Can polyisocyanurate nanofoam challenge aerogels? *)

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Abstract: After 40 years of development polyisocyanurate (PIR) insulation foams have become commercially successful commodity products with very desirable properties, like very low thermal conductivity, good fire resistance, low density and cheap, efficient manufacturing technologies. The industry strives to further improve their thermal resistance by reducing average cell size. However this approach has its theoretical limits due to the Knudsen effect and detrimental effects of cell size reduction on dimensional stability and aged thermal resistance of the foams. Further significant improvement of the PIR foams may be possible by changing their structure from closed cell micro-foams to open cell nanofoams, similar to morphology of silica aerogels and other polymeric aerogels.

Keywords: polyisocyanurate foam, polymeric foams, polyurethane foam, thermal conductivity, cell size, nanofoam, insulation foam, polymeric aerogel.

Czy nanopianka poliizocyjanurowa może rzucić wyzwanie aerożelom?

Streszczenie: W wyniku 40 lat intensywnych badań izolacyjnych pianek poliizocyjanurowych (PIR), służących poprawie ich pożądanych właściwości, stały się one bardzo popularnymi produktami. Cenionymi właściwościami pianek PIR, uzyskiwanych za pomocą tanich i efektywnych technologii produkcji, są: mała przewodność cieplna, dobra odporność ogniowa i mała gęstość. Wytwórcy dążą do dalszej poprawy ich oporności cieplnej przede wszystkim poprzez zmniejszanie średniej wielkości komórek. Jednak metoda ta ma swoje ograniczenia wynikające z efektu Knudsena, a także szkodliwego wpływu zmniejszania wielkości komórek na stabilność wymiarową i długoterminową oporność cieplną pianek. Inną metodą poprawy właściwości pianek PIR może być zmiana ich struktury z nanopianek zamknięto-komórkowych do otwarto-komórkowych, podobnych w swojej morfologii do krzemowych aerożeli i innych aerożeli polimerowych.

Słowa kluczowe: pianki poliizocyjanurowe, pianki polimerowe, pianki poliuretanowe, przewodność cieplna, wielkość komórek, nanopianki, pianki izolacyjne, aerożele polimerowe.

Polyisocyanurate (PIR) products started to claim nowadays the prominent place in the polyurethane (PUR) insulation industry. Despite the general perception of being a novelty material, PIR technology is already over 40 years old. In this time it went through a long evolution [1], which finally produced a very desirable material, with exceedingly good insulation value, fire resistance, and strength.

Producers of commercially available PIR products claim thermal conductivity (λ) declared of 0.021 W/(deg·m) (according to EN 13165 standard) — the best value among all commodity insulation materials. These products achieve high ratings in various fire tests: B-2 (DIN 4102), Euroclass B and C (EN 13823), FM, LPCB 1181, BS 476 Class O. They are very light, with density below 26—27 kg/m^3, yet still stable and shrinkage resistant. Some producers are able to manufacture > 20 cm thick boards. Thin boards can be produced at the speed exceeding 70 m/min. This makes the technology very economic and allows PIR to be competitively priced in the whole thermal insulation market.

Despite these already impressive properties, the industry still strives to do better. One of the main properties, which everybody aspires to improve even further, is thermal resistance.

THERMAL CONDUCTIVITY OF PIR FOAMS VERSUS CELL SIZE

Thermal conductivity of polymeric foams (λ) depends on the thermal conductivity of the polymer matrix (λ_p), thermal conductivity of the cell gas (λ_g) and the heat transfer through radiation (λ_r) and convection (λ_c):

$$\lambda = \lambda_p + \lambda_g + \lambda_r + \lambda_c \qquad (1)$$

Currently achievable density of PIR foam is very low, which means that there is little of the polymer in the foam

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[**)] Author for correspondence; e-mail: gm@polychemtech.com and thermal conductivity of the solid phase can be practically ignored. Two other major factors which bear more and more contribution to the λ of foam at this low density are: the thermal conductivity of the cell gases and the foam morphology, i.e. average size of the cells.

The efforts to improve λ of PUR/PIR foams concentrate nowadays mainly on the latter factor — reducing the average cells size [2—5]. In theory by reducing the cell size, it is possible to improve thermal conductivity of foams down to 5—8 mW/(deg · m) [6].

There has been a lot of research and development already done on reducing the PUR/PIR foam cell size, using special surfactants, nucleation additives and by redesigning the formulations. For instance the latest Bayer development published at [4] claims that Bayer's scientists managed to reduce the cell size by 40 %. This delivered improvement of thermal conductivity by 10 %.

