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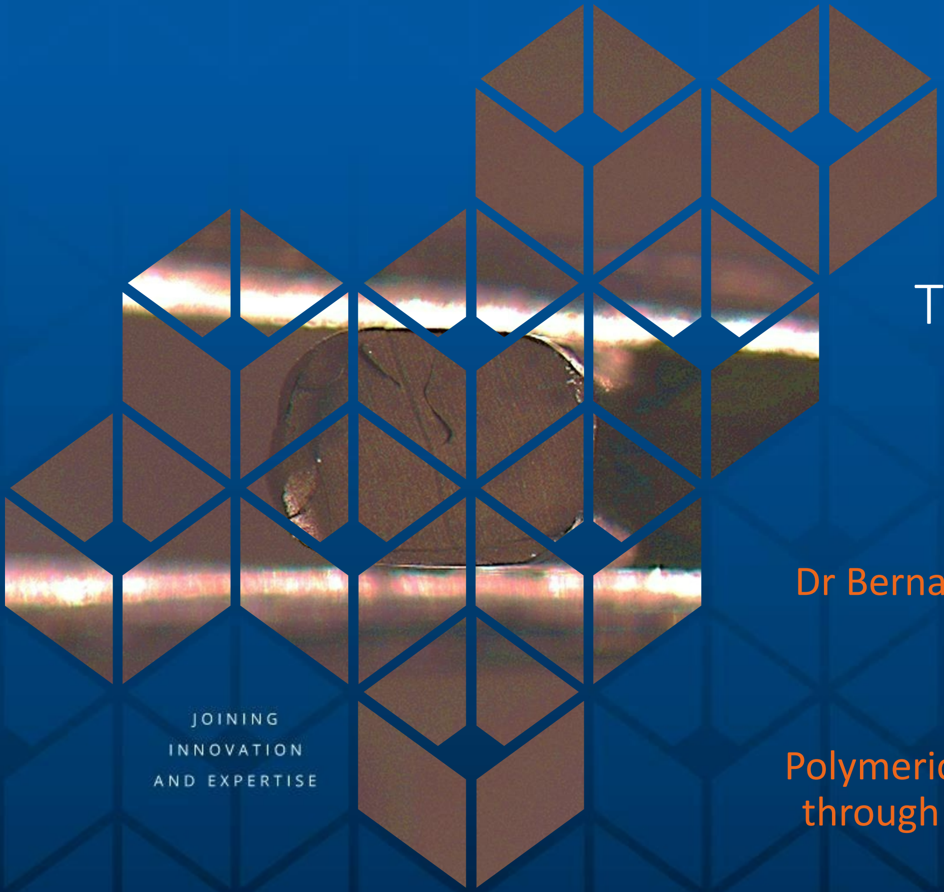

JOINING
INNOVATION
AND EXPERTISE

The permeation of carbon dioxide or hydrogen into elastomers

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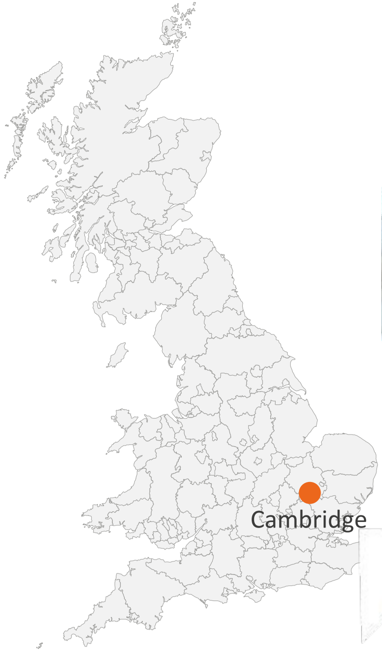
Technology Fellow

Polymeric Materials and Ageing through Permeation Processes

Presentation plan

- Introduction
- Aims for permeation measurements
- What is a permeation test and how useful is the measurement?
- Controlling the boundary measurements for exposure
- An example of CO_2 ageing through permeation data, with and without impurities
- Hydrogen transport
- Recommendations

