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

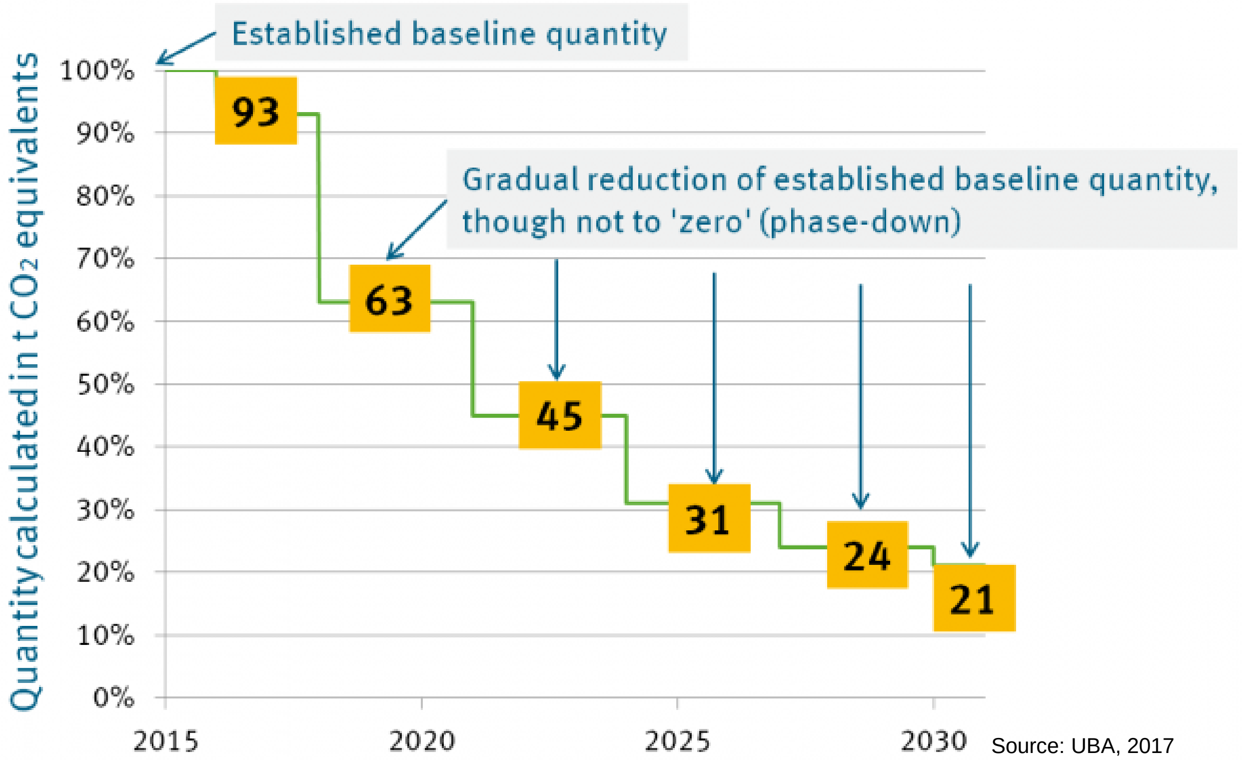
Motivation

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



Source: UBA, 2017

F-Gas Regulation: Reduction of CO_2-equivalents of refrigerants

