larger spacing between the EPDM molecules and thus a lower bonding strength between the molecules. Hence, the higher amount of plasticizers in the EPDM 2 composition enables the refrigerants to be better absorbed. The lower amount of carbon black within EPDM 2 enhances this effect, because carbon black generally enforces the bonding strength between the molecules.



(a) (b)

Fig. 2 Relative change in weight directly after exposure (a) and after subsequent drying (b)

Furthermore, it is noticeably that for both EPDM compositions, the swelling after exposure to R1233zd-E is significantly larger than for the other refrigerants. This can also be confirmed by the changes in weight and Shore A hardness. Within the investigated fluids, R1233zd-E is the only refrigerant containing chlorine in its chemical structure, which may be the explanation for this fact. This finding is interesting especially because R1233zd-E is a promising low-GWP replacement for R245fa, at least from a thermodynamic point of view. In this context, a similar material compatibility of R245fa and R1233zd-E is desirable. However, the measurements show a large difference in swelling as well as in weight and in hardness change between both fluids.



(a) (b)

Fig. 3. Relative change in Shore A hardness directly after exposure (a) and after subsequent drying (b)

Besides R1233zd-E also R1234yf causes high swelling of EPDM, especially of the EPDM 2 sample. Compared to the saturated R245fa, the exposure of EPDM 2 leads to larger weight gain and softening for both unsaturated refrigerants. This contrasts with the case of FKM, where the exposure to the HFO leads to a smaller change in the respective properties.

For further anlaysis the hardness change directly at the samples surface (cf. fig. 4) is investigated. Comparing the change in Shore A hardness after drying (cf. fig. 3 (b)) with the change in indentation depth according to IRHD, it becomes apparent that the softening effect observed for the FKM and EPDM samples is much higher at the surface than for the mean value along the samples thickness. While the Shore A hardness of FKM after exposure to R1233zd-E and subsequent drying is decreased by 4.3 %, the change in indentation depth according to IRDH is 27.2 %. This supports the assumption, that the major chemical interaction takes place at the surface.

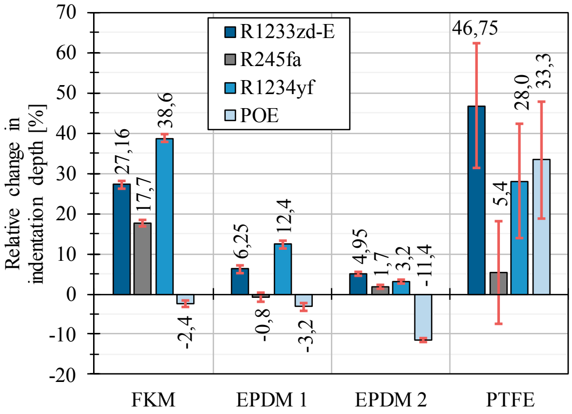


Fig. 4. Relative change in indentation depth according to IRDH after drying

Looking at the compatibility of PTFE, the change in volume, weight and Shore A hardness after exposure to the refrigerants is low compared to the other polymers. However, the degree of interaction with the fluids at the surface is quite high, which can be obtained from the large change in indentation depth especially for the HFO and the POE (cf. fig. 4). Here it has to be noted, that the change in indentation depth is refered to the state after the drying procedure. Unfortunately, no measurements have been made directly after the exposure because of unavailability of the measuring instrument. The reason for the high degree of interaction at the surface of the PTFE samples might be explained with the production process of PTFE. During this process the thermoplastics mostly get an amorphous outer layer due to the rapid cooling of the surface material at the “cold” tool surface. PTFE is processed mostly by sintering within hot tools. But after demolding the surfaces cool down more rapidly and the post cristallysation is lower than in the bulk material. This amormous surface enables the fluids to better interact with the polymer. Therefore, the change in small load hardness of the PTFE samples is much higher than the change in Shore A hardness, which mainly accounts for the hardness of the bulk material. To overcome this effect, the temperature gradient within the material should be controlled during cooling.