Introduction



TWI ltd
Head office
Established in 1946

Dr Trevor Gooch
(contribution 1965-2000)
corrosion laboratory

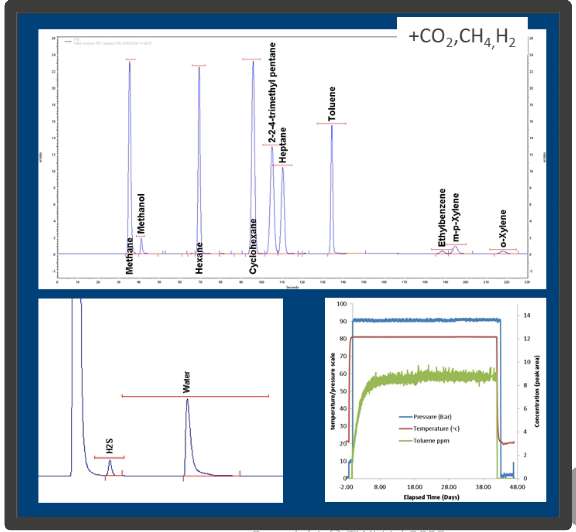
International Membership base
- Performance of materials
- Contracted for confidential project or research

Consultants, Engineers and Experimentalists
- Understand the question
- Design a non-standard experiment with known boundary conditions
- Interpret data for use at all readiness levels

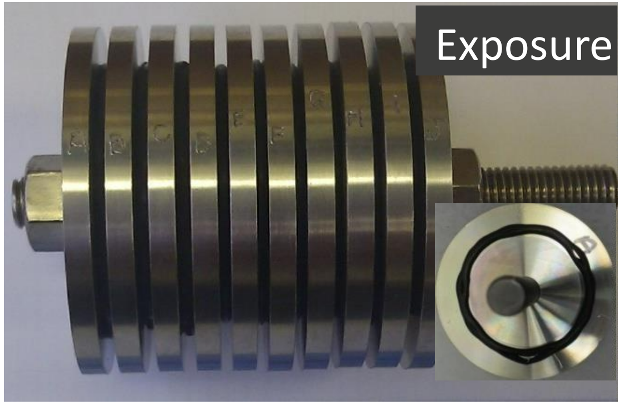
Permeation facility
- Developed since 2012
- Mixtures - CO_2, H_2,CH_4, O_2, H_2O (water, vapour), H_2S, NH_3, toluene, cyclohexane, heptane, xylene (NO_x and SO_X).
- Pressure, temperature and extended duration

A service to our Members - our aims

- Material selection
  - Change in properties over lifetime as a design input for a third party.
- Establish a permeation test as an ageing test
  - Small volumes of fluids (gases, mixtures or liquids)
  - Varying fluids, temperatures and pressure
    - increase and reduction
  - Different length scales
  - Lasting a few months
  - Data interpretation to include transport coefficients
    - activation energy for permeation
    - hole affinity constants

