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# Synthesis and characterization of melamine–formaldehyde rigid foams for vacuum thermal insulation

V. Nemanič [a,*], B. Zajec [a,1], M. Žumer [a], N. Figar [b], M. Kavšek [b], I. Mihelič [b]

[a] Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia
[b] Melamin, Tomšičeva 9, 1330 Kočevje, Slovenia

## HIGHLIGHTS

- Novel open pore melamine–formaldehyde (MF) rigid foam was synthesized.
- High thermal stability up to 200 °C and an extremely low outgassing rate was achieved.
- The base thermal conductivity at low pressure equal to 0.006 W m$^{-1}$ K$^{-1}$ at 300 K.
- These properties are sought-after for the core material in vacuum thermal insulations with long-term service life.
- Such a low outgassing rate previously attributed solely to inorganic materials having a much higher density.

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## ABSTRACT

A novel core material for vacuum thermal insulation, the melamine–formaldehyde (MF) rigid foam was processed from an emulsion of the melamine–formaldehyde resin at temperatures between 130 °C and 150 °C, using pentane as the blowing agent. The achieved porosity was between 92% and 98%. Open pore structure with desired mechanical properties was achieved by variations of the initial chemical composition of liquid reactants and controlled foaming and hardening, employing classical heating. The average pore size was determined directly by SEM and indirectly by measuring the thermal conductivity in a wide pressure range from $10^{-3}$ mbar to the atmosphere. Optimization of the synthesis resulted in the base thermal conductivity equal to only 0.006 W m$^{-1}$ K$^{-1}$ and an extremely low outgassing rate. The long-term pressure-rise measurements indicate that these MF rigid foams could be the first organic candidates applied as the core material in Vacuum Insulating Panels (VIPs) whose performance may be comparable to selected inorganic core materials. Their further advantages compared to conventional organic foams are their stability, as they can withstand a temperature in excess of 200 °C, and good fire resistance.



## 1. Introduction

Core materials for Vacuum Insulation Panels (VIPs) must fulfill several specific requirements. They should have a high porosity with small interconnected open pores and structural stability, since they must withstand the high mechanical load exerted by the atmospheric pressure. Small pores are desired since the same low thermal conductivity can be maintained at a higher internal pressure compared to the same bulk material with larger pores. Beside this, chemical stability, expressed by low outgassing rates over the projected operational time, must be achieved, too. These extreme requirements seem to meet in VIPs for building applications where the expected service lifetime is ~100 years [1–3]. A combined vacuum-thermal treatment at elevated temperatures is an obvious step of the core preparation and nowadays only inorganic materials seem to fulfill these requirements. The core density of such VIPs is of the order of $\rho \sim 200$ kg m$^{-3}$, while the resulting base thermal conductivity could be as low as 0.002 W m$^{-1}$ K$^{-1}$ for glass fibers, and ~0.005 W m$^{-1}$ K$^{-1}$ for nanoporous silica [1,2,4]. Organic polymer foams used as conventional thermal insulation materials have a substantially lower density, $\rho$ = 30–50 kg m$^{-3}$, and seem to be attractive also as core materials for VIPs in buildings. Unfortunately, their main drawbacks, like low tolerable processing temperature, relatively high outgassing rate, high flammability and low softening point, restrain them to applications where the service lifetime scale is only a few years. Anyhow, organic materials with better properties are continuously searched [5,6].

In the present work we report on the processing and characterization of melamine–formaldehyde (MF) rigid foams with densities from $\rho$ = 30–115 kg m$^{-3}$. Selected MF foam samples with the

* Corresponding author. Tel.: +386 14773409.
*E-mail address:* vincenc.nemanic@ijs.si (V. Nemanič).
[1] Current address: Slovenian National Building and Civil Engineering Institute, Dimičeva 12, 1000 Ljubljana, Slovenia.

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density between $\rho$ = 55–75 kg m$^{-3}$ were tested as VIP core materials. They excel in thermal stability and low outgassing rate, both comparable to inorganic core materials which have substantially higher densities. The highly porous microstructure is manifested by a base thermal conductivity $\lambda_0 \sim 0.006$ W m$^{-1}$ K$^{-1}$.

## 2. Experimental

The development and optimization of the novel rigid foam was a complex process. Several parameters determined during a particular measurement cycle had to be either preserved or slightly changed to make a small improvement of some particular foam property in the next synthesis. Some foam properties could be determined easily, soon after the synthesis, while some others, like the outgassing rate and thermal conductivity at low pressures, required several days or weeks. Determination of the outgassing rate of any VIP core material is at the limit of the present-day techniques, developed and applied mainly in the vacuum practices [7]. MF foams withstand 200 °C without a noticeable change of their properties, thus a moderate heating cycle at 150 °C in vacuum was introduced in our testing schedule, after the foams had been dried in the air. The MF foam sample was mounted and welded into a stainless steel envelope, which was tight and completely impermeable for all atmospheric gases. By adding a suitable inert pressure gas sensor, like the spinning rotor gauge (SRG), (Leybold, VM 212), pressure change d$p$/d$t$ could be monitored at any time after processing and sealing. In the first set of experiments, only the outgassing rate at room temperature was monitored, which enabled selection of the most promising MF types. In the second set of experiments, the base thermal conductivity $\lambda_0$ at "zero" gas pressure ($p < 10^{-2}$ mbar) of a previously approved MF foam type could be measured, too. We avoided flexible polymer foil envelopes, where pinholes, gas permeation through the sealing area, low tolerable thermal treatment temperature, etc. introduce a serious limitation in obtaining the true core material outgassing rate [8].

