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Material compatibility of ORC working fluids with polymers

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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.

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

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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,