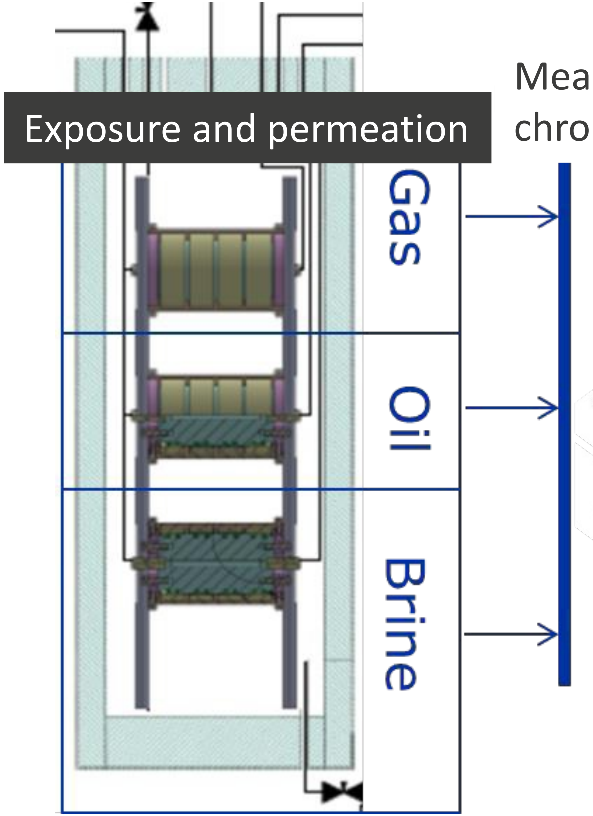


Controlling the boundary conditions - Fluid to outer surface of O-rings

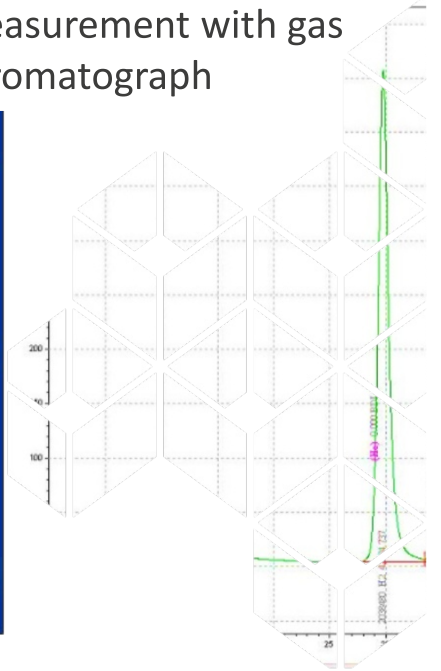


100mm

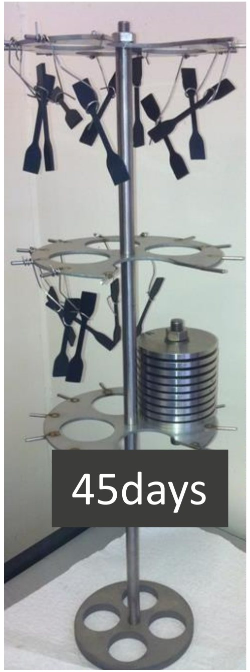
200mm

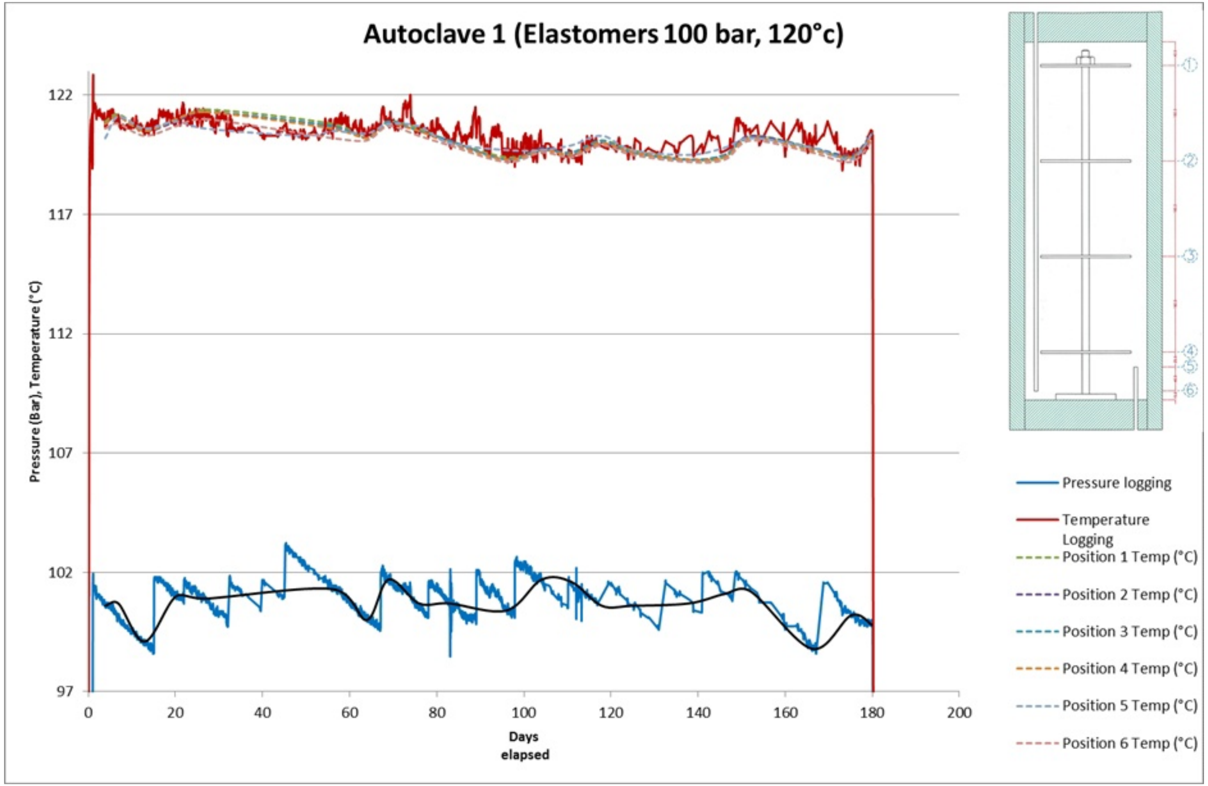