These facts explain that the progress over three years could only be achieved by a careful build-up of a database. We present in this section the following main four separated blocks:

### 2.1. Synthesis and thermal processing of the foam

For preparation of the foams, a reacting mixture was formed from an emulsion of Meldur®MP (melamine–formaldehyde resin partially soluble in water with the concentration range between 60% and 65%), *n*-pentane, sodium lauryl ether sulphate (SLES) and formic acid. This type of foam was labelled as the unmodified version. 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 and 150 °C for 30 min. Final curing and water removal was carried out at temperatures from 170 °C to 190 °C. Two types of dimensions of samples were prepared for further analysis: cylinders with the diameter 150 mm and thickness 20 mm, and square blocks with the dimension 200 × 200 × 24 mm$^3$. In the same manner as described above we also studied foams prepared with the sulphonated melamine–formaldehyde resin Meldur®MPS (completely soluble in water with the concentration range between 60% and 65%). This type of foam was labelled as the modified version. The morphology of each newly synthesized MF rigid foam type was inspected by the scanning electronic microscopy (SEM). The compression strength measurements were carried out on the dynamometer TIRAtest 2705, according to EN 826, while thermal conductivity in the air was measured by the heat flow meter apparatus Stirolab LM.305, according to EN 12667.

### 2.2. Outgassing rate measurements

Cylindrically-shaped samples with the diameter 150 mm and thickness 20 mm were mounted into cylindrical envelopes made of stainless steel with a wall thickness of 0.5 mm. These envelopes were equipped with two appendages; a spinning rotor gauge (SRG) thimble connected through a 500 mm long bellows for monitoring of the outgassing rate, and a Cu-tube pumping connection (inner diameter = 5 mm), positioned in the center of the top-side of the envelope. Empty envelopes with an area $A$ = 450 cm$^2$ and volume $V$ = 360 cm$^3$ were thermally pre-treated in the air and subsequently in vacuum to get a very low background outgassing rate [9].

It should be emphasized that the outgassing rate of any investigated material according to the recommended practices must be given in prescribed specific units, related to as per gram or per unit area [7]. Anyway, the simple recorded parameter d$p$/d$t$ is often used for a VIP's service life projection [8]. This seems to be correct as it is difficult, sometimes even impossible, to distinguish between contributions of the core material and the envelope. As we have measured also all the empty envelopes before the particular MF foam sample have been inserted, we could determine the contribution of the core alone by subtracting the background. It was assumed that the outgassing rate of the envelope itself has been preserved and that it has not been affected by the gases released from the MF foam.

MF foams with densities from $\rho$ = 30–115 kg m$^{-3}$ were evaluated. Besides the variation of density, samples with various sulphur contents were studied, too. The final encapsulation into the stainless steel envelope was performed by welding in about 30 min after the thermal treatment in the air was concluded. A preliminary He leak test for tightness followed. The connecting UHV vacuum valve included a thin stainless steel net (mesh#300), which prevented contamination of the vacuum system with powder particles. The initial pump-down with a rotary pump was performed very slowly (~10 min) in order to minimize turbulence which could displace particles from the MF foam sample. Then a turbo molecular pump was switched on and the pressure in the vacuum system was monitored by a Bayard–Alpert ionization gauge. Typically an overnight evacuation at room temperature followed before a detailed He leak test by the quadrupole mass spectrometer could be performed. Subsequent thermal treatment procedure included a ramping phase (30 °C/h), dwell at 150 °C (typically 4 h), and cooling (60 °C/h) to room temperature overnight. Finally, an additional He leak test was performed at increased sensitivity (base pressure ~2 × 10$^{-7}$ mbar).

### 2.3. Base thermal conductivity $\lambda_0$

For these measurements, only selected samples with a low outgassing rate within the range of densities $\rho$ = 55–75 kg m$^{-3}$ were prepared. A square thin-walled stainless steel envelope was designed, consisting of a frame made of 0.5 mm thick U-profile and a covering stainless steel foil of thickness 100 μm. The outgassing rates of empty envelopes were not measured directly, since the atmospheric pressure would deform the thin stainless steel foil. Therefore, almost identical, just smaller envelopes with dimension 100 × 100 × 20 mm$^3$, containing an inner stainless steel support, were prepared in parallel to determine the background outgassing rate.

The same two appendages as in the outgassing rate measurements were welded to the frame. The design of this envelope is not suitable for a VIP because of the thick U-profile edge, but it enables measuring of the perpendicular component of the base thermal conductivity $\lambda_0$ of the sample. Each sample with the size ~200 × 200 × 24 mm$^3$ was dried at 150 °C in air for 17 h before