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Synthesis and characterization of melamine – formaldehyde rigid foams

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IVIS 2013 **20^{th} Sept 2013**

Outline of the talk

- life expectance of VIPs
- synthesis of melamine – formaldehyde (MF) rigid foams
- mechanical & thermal properties of MF foams as VIP core
- outgassing rate measurements of the envelope and core
- results
- potential applications
- summary

Life expectance of VIPs

Life expectance of any sealed vacuum element is determined by mechanisms which increase the pressure to the **tolerable level.**

Tolerable pressure level inside a VIP is determined by the **microstructure of the core**, while the “pressure rise d*p*/d*t*” by:

- leaks
- permeation
- outgassing

envelope

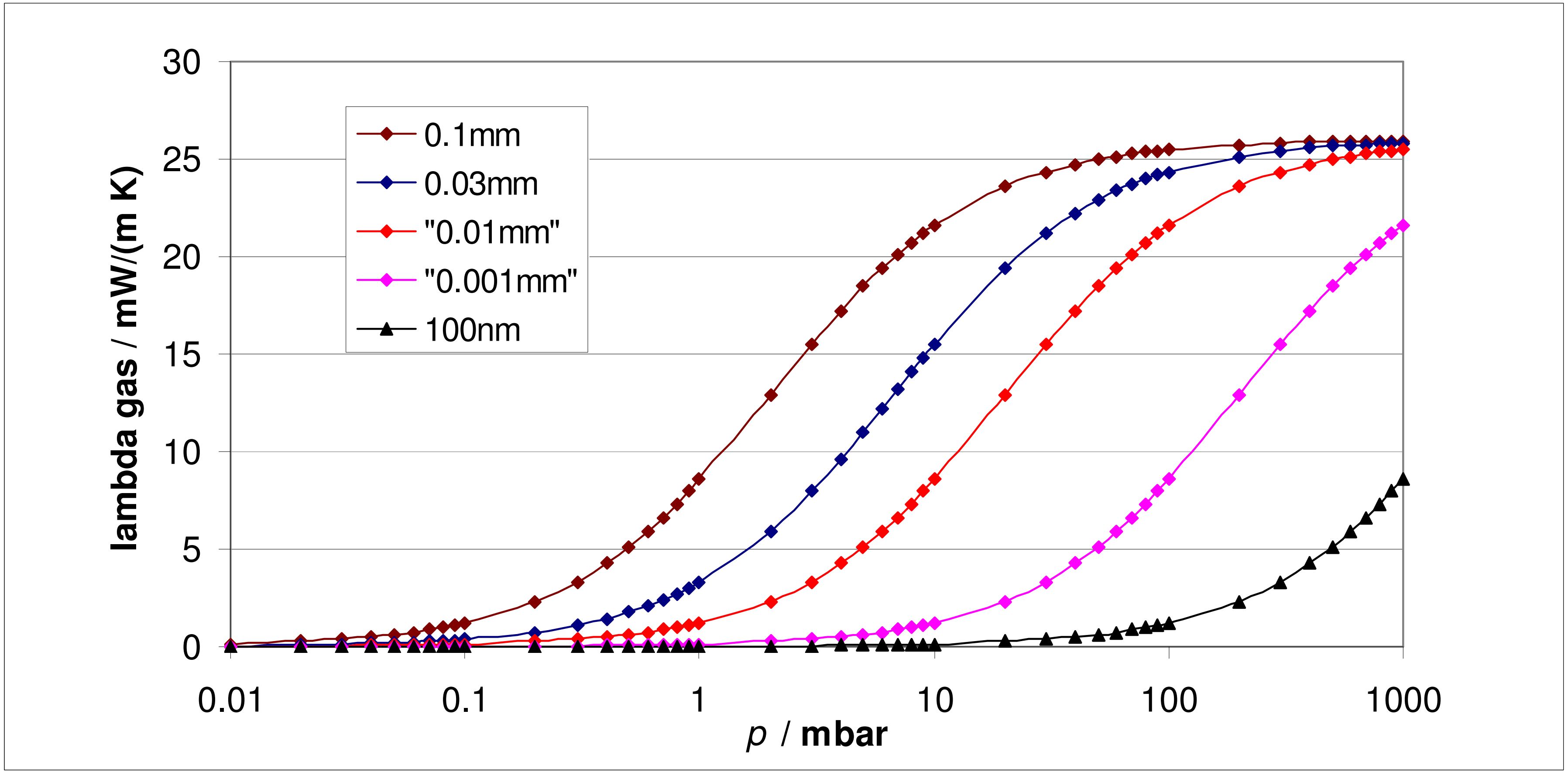
and

- **outgassing of the core**

During the synthesis of a novel core material, a testing method was needed where contributions of the envelope were negligible.