4. Conclusion

In this study, the material compatibility of the polymers EPDM, FKM and PTFE with the refrigerants R245fa, R1233zd-E and R1234yf as well as with a POE lubricant has been evaluated. Therefore, the changes in volume, weight, Shore A as well as in small load hardness according to IRHD are determined directly after the exposure to the fluids and after a subsequent drying period. The exposure time has been set to 28 days at 23 °C and the drying period was two months at 23 °C. Based on the experimental analysis the following conclusions can be drawn:

- Large change in volume, weight, Shore A and small load hardness for FKM exposed to fluorinated refrigerants, which is even worse for the saturated R245fa compared to the unsaturated HFO.
- POE causes only small changes in the investigated properties of all polymers. Concerning the change in volume, this lubricant causes slight shrinking. However, due to small concentrations of POE in real application, the observed effect is likely to be negligible.
- R245fa causes less than 3 % changes of the investigated properties for both EPDM compositions.
- The composition of EPDM in terms of carbon black and plasticizer influences the compatibility with the investigated refrigerants.
- In contrast to R245fa, its low-GWP alternative R1233zd-E leads to considerable changes of the EPDM samples in all investigated properties.
- All investigated fluids cause only slight changes in volume, weight and Shore A of the PTFE samples. The change in small load hardness, however, suggests a high degree of interaction at the surface when exposed to the investigated HFO and POE.

Furthermore, this study pointed out the importance of material compatibility testing especially investigating the behavior of new generation refrigerants, which are used as alternatives for state-of-the-art fluids. The unsaturated characteristic of these HFO may lead to considerable changes in material compatibility compared to the hydrofluorocarbons (HFC). The limited number of investigated refrigerants and polymer samples, however, makes it difficult to draw generally applicable conclusions. Thus, further material samples and refrigerants are planned to be investigated under consistent testing conditions. In addition, the temperature dependency of the material compatibility has not been studied in this work, but it can provide further relevant information. At higher temperatures, mass transport phenomena, such as diffusion, are typically enhanced, leading to the assumption of a larger change in the investigated properties. This has to be investigated in future work.

Acknowledgements

Funding from the Bavarian State Ministry of Education, Science and the Arts in the frame of the project Geothermie-Allianz Bayern is gratefully acknowledged.

References

[1] Eyerer S, Wieland C, Vandersickel A, Spliethoff H. Experimental Study of an ORC (Organic Rankine Cycle) and Analysis of R1233zd-E as a Drop-In Replacement for R245fa for Low Temperature Heat Utilization. *Energy* 2016;103:660–71.

[2] Quoilin S, van Den Broek M, Declaye S, Dewallef P, Lemort V. Techno-Economic Survey of Organic Rankine Cycle (ORC) Systems. *Renewable and Sustainable Energy Reviews* 2013;22:168–86.

[3] Macchi E, Astolfi M (eds). *Organic Rankine Cycle (ORC) Power Systems - Technologies and Applications.* 1st ed.: Woodhead Publishing; 2016.

[4] Han X, Yuan X, Xu Z, Wang X, Chen G, Xu X. Research on Compatibility Between Ethyl Fluoride with/Without Lubricant Oils, and Plastics and Elastomers. *Industrial & Engineering Chemistry Research* 2014;53:14650–8.

[5] Honeywell. *Solstice yf Properties and Materials Compatibility*; 2015.

[6] Honeywell. *Honeywell Enovate 245fa: Technical Information*; 2017.

[7] Leck TJ. Evaluation of HFO-1234yf as a Potential Replacement for R-134a in Refrigeration Applications. In: *3rd IIR Conference on Thermophysical Properties and Transfer Processes of Refrigerants, USA, Boulder*; 2009.

[8] Majurin J, Staats SJ, Sorenson E, Gilles W. Material Compatibility of HVAC&R System Materials with Low Global Warming Potential Refrigerants. *Science and Technology for the Built Environment* 2015;21:491–501.

[9] Eyerer P, Schäfer R. *Mikrohärteprüfung an elastomeren Formteilen: Mitteilung aus dem Zentrallabor der Elring Dichtungswerke*; 1973.

[10] Eyerer P. Kleinlast- und Mikrohärteprüfung (Eindringverfahren) an nichtmetallischen Werkstoffen: Low Load Indentation Testing of Nonmetally Materials. *VDI Berichte* 1978;No. 308.

[11] Eyerer S, Liu W, Irl M, Ausfelder S, Dichtl E-M, Wieland C, Spliethoff H. Experimental Study of an ORC with Uncertainty Analysis and Inter-Model Comparison for Thermodynamic Properties of R1233zd-E. In: *Heat Powered Cycles Conference, UK, Nottingham, 26-29 June*; 2016.

[12] ISO 175:2011-03. Plastics – Methods of Test for the Determination of the Effects of Immersion in Liquid Chemicals.