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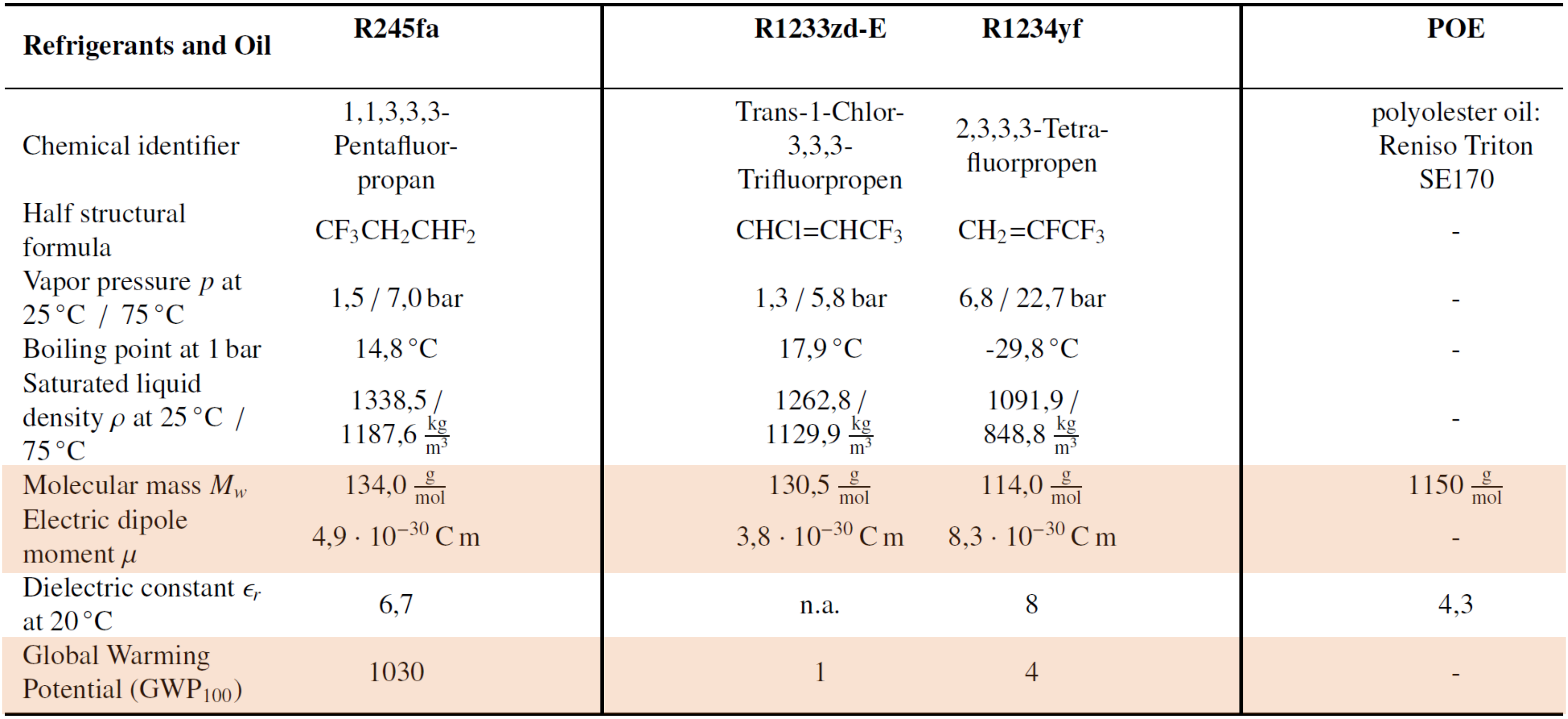
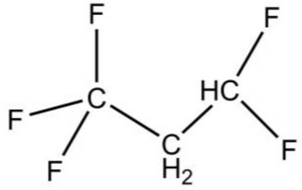
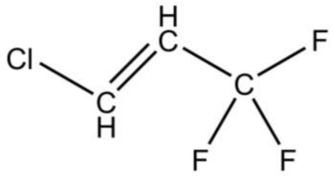
Investigated fluids and polymers