Life expectance of VIPs

When the mean pore size of the core is macroscopic size, pressure requirements are more stringent than in nanostructured core materials.



Life expectance of VIPs

For a particular core, pressure in the VIP should not exceed the specified value $\boldsymbol{p}_{\mathbf{max}}$ within the expected lifetime Δt.

$$p_{\max} = \frac{dp}{dt} \cdot \Delta t$$

An assumption for the VIP's lifetime is most often made by the projection assuming the constancy of the initial dp/dt.
The "initial" means 24 h – 48 h when the accuracy of dp/dt determination is sufficiently high.*

* *Redhead P.* **Recommended practices for measuring and reporting outgassing data**. *J Vac Sci Technol A 2002; 5: 1667-75.*

Synthesis of MF rigid foams

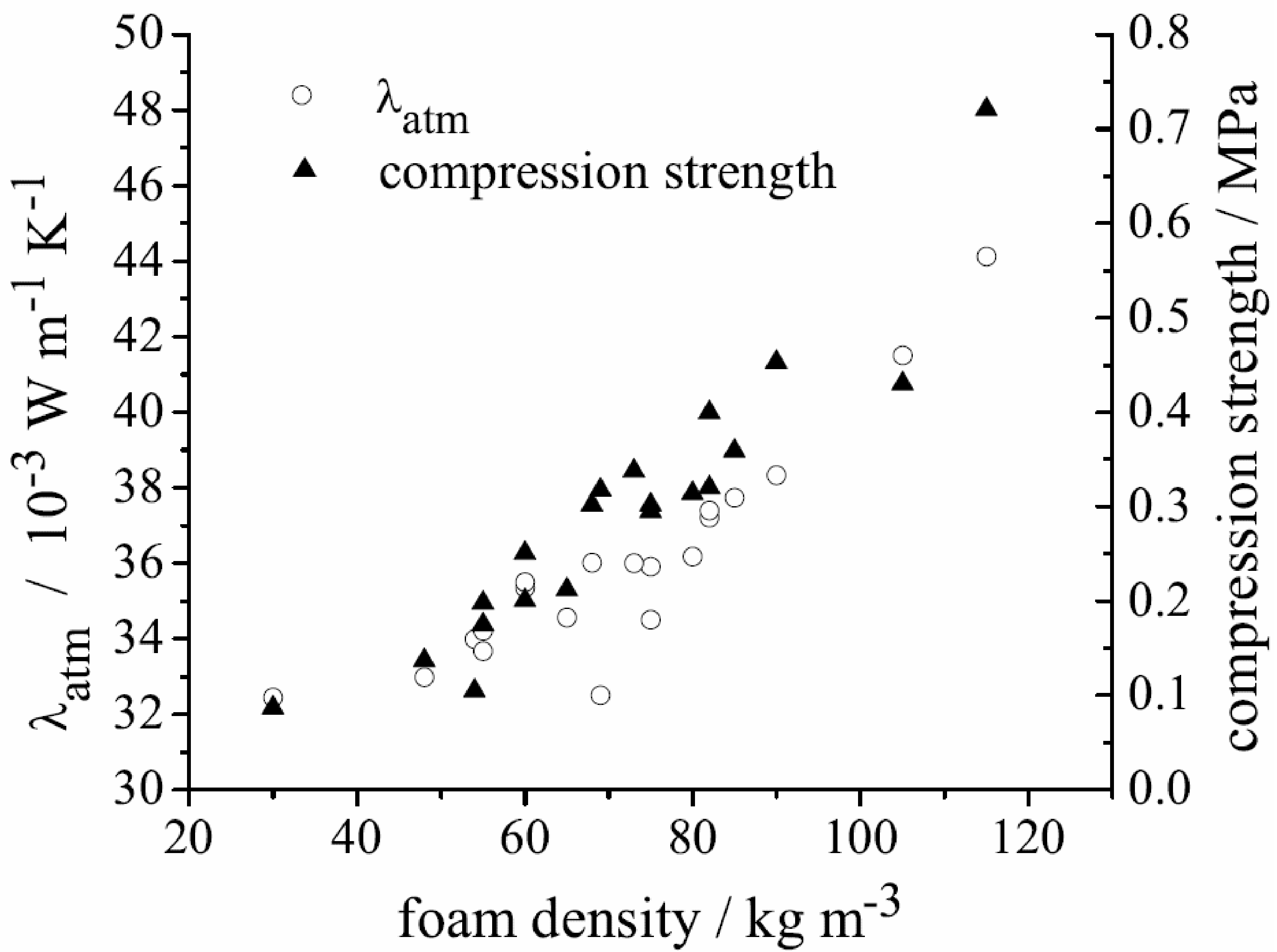
Reacting mixture – emulsion made of:

- Meldur® (water solution 60 % - 65 % MF resin)
- n-pentane
- sodium lauryl ether sulphate (SLES)
- formic acid

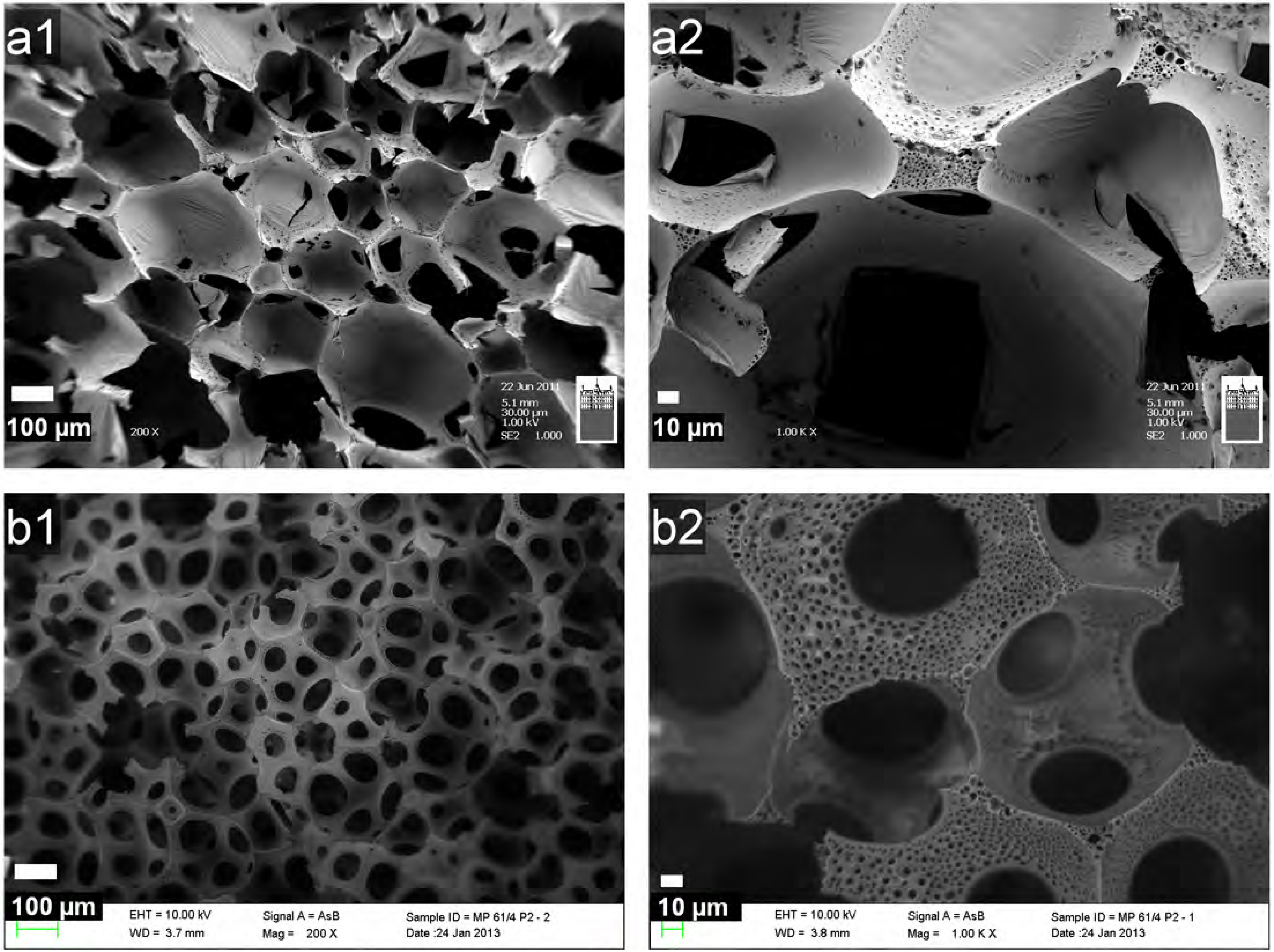
Foam density was controlled by variation of the pentane content in the emulsion and with different heating schedules