Measurement with gas chromatograph



Controlling the boundary conditions - 19L volume CO_2 with 1.5%H_2S experiments (in the past)





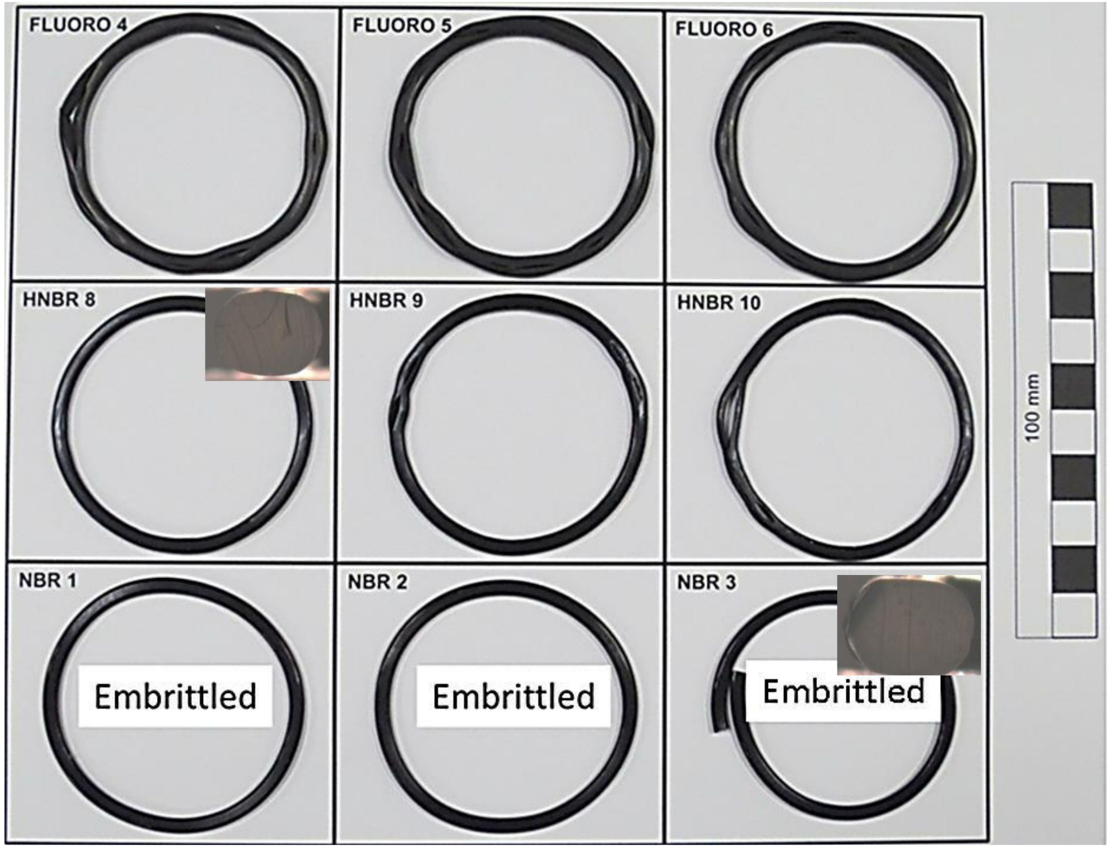
Exposure to supercritical CO_2 with 1.5% H_2S in large volume autoclave