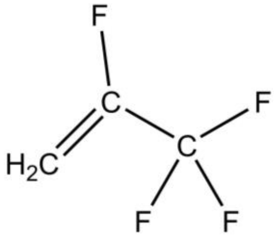
	HFC	HFO		Lubricant
Refrigerants and Oil	**R245fa**	**R1233zd-E**	**R1234yf**	**POE**
Chemical identifier	1,1,3,3,3-Pentafluorpropan	Trans-1-Chlor-3,3,3-Trifluorpropen	2,3,3,3-Tetrafluorpropen	polyolester oil: Reniso Triton SE170
Half structural formula	$CF_3CH_2CHF_2$	$CHCl{=}CHCF_3$	$CH_2{=}CFCF_3$	-
Vapor pressure p at 25 °C / 75 °C	1,5 / 7,0 bar	1,3 / 5,8 bar	6,8 / 22,7 bar	-
Boiling point at 1 bar	14,8 °C	17,9 °C	-29,8 °C	-
Saturated liquid density ρ at 25 °C / 75 °C	1338,5 / 1187,6 $\frac{kg}{m^3}$	1262,8 / 1129,9 $\frac{kg}{m^3}$	1091,9 / 848,8 $\frac{kg}{m^3}$	-
Molecular mass M_w	134,0 $\frac{g}{mol}$	130,5 $\frac{g}{mol}$	114,0 $\frac{g}{mol}$	1150 $\frac{g}{mol}$
Electric dipole moment μ	$4{,}9 \cdot 10^{-30}$ C m	$3{,}8 \cdot 10^{-30}$ C m	$8{,}3 \cdot 10^{-30}$ C m	-
Dielectric constant ϵ_r at 20 °C	6,7	n.a.	8	4,3
Global Warming Potential (GWP_{100})	1030	1	4	-



R245fa



R1233zd-E



R1234yf

For comparison:

acetone: very polar solvent μ = $9{,}6 \cdot 10^{-30}$ C m

n-hexane: non-polar solvent μ = $0 \cdot 10^{-30}$ 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

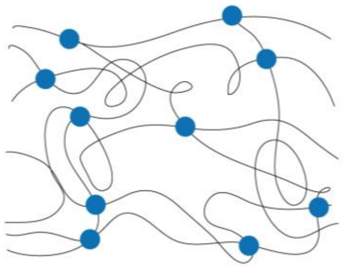
Application of polymers within the ORC
static and dynamic seals (i.e. O-rings, radial shaft seals , valve seals)
other parts in components (i.e. diaphragm in diaphragm pumps, stator in eccentric screw pumps)

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)**

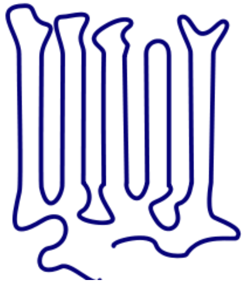
} elastomers



amorphous,
cross-linked

- **Polytetrafluoroethylene (PTFE)** } thermoplastic

amorphous,
not cross-linked



crystalline,
not cross-linked

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Relevant theoretical mechanisms for the fluid-polymer interaction

Physical interaction:	**during exposition**	**after desorption**
Diffusion of refrigerants molecules within the polymer matrix	m, V ↑ H ↓ ε ↑	m, V, H, ε →
Plasticizer and other low-molecular additives evaporate at high temperatures	m, V ↓ H ↑ ε ↓	m, V ↓ H ↑ ε ↓
Chemical interaction:		
Plasticizer and other low-molecular additives dissolves in the refrigerant	m, V↓ H ↑ ε ↓	m, V ↓ H ↑ ε ↓
Increase of the degree of cross-linking (for elastomers)	m, V→ H ↑ ε ↓	m, V→ H ↑ ε ↓
Degradation of cross-linking points (for elastomers)	m, V→ H ↓ ε ↑	m, V→ H ↓ ε ↑
Decrease of the degree of crystallization (for thermoplastics)	m, V→ H ↓ ε ↑	m, V→ H ↓ ε ↑
Decrease of the degree of polymerization (for thermoplastics)		

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Experimental procedure

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

pressure vessel

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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Results

Fluoric rubber (FKM)

Significant swelling of FKM for all refrigerants (similar chemical structure)

R245fa causes largest swelling (only saturated refrigerants)