Foaming and curing proceeded with heating in a conventional oven in the range of temperatures between 130 °C and 150 °C for 30 minutes.
Final curing and water removal was carried out at temperatures from 170 °C to 190 °C.

Mechanical & thermal properties of MF foams

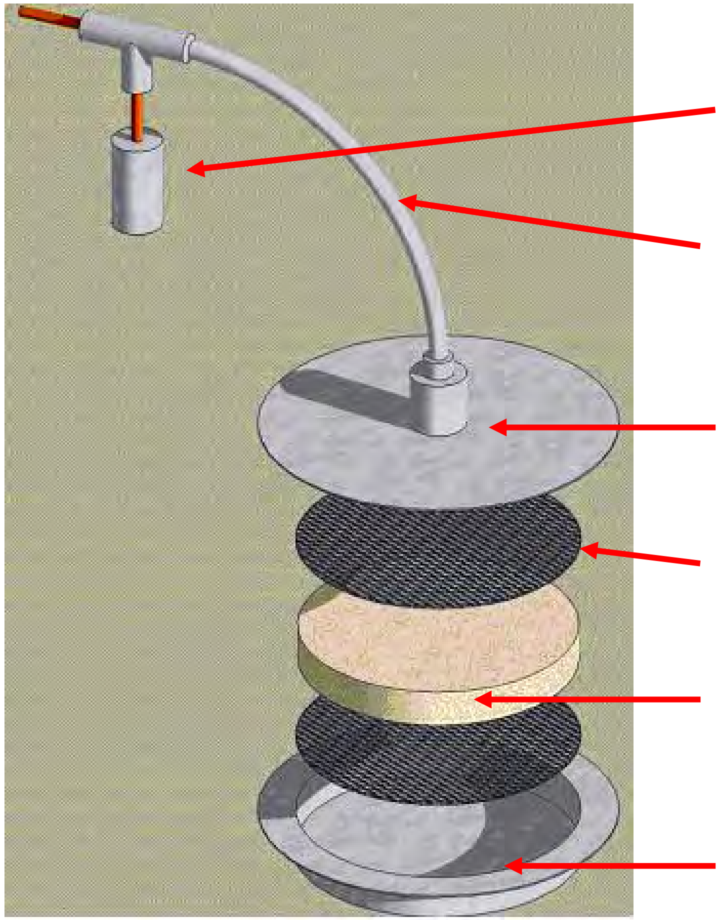


Mechanical & thermal properties of MF foams



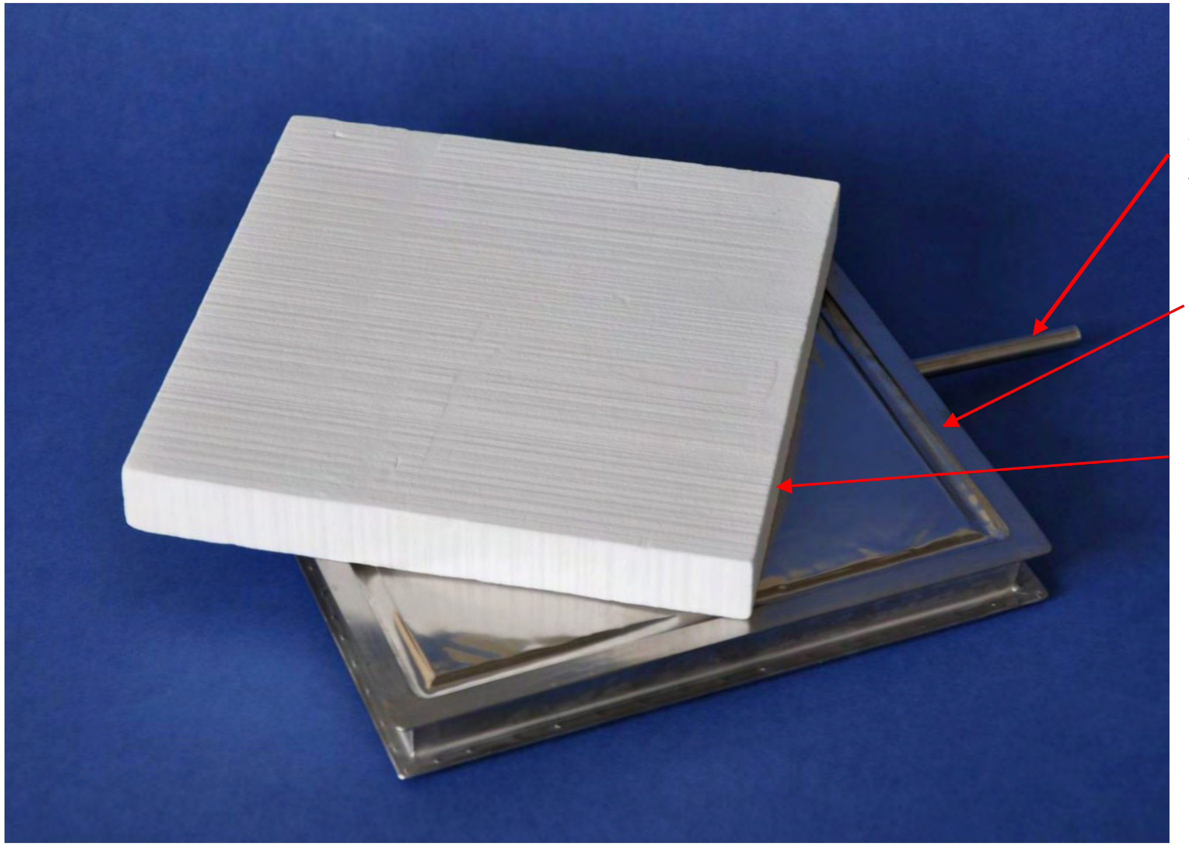
Outgassing rate measurements of the envelope/core

preliminary tests for obtaining data on outgassing of MF foams ⇒ stainless steel envelope without / with MF sample.



Outgassing rate measurements of the envelope/core

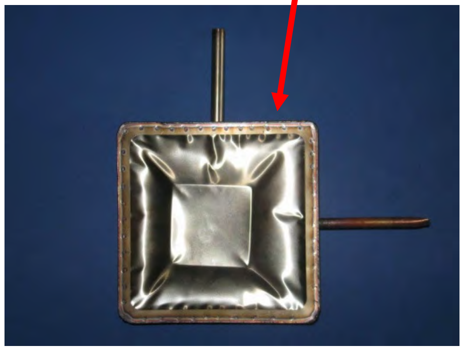
next step: thin walled square envelope without / with MF sample $\Rightarrow$ thermal conductivity λ_0 measured at very low pressure after pinch-off



pressure gauge (SRG)