NBR brittle at 45 days and 180days

Polymer	+D wt%	+D wt%*	+Dd%	+Dd%
	45 days	180 days	45 days	180 days
NBR	7.13 ±0.04	7.56 ±0.01	1.29 ±0.09	1.42 ±0.24
HNBR (G8.9.1)	4.39 ±0.01	7.47 ±0.06	-0.07 ±0.25	1.74 ±0.11
FLUOROELAST	2.75 ±0.02	3.54 ±0.04	1.98 ±0.17	2.88 ±0.06

Polymer	σ_m MPa Unaged	σ_m MPa 45 days	σ_m MPa 180 days	ε_{tb} unaged	ε_{tb} 45 days	ε_{tb} 180 days
NBR	23.1±1.0	6.0 ±0.19	7.4 ±0.3	2.30 ±0.10	0.65 ±0.08	0.02±0
HNBR (G8.9.1)	32.0 ±2.9	29.5 ±2.5	34.7 ±1.4	2.04 ±0.13	0.88 ±0.8	0.40 ±0.03
Fluoroelastomer	15.6 ±1.4	11.9 ±0.4	10.4 ±1.3	0.89 ±0.11	0.52 ±0.01	0.44 ±1.34

O-rings after RGD in CO_2 with 0.186% H_2S at 120 °C and 100 barg



FLUORO	+D wt% RGD (15 days)
4	0.31
5	0.31
6	0.28
HNBR	
8	0.22
9	0.21
10	X
NBR	
1	0.25
2	0.22
3	0.23

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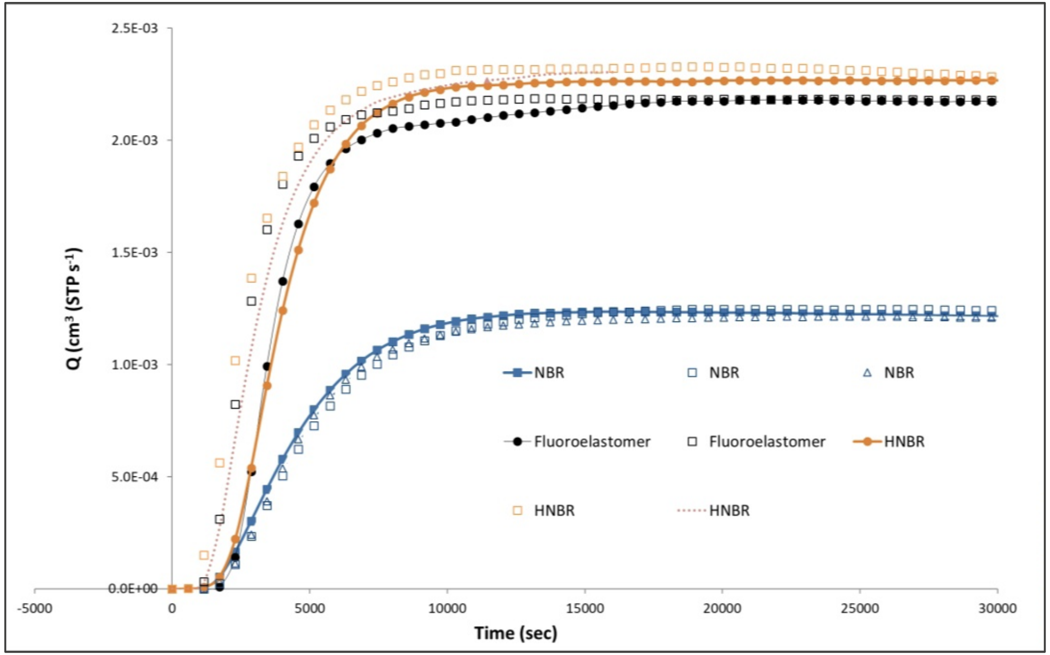
Permeation data on disc experiments (120 °C and 100barg, supercritical CO_2)



Elastomer	K ($x10^{-6}$)*	D ($x10^{-6}$)**	S ***
HNBR	2.3	2.1	1.03
HNBR	2.2	2.6	0.85
HNBR	2.2	2.4	0.95
Fluoroelastomer	1.9	-	-
Fluoroelastomer	1.9	2.4	0.78
NBR	1.2	1.8	0.66
NBR	1.2	1.6	0.79
NBR	1.2	1.6	0.73