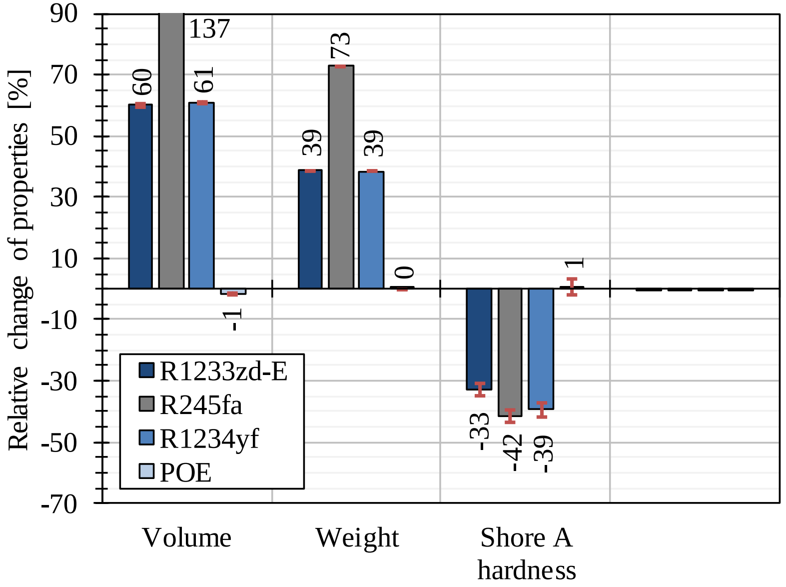
Decrease of Shore hardness is in good agreement with theory

No change in properties with POE

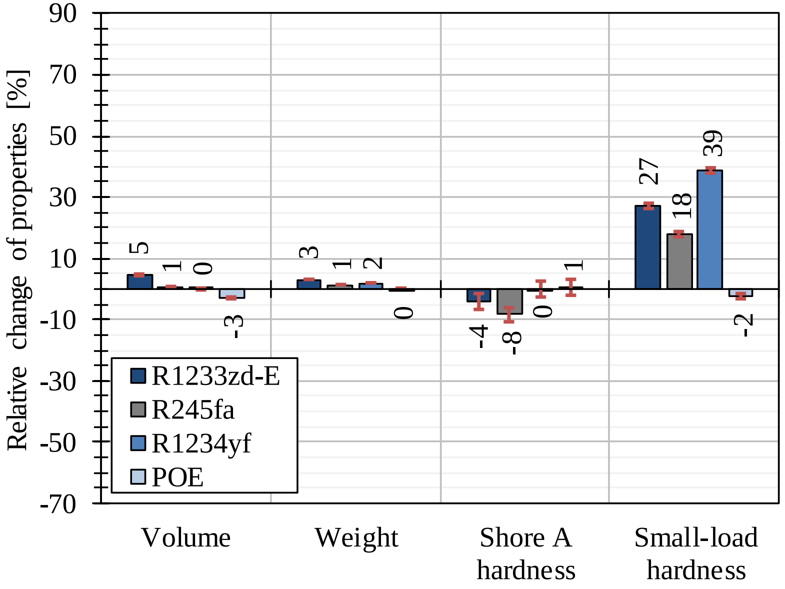
Almost no remaining change in volume and weight after drying
→ Mainly physical polymer-fluid interaction with absorption and desorption of the refrigerant