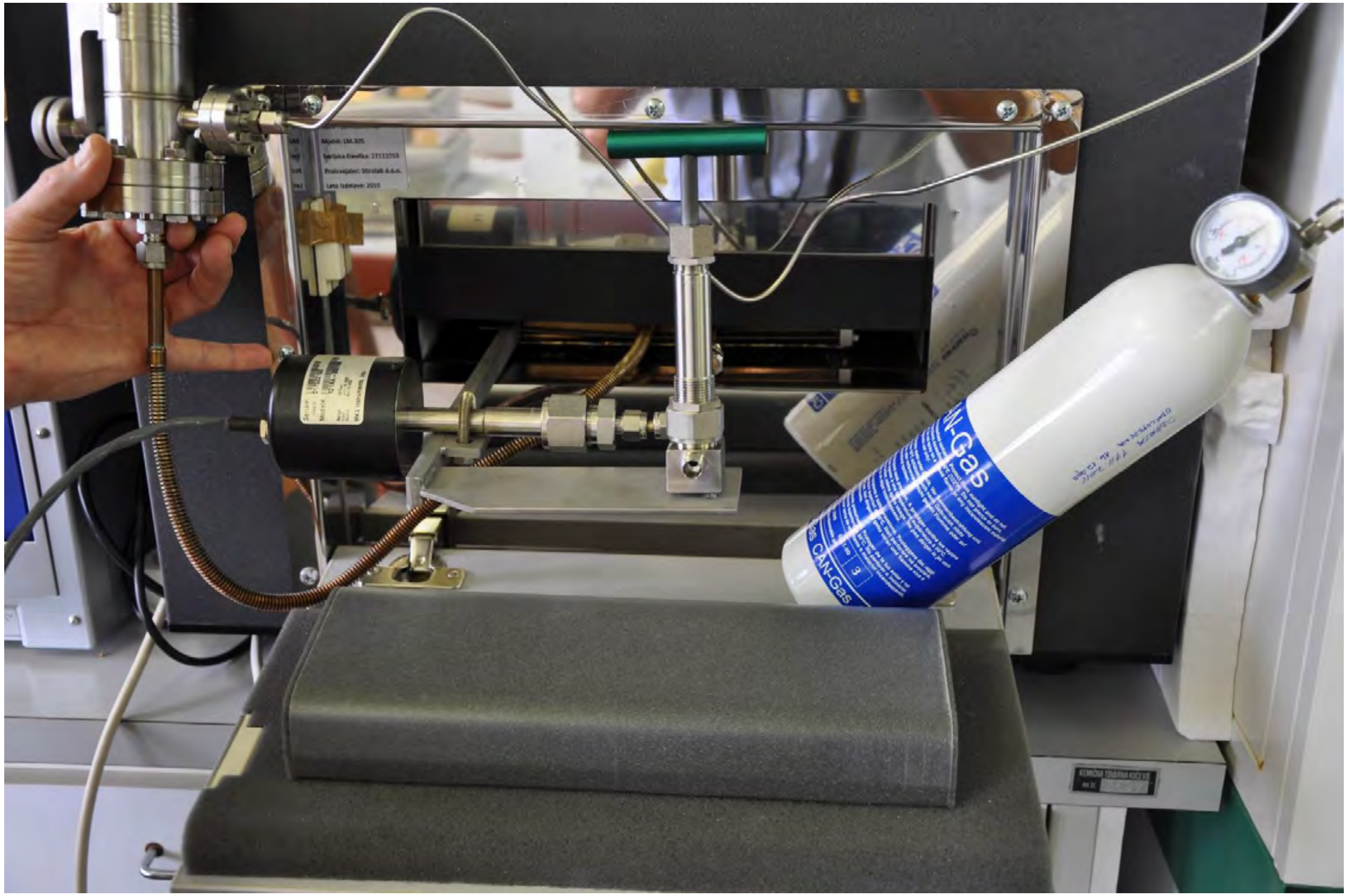
square st. steel envelope

MF foam



Outgassing rate measurements of the envelope/core

thermal conductivity versus pressure measured after bake-out by admitting controlled amount of Ar



Outgassing rate measurements of the envelope/core

preparation steps of FM foam samples

- water removal at 150 ℃ for 17 h in the air
- envelope welding
- He leak testing
- bake-out ~4 h at 150 ℃, high vacuum
- cooling to room temperature
- Cu tube pinch-off
- SRG measurements for 24 h

Results

dp/dt, specific outgassing rate q_{m}, and thermal conductivity λ_0 for selected MF samples with density from 55 - 82 kg m^{-3}

Sample	ρ	dp/dt*	q_{m}	λ_0
number	kg m^{-3}	x10^{-9} mbar s^{-1}	$\times$10^{-11} mbar L s^{-1} g^{-1}	x10^{-3}W m^{-1} K^{-1}
1	55	4.9	11.1	5.9
2	60	4.7	9.8	6.2
3	68	4.4	8.1	5.9
4	73	2.8	4.8	6.9
5	75	2.2	3.7	6.6
6	82	2.9	4.4	7.6

*empty envelope contributes dp/dt ~ 1x10^{-11} mbar s^{-1} which corresponds to extremely low q ~5x10^{-15} mbar L s^{-1} cm^{-2}

Dissertation zur Erlangung des Doktorgrades
der Mathematisch-Naturwissenschaftlichen Fakultät
der Universität Augsburg
vorgelegt von

Daniel Schultheiß

Literature Survey of Outgassing Rates

16. April 2007

OPUS Augsburg
der Online-Publikationsserver der Universität Augsburg

If not noted, the outgassing rates, q_G, are measured at room temperature (RT). The unit of the area specific outgassing rates is $\mathrm{mbar\,l\,s^{-1}\,m^{-2}}$. The term "$xx$ h at yyy °C" denotes the bake-out at yyy °C for xx hours.

