Material compatibility of ORC working fluids with polymers

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Agenda

1) Motivation

2) Investigated fluids and polymers

3) Relevant theoretical mechanisms for fluid-polymer interaction

4) Experimental procedure

5) Results

6) Conclusion and Outlook
Motivation

Modern working fluids with low GWP and no ODP are available

Application of these Fluids is politically enforced (i.e. F-Gas Regulation, MAC Directive)

Modern fluids have similar thermophysical properties compared to State-of-the-Art fluid
→ From a thermodynamic perspective:
   Possible application of these fluids

But: Thermal stability and material compatibility is often not fully investigated

F-Gas Regulation: Reduction of CO$_2$-equivalents of refrigerants

Source: UBA, 2017
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Investigated fluids and polymers

<table>
<thead>
<tr>
<th>Refrigerants and Oil</th>
<th>HFC</th>
<th>HFO</th>
<th>Lubricant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical identifier</td>
<td>1,1,3,3,3- Pentafluoropropan</td>
<td>Trans-1-Chlor-3,3,3-Tetrafluoropropene</td>
<td>POE</td>
</tr>
<tr>
<td>Half structural formula</td>
<td>CF₃CH₂CHF₂</td>
<td>CHCl=CHCF₃</td>
<td>CH₂=CFCF₃</td>
</tr>
<tr>
<td>Vapor pressure ρ at 25°C / 75°C</td>
<td>1.5 / 7.0 bar</td>
<td>1.3 / 5.8 bar</td>
<td>6.8 / 22.7 bar</td>
</tr>
<tr>
<td>Boiling point at 1 bar</td>
<td>14.8°C</td>
<td>17.9°C</td>
<td>-29.8°C</td>
</tr>
<tr>
<td>Saturated liquid density ρ at 25°C / 75°C</td>
<td>1338.5 / 1187.6 kg m⁻³</td>
<td>1262.8 / 1129.9 kg m⁻³</td>
<td>848.8 kg m⁻³</td>
</tr>
<tr>
<td>Molecular mass Mᵥ</td>
<td>134.0 g mol⁻¹</td>
<td>130.5 g mol⁻¹</td>
<td>114.0 g mol⁻¹</td>
</tr>
<tr>
<td>Electric dipole moment μ</td>
<td>4.9 ⋅ 10⁻³⁰ C m</td>
<td>3.8 ⋅ 10⁻³⁰ C m</td>
<td>8.3 ⋅ 10⁻³⁰ C m</td>
</tr>
<tr>
<td>Dielectric constant εᵣ at 20°C</td>
<td>6.7</td>
<td>n.a.</td>
<td>8</td>
</tr>
<tr>
<td>Global Warming Potential (GWP₁₀₀)</td>
<td>1030</td>
<td>1</td>
<td>4</td>
</tr>
</tbody>
</table>

For comparison:
acetone: very polar solvent μ = 9.6 ⋅ 10⁻³⁰ C m
n-hexane: non-polar solvent μ = 0 ⋅ 10⁻³⁰ C m

Thesis:
Double bound within the molecule changes the chemical behavior of the fluid and may cause different compatibility properties.
Investigated fluids and polymers

Polymers, especially elastomers tend to swell and change their mechanical properties when exposed to refrigerants.

Application of polymers within the ORC
- static and dynamic seals (i.e. O-rings, radial shaft seals, valve seals)
- other parts in components (i.e. diaphragm in diaphragm pumps, stator in eccentric screw pumps)

Practical question:
Which polymers are resistant against the modern refrigerants?

Investigation of four different Polymers:
- Two compositions of ethylene-propylene-diene rubber (EPDM):
  - EPDM 1 with more black carbon and less plasticizer than EPDM 2
- fluoric rubber (FKM)
- Polytetrafluoroethylene (PTFE)

Amorphous, cross-linked
- elastomers

Amorphous, not cross-linked
- thermoplastic

Crystalline, not cross-linked
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Relevant theoretical mechanisms for the fluid-polymer interaction

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<tr>
<th>Physical interaction:</th>
<th>during exposition</th>
<th>after desorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusion of refrigerants molecules within the polymer matrix</td>
<td>m, V ↑ H ↓ ε ↑</td>
<td>m, V, H, ε →</td>
</tr>
<tr>
<td>Plasticizer and other low-molecular additives evaporate at high temperatures</td>
<td>m, V ↓ H ↑ ε ↓</td>
<td>m, V ↓ H ↑ ε ↓</td>
</tr>
</tbody>
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<tr>
<td>Plasticizer and other low-molecular additives dissolves in the refrigerant</td>
<td>m, V ↓ H ↑ ε ↓</td>
<td>m, V ↓ H ↑ ε ↓</td>
</tr>
<tr>
<td>Increase of the degree of cross-linking (for elastomers)</td>
<td>m, V→ H ↑ ε ↓</td>
<td>m, V→ H ↑ ε ↓</td>
</tr>
<tr>
<td>Degradation of cross-linking points (for elastomers)</td>
<td>m, V→ H ↓ ε ↑</td>
<td>m, V→ H ↓ ε ↑</td>
</tr>
<tr>
<td>Decrease of the degree of crystallization (for thermoplastics)</td>
<td>m, V→ H ↓ ε ↑</td>
<td>m, V→ H ↓ ε ↑</td>
</tr>
<tr>
<td>Decrease of the degree of polymerization (for thermoplastics)</td>
<td>m, V→ H ↓ ε ↑</td>
<td>m, V→ H ↓ ε ↑</td>
</tr>
</tbody>
</table>
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Experimental procedure