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

directly after exposure



after drying period



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

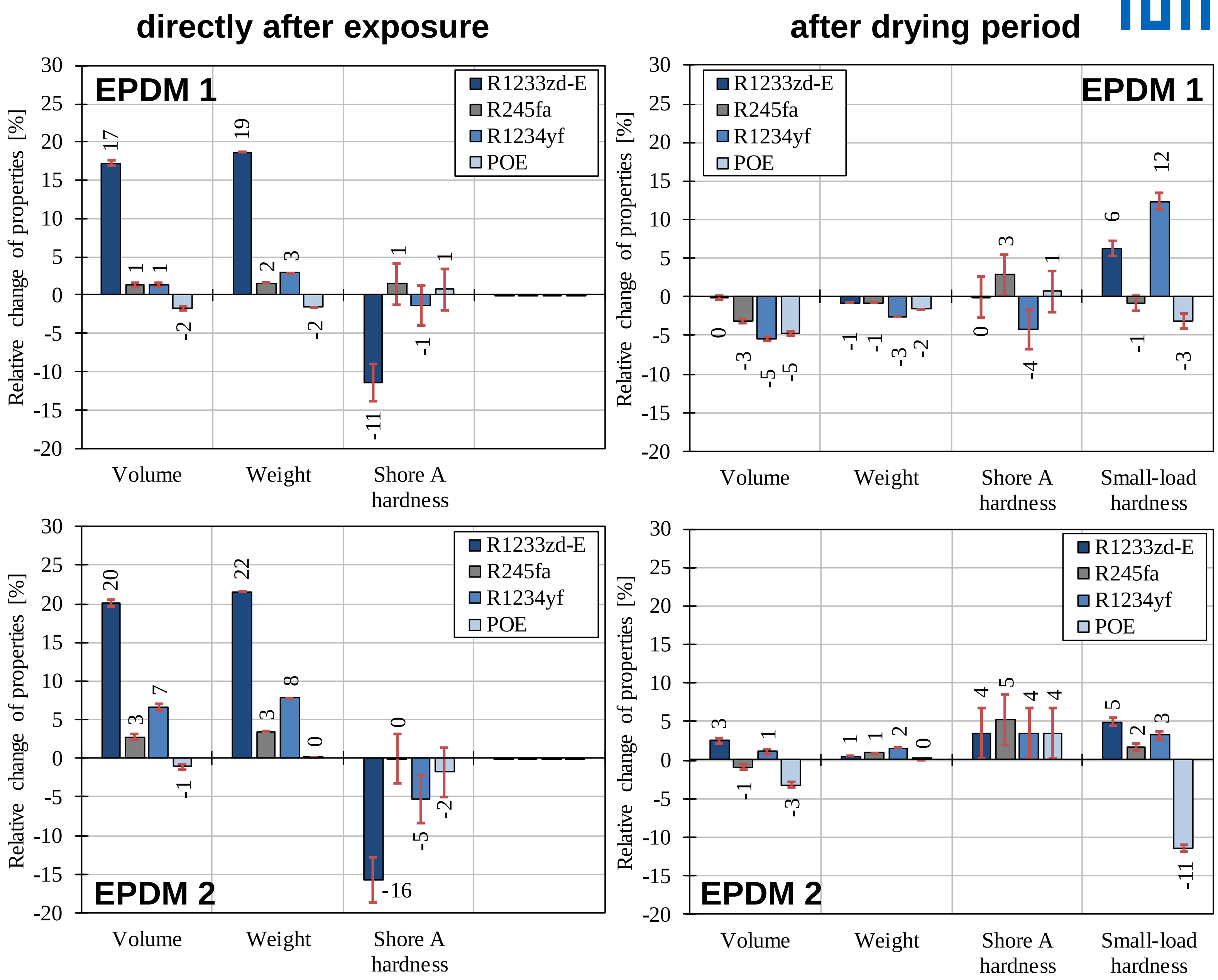
Significant swelling of both EPDM samples exposed to R1233zd-E