*$cm^3(STP)s^{-1}\ cm\ cm^{-2}\ bar^{-1}$
$cm^2\ s^{-1}$, * $cm^3(STP)\ cm^{-3}$ (polymer)bar^{-1}

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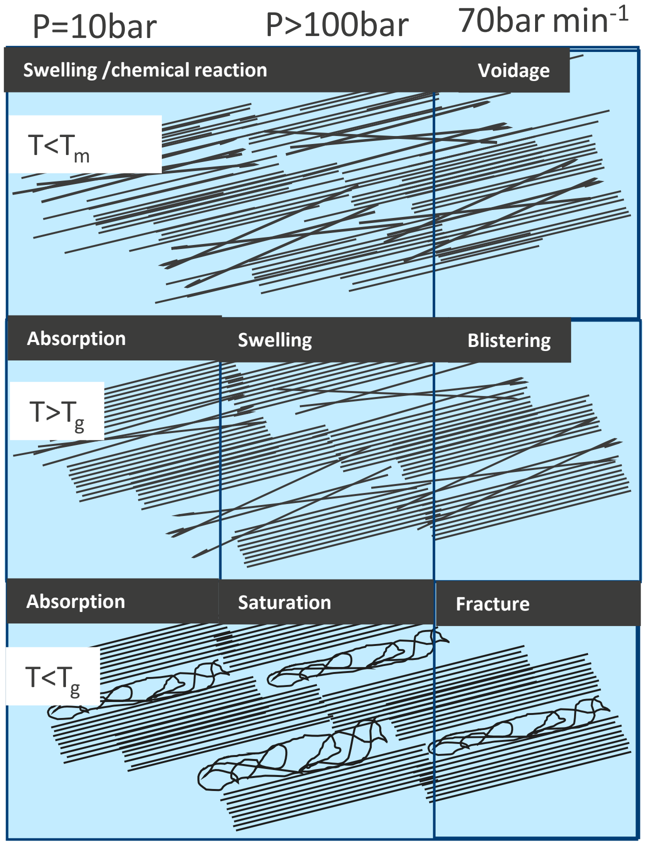
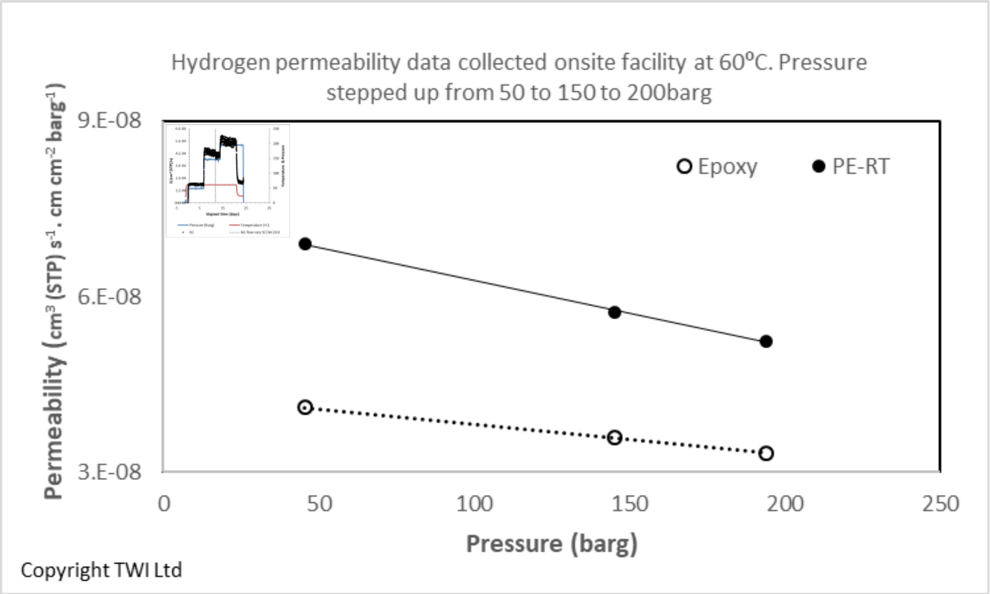
Polymer morphology - hydrogen interactions