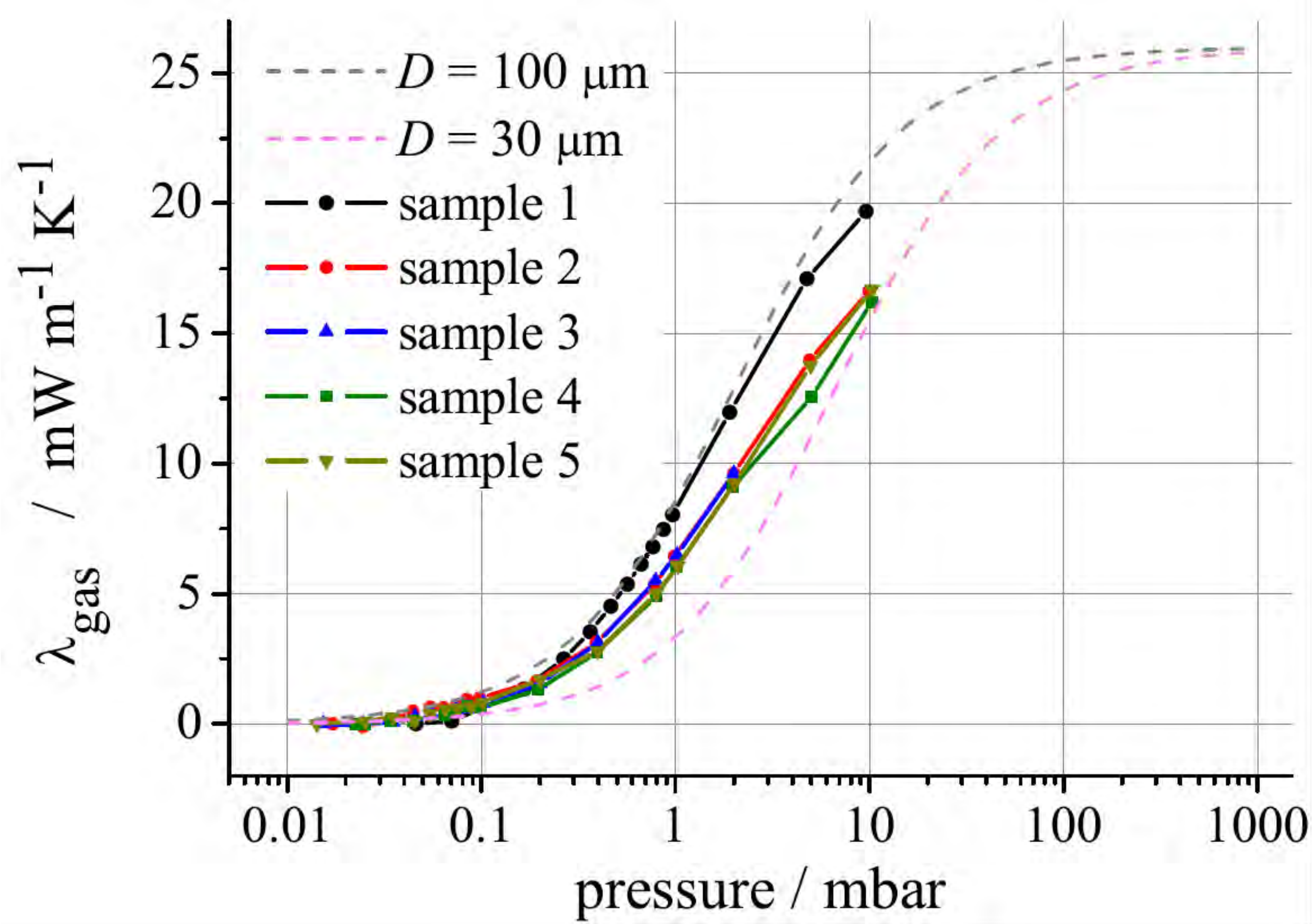
Table B.6: Area specific outgassing rates of polymers