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



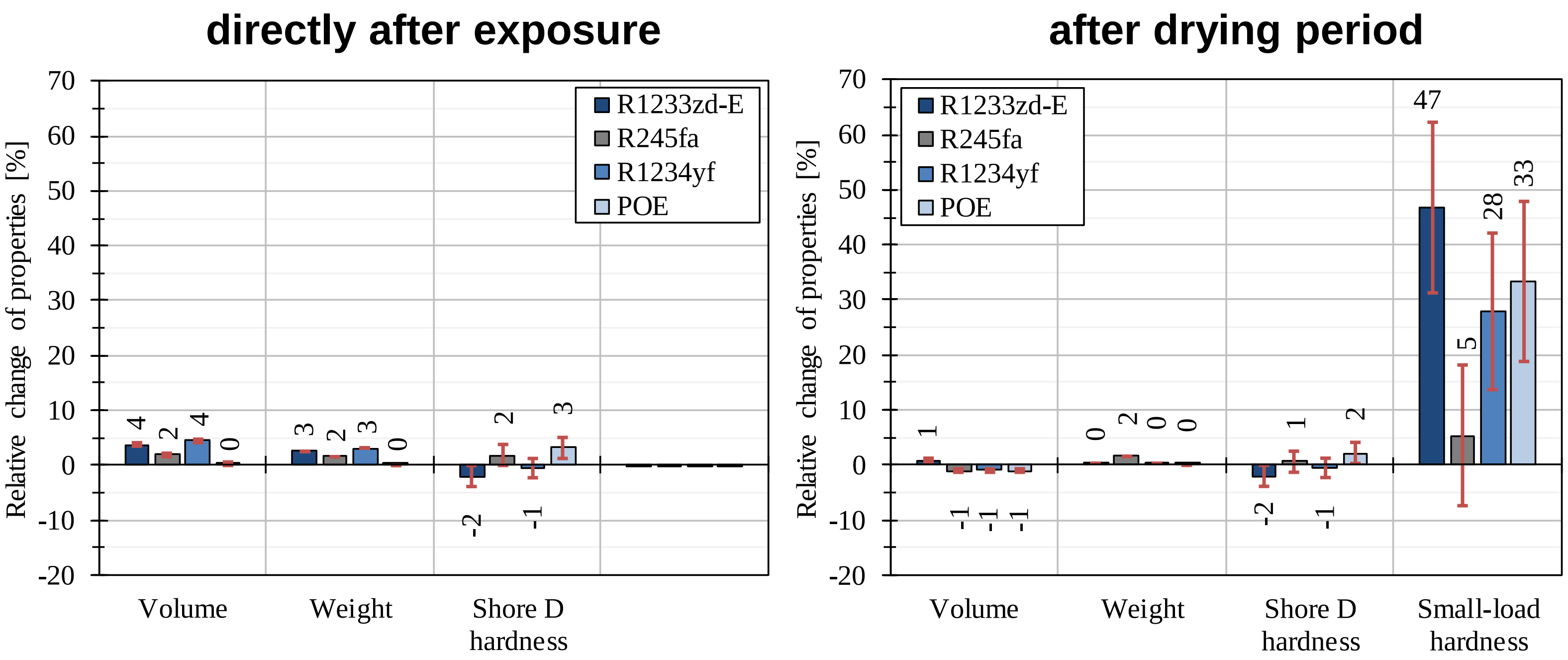
Results

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

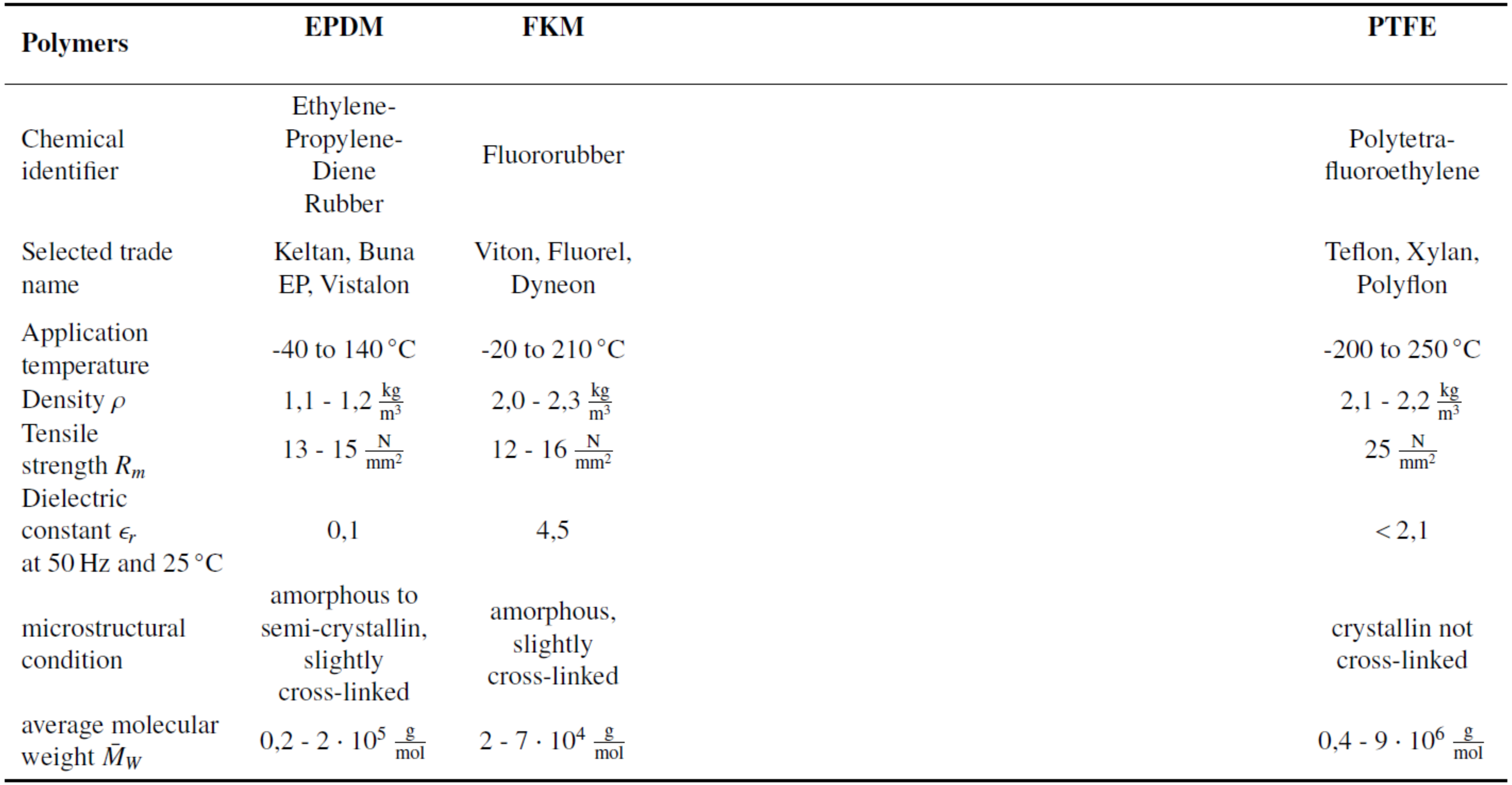
Thank you for your attention!

Questions and discussion!

References

(UBA 2017)	Umwelt Bundesamt: https://www.umweltbundesamt.de/en/topics/economics-consumption/products/fluorinated-greenhouse-gases-fully-halogenated-cfcs/statutes-regulations/eu-regulation-concerning-fluorinated-greenhouse#textpart-1; last access date: 04.09.2017

Backup



Polymers	**EPDM**	**FKM**	**PTFE**
Chemical identifier	Ethylene-Propylene-Diene Rubber	Fluororubber	Polytetra-fluoroethylene
Selected trade name	Keltan, Buna EP, Vistalon	Viton, Fluorel, Dyneon	Teflon, Xylan, Polyflon
Application temperature	-40 to 140 °C	-20 to 210 °C	-200 to 250 °C
Density ρ	1,1 - 1,2 $\frac{kg}{m^3}$	2,0 - 2,3 $\frac{kg}{m^3}$	2,1 - 2,2 $\frac{kg}{m^3}$
Tensile strength R_m	13 - 15 $\frac{N}{mm^2}$	12 - 16 $\frac{N}{mm^2}$	25 $\frac{N}{mm^2}$
Dielectric constant ϵ_r at 50 Hz and 25 °C	0,1	4,5	$< 2,1$
microstructural condition	amorphous to semi-crystallin, slightly cross-linked	amorphous, slightly cross-linked	crystallin not cross-linked
average molecular weight $\bar{M}_W$	0,2 - 2 $\cdot 10^5 \frac{g}{mol}$	2 - 7 $\cdot 10^4 \frac{g}{mol}$	0,4 - 9 $\cdot 10^6 \frac{g}{mol}$