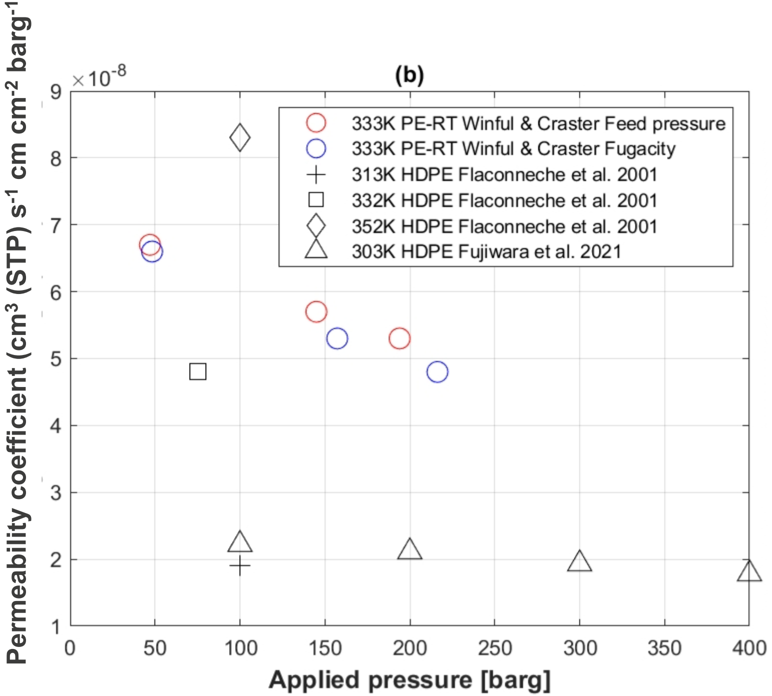
- Mainly transported through the amorphous regions as molecular hydrogen
- What about impurities?
- **Can displace other dissolved gases?**
- **Will hydrogen cause additives to be displaced?**
- **Possibility for reaction where residual catalysts are present. Atomic hydrogen generated locally?**
- Swelling and decompression damage at higher pressures

	Diam. (pm)
H_2	289
CH_4	380
O_2	346



Example of permeation of hydrogen through polymers





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Summary

- The boundary conditions on the specimens on exposure to CO_2 alters the outcomes
  - Differences in mass uptake
  - Rapid gas decompression damage
  - Compression set
- At early times, on development of the permeation steady state, there is no evidence of ageing
- The inclusion of an impurity such as H_2S in the CO_2 perturbs the supply of CO_2 at the elastomer surface.
- In detailed study of transport, the fugacity of the CO_2 needs to be allowed for. This is not a concern in hydrogen experiments.

Recommendations

- Establish a permeation test as an ageing test
  - Small volumes of fluids (gases, mixtures or liquids)
  - Varying fluids, temperatures and pressure
    - increase and reduction
  - Different length scales
  - Lasting a few months
  - Data interpretation to include transport coefficients
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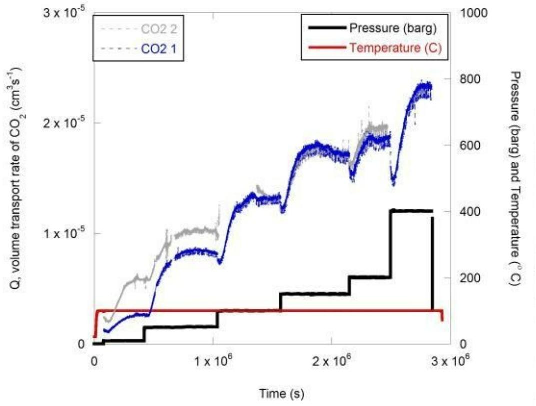

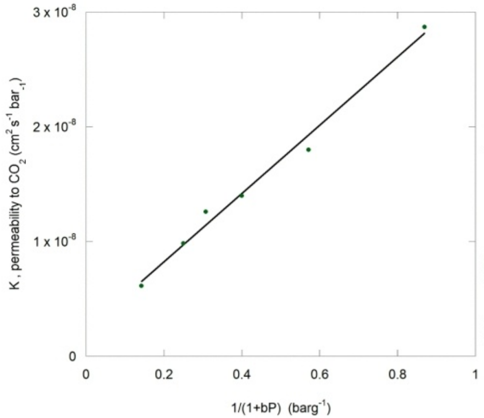

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