material	preparation / treatment	q_G	ref.
1338 (epoxy)	24 h at 140 °C, 10 h at RT	3.1E-05	[208]
828 (epoxy)	24 h at 140 °C, 10 h at RT	2.0E-04	[208]
Araldite	10 h at RT	1.0E-02	[195]
Araldite	10 h at RT	4.7E-03	[96]
Araldite		1.2E-02	[30]
Araldite		1.5E-02	[30]
Araldite AT1	51 h at RT	6.0E-04	[209]
Araldite CT200+HT901	51 h at RT, 98 h at 100 °C	2.7E-06	[209]
Araldite MY740	51 h at RT	2.0E-04	[209]
Boron nitride M	clean in alcohol, dry air, 100 h at RT	3.0E-03	[121]
Butyl	4 h at RT	5.3E-03	[96]
CY-179 (epoxy)	24 h at 140 °C, 10 h at RT	4.5E-05	[208]
ERL4221 (epoxy)	24 h at 140 °C, 10 h at RT	2.0E-04	[208]
Kel-F	10 h at RT	2.3E-04	[96]
Kel-F		4.0E-04	[30]
Lexan (polycarbonate resin)	clean in alcohol, dry air, 100 h at RT	1.2E-03	[121]
Mycalex	51 h at RT	1.0E-05	[209]
Mylar	10 h at RT	2.0E-03	[195]
Mylar	10 h at RT	5.3E-03	[96]
Neopren		3.0E-02	[30]
Neoprene	4 h at RT	2.4E-01	[96]

SS	1 h at RT	3.1E-03	[30]
SS	2 h at RT	7.7E-06	[129]
SS	2 h at RT	6.3E-05	[194]
SS	5 h at RT	1.0E-04	[195]
SS	10 h at RT	1.0E-05	[96]
SS	20 h at 150 °C	8.4E-07	[128]
SS	21 h at 200 °C	1.3E-10	[196]
SS	22 h at 212 °C	1.0E-10	[196]
SS	100 h at 430 °C, 100 h at 480 °C	3.0E-12	[196]
SS	electropolished	3.0E-08	[197]
SS	electropolished, 1 h at RT	4.3E-05	[30]
SS	mechanically polished, 1 h at RT	1.7E-05	[30]
SS	sand-blasted, 1 h at RT	8.3E-05	[30]
SS (304)	30 h at 250 °C	4.0E-08	[96]
SS (304)	baked and cleaned	1.3E-08	[198]
SS (304)	oxidized (3.5 nm CrOxide)	1.6E-10	[199]
SS (304)	venting with N_2, 8 h at 180 °C	2.0E-09	[200]
SS (316)	baked and cleaned	1.3E-08	[198]
SS (316L)	10 h at 20 °C, 40 h at 140 °C, 50 h at 20 °C	7.7E-09	[201]
SS (401)	24 h at 300 °C	2.4E-07	[120]
SS (U15C)	45 h at 360 °C	1.9E-08	[126]
SS (U15C)	baked in situ at 360 °C for 24 h	3.7E-10	[126]

Results

gaseous part of thermal conductivity for 5 selected MF samples



Potential applications

Several VIP types have been studied and tested in the last 20 years with specific advantages and drawbacks:

- plastic open cellular rigid foams in plastic metallized envelope
- microporous inorganic powder in plastic (+ thin Al) envelope
- glassfibers in stainless steel foil

At present,

• inorganic ***nanostructured board*** or ***glass micro-fibers*** in laminated plastic envelope seems to be the most promising options, for buildings?

In the future:

- organic nanostructured open cellular rigid foams
- fire-resistant organic foams

Potential applications

MF foams tested so far exhibit some potentially interesting properties

⇒ they seems to be suitable as core material for VIPs

- they can be synthesized by rather simple chemistry (a pilot plant for soft and rigid MF foams is under construction)
- after water removal and moderate vacuum treatment, extremely low outgassing rate is obtained
- thermal conductivity is within the range of other organic foams
- they exhibit a very good fire resistance

Potential applications

MF foams exhibit “low flammability” by EU fire classification standard for buildings (DIN 4102-1), (i.e. class B1). Many organic core materials are flammable and need additives to improve flame resistance.

Summary

- Novel open cell MF foams were synthesized on laboratoratory scale
- Chemical, mechanical and thermal properties were studied
- Selected MF foams fulfill requirements as core materials in VIPs
- As they are fire-resistant, they might be applied in buildings
- .... many properties still need to be improved and optimized

IVIS organisers comment: the related full paper is now available on
http://dx.doi.org/10.1016/j.apenergy.2013.09.071
Nemanic et al, Applied Energy 114 (2014) 320–326