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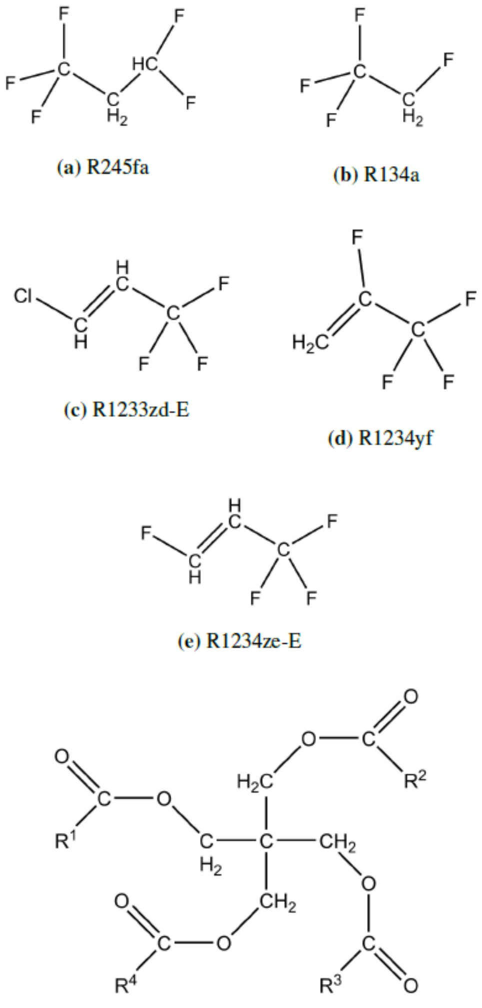


(a) R245fa

(b) R134a

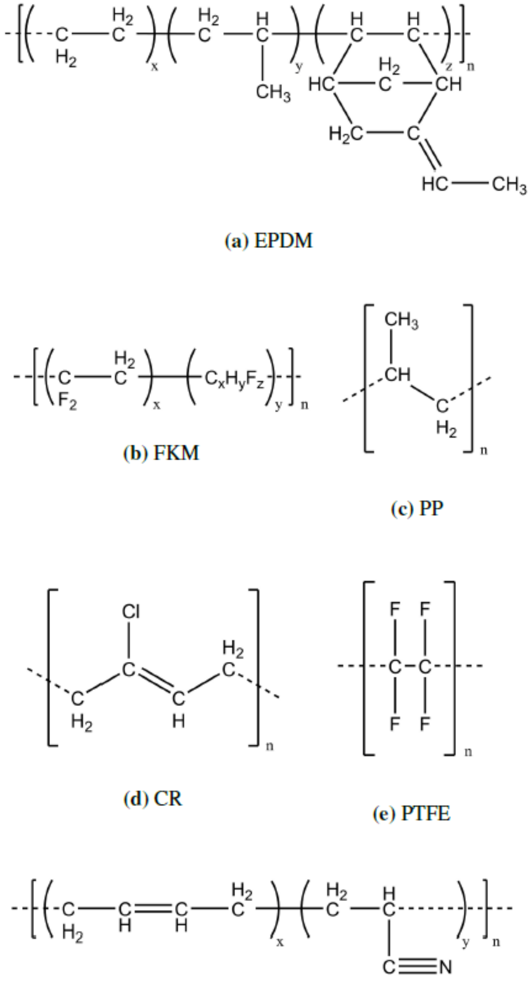
(c) R1233zd-E

(d) R1234yf

(e) R1234ze-E

(f) Polyolester oil

Figure 1 – Structural formulas of the investigated pure fluids



(a) EPDM

(b) FKM

(c) PP

(d) CR

(e) PTFE

(f) NBR

Figure 2 – Structural formulas of the investigated polymers