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</tr>
</thead>
<tbody>
<tr>
<td>Conditioning before exposure</td>
<td>No conditioning</td>
<td>Cleaning with acetone and deionized water; Drying at 125°C</td>
<td>Nothing reported</td>
<td>Storage at 23 °C and 50 % rel. humidity</td>
<td>Storage at 23 °C and 50 % rel. humidity, no further cleaning</td>
</tr>
<tr>
<td>Exposure period and temperature</td>
<td>21 – 28 d 85 °C – 127 °C</td>
<td>14 d 60 °C</td>
<td>24 h -</td>
<td>24 h, 7 d or 16 w 23 °C or 70 °C or depending on appl.</td>
<td>28 d 23 °C</td>
</tr>
<tr>
<td>Drying period and temperature</td>
<td>24 h 85 °C – 127 °C</td>
<td>no drying</td>
<td>no drying</td>
<td>50 °C or depending on appl.</td>
<td>8 w 23 °C and 50 % rel. humidity</td>
</tr>
</tbody>
</table>

Exposition of the polymer samples in liquid fluid (saturated state)

Drying / Desorption: conditioned air

Evaluation of change in volume, weight, Shore hardness and small-load hardness directly after exposition and after subsequent drying period
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Significant swelling of FKM for all refrigerants (similar chemical structure)

R245fa causes largest swelling (only saturated refrigerants)

Decrease of Shore hardness is in good agreement with theory

No change in properties with POE

Almost no remaining change in volume and weight after drying

→ Mainly physical polymer-fluid interaction with absorption and desorption of the refrigerant

Remaining increase in hardness at the surface for all refrigerants → Damages due to desorption

FKM not compatible with all investigated fluids due to large swelling
Results

Ethylene-propylene-diene rubber (EPDM)

EPDM 1 has more black carbon and less plasticizer than EPDM 2.

Significant swelling of both EPDM samples exposed to R1233zd-E.

Volume, weight and hardness change are in good agreement with each other.

Remaining weight and volume loss after drying for EPDM 1 with all fluids → Dissolution of plasticizer or other low-molecular additives.

EPDM 1 not compatible with all fluids due to dissolution of plasticizer.

Special attention should be paid for the application of R1233zd-E.
Results
Polytetrafluoroethylene (PTFE)

Only slight swelling of PTFE directly after exposure to all investigated fluids

Almost no remaining change in volume, weight and Shore hardness after drying

Significant softening at the samples surface after being exposed to HFO and POE

→ PTFE typically have an amorphous structure at the outer layer due to the production process and a crystalline structure in the bulk

→ higher interaction with amorphous structure than with crystalline structure

PTFE is compatible with all refrigerants and POE. However, special attention should be payed to surface effects.
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Conclusion

- Four investigated fluids: R245fa, R1233zd-E, R1234yf and POE
- Four investigated Elastomers: FKM, two types of EPDM, PTFE
- FKM not compatible with all investigated fluids due to large swelling
- Special attention should be paid for the application of R1233zd-E, especially in comparison to R245fa
- Polymer composition plays an important role for material compatibility
- PTFE is compatible with all refrigerants and POE. However, special attention should be payed to surface effects

Outlook

Investigation of other refrigerants (R134A, R1234ze-E, R450A, R513A) and polymers (chlorobutadiene rubber, nitrile butadiene rubber, polypropylene)

Analysis of possible temperature dependency and experiments with supercritical fluid states.

Analysis of the polymers samples with pyrolysis and thermogravimetric analysis to account for the influence of the composition
Thank you for your attention!

Questions and discussion!
References

## Polymers

<table>
<thead>
<tr>
<th>Polymers</th>
<th>EPDM</th>
<th>FKM</th>
<th>PTFE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical identifier</td>
<td>Ethylene-Propylene-Diene Rubber</td>
<td>Fluororubber</td>
<td>Polytetra-fluoroethylene</td>
</tr>
<tr>
<td>Selected trade name</td>
<td>Keltan, Buna EP, Vistalon</td>
<td>Viton, Fluorel, Dyneon</td>
<td>Teflon, Xylan, Polyflon</td>
</tr>
<tr>
<td>Application temperature</td>
<td>-40 to 140 °C</td>
<td>-20 to 210 °C</td>
<td>-200 to 250 °C</td>
</tr>
<tr>
<td>Density $\rho$</td>
<td>1.1 - 1.2 kg/m$^3$</td>
<td>2.0 - 2.3 kg/m$^3$</td>
<td>2.1 - 2.2 kg/m$^3$</td>
</tr>
<tr>
<td>Tensile strength $R_m$</td>
<td>13 - 15 N/mm$^2$</td>
<td>12 - 16 N/mm$^2$</td>
<td>25 N/mm$^2$</td>
</tr>
<tr>
<td>Dielectric constant $\varepsilon_r$</td>
<td>0.1</td>
<td>4.5</td>
<td>&lt; 2.1</td>
</tr>
<tr>
<td>at 50 Hz and 25 °C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>microstructural condition</td>
<td>amorphous to semi-crystallin, slightly cross-linked</td>
<td>amorphous, slightly cross-linked</td>
<td>crystallin not cross-linked</td>
</tr>
<tr>
<td>average molecular weight $M_W$</td>
<td>0.2 - 2 · 10$^5$ g/mol</td>
<td>2 - 7 · 10$^4$ g/mol</td>
<td>0.4 - 9 · 10$^6$ g/mol</td>
</tr>
</tbody>
</table>
Figure 1 – Structural formulas of the investigated pure fluids

Figure 2 – Structural formulas of the investigated polymers