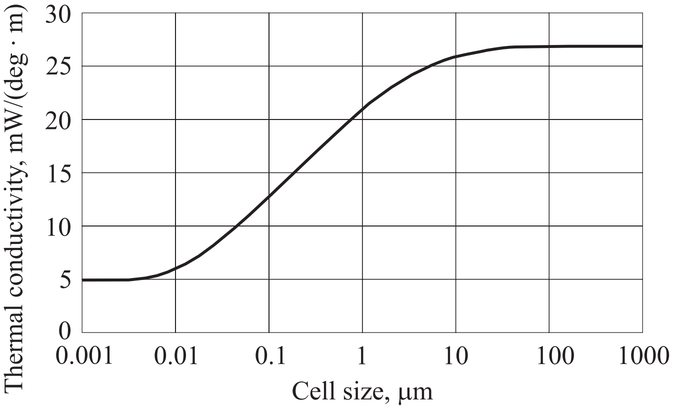

Fig. 1. Thermal conductivity of PUR foams as a function of the average cell size

The reason for this relatively slow, non-linear progress is shown in Fig. 1 depicting the Knudsen effect [6]. Visible improvement (decrease) of thermal conductivity is expected only when the average cell size becomes smaller than 1 µm. Significant improvement may be achieved only when the cells become smaller than 0.1 µm. Currently the average cell size in PUR/PIR foams is about 100—200 µm, so to achieve good thermal resistance, up to 1000-fold reduction of cell size is needed.

DIMENSIONAL STABILITY OF PIR FOAMS VERSUS CELL SIZE

However at a constant and already very low density foam (only commercially acceptable option), in finer closed foam cell the same amount of polymeric mass has to be spread over much wider area. The cell walls and to some extent also the struts are getting thinner and thinner. The thinner the walls the quicker gas exchange through the walls. The thinner the struts the lower compressive strength of the foam and its dimensional stability are.

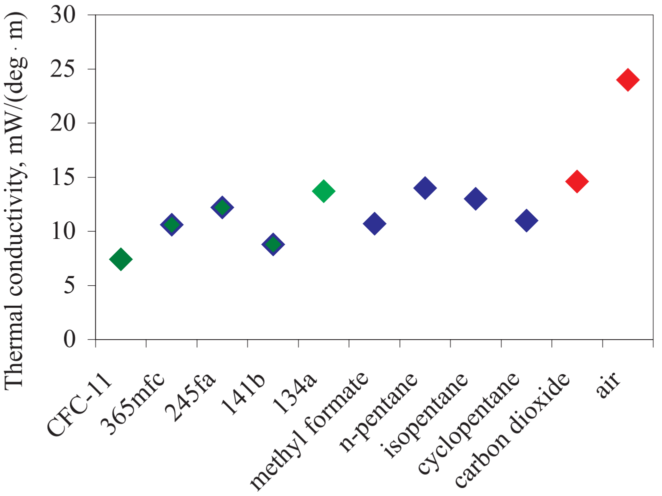

Fig. 2. Thermal conductivity of gases found in PUR/PIR foams (CFC-11 — trichlorofluoromethane, 365mfc — 1,1,1,3,3-pentafluorobutane, 245fa — 1,1,1,3,3-pentafluoropropane, 141b — 1,1-dichloro-1-fluoroethane, 134a — 1,1,1,2-tetrafluoroethane)

Fig. 2 shows thermal conductivity of blowing agents used to produce PIR foams [7—11]. Carbon dioxide has relatively good thermal resistance. It is only slightly worse than those of *n*-pentane or isopentane, the most common blowing agents used in PIR foams. Its thermal conductivity is also 60 % lower than that of the air. Unfortunately the use of carbon dioxide as a blowing or co-blowing agent is limited due to its high diffusion rate out of PUR matrix, much higher than the diffusion rate of air into the foam. The mismatch of the diffusion rates may deepen the partial vacuum already present inside cooled down, closed cell foam, which in turn can cause permanent foam shrinkage or even total foam collapse. More importantly, because the carbon dioxide migration is still relatively slow, shrinkage may become apparent only after a few days or even months, thus after the material has been already installed in its final application. Rectifying potential complaints then may be much more expensive than just the cost of the substandard products.

In low density foam the accelerated gas exchange and replacing carbon dioxide with air, not only decreases the dimensional stability, but may also worsen, more than expected, the aged thermal resistance of the material.

There is a complex, four variables relationship between foam cell size, thermal conductivity, mechanical strength and density (thus price) of the conventional PUR/PIR foams. These four properties are very tightly linked together. They affect each other and limit each other. After 40 years of constant and intensive R&D work on PIR improvement, it can be proudly said that the industry managed to get very close to the optimum point of this four dimensional relationship. It also means that the industry has reached almost „the end of the road". There is not much left what can be done to improve drastically the „classic", closed cell PUR/PIR foams as we know them today.

AN AEROGEL AS A MODEL MATERIAL FOR FURTHER PIR DEVELOPMENT

Fortunately there is another material, which can be an inspiration for further development of PIR insulation — the aerogel.

In its purest form it is a beautiful, magical material. It is the lightest solid material on the earth. It can have thermal conductivity as low as 4 mW/(deg · m). It is made of 5 % of sand and 95 % of air, so it is totally non-burning, ecological and in 100 % recyclable. It looks like an ideal insulating material. It would be if not for two major caveats: the price (it is also one of the most expensive materials on the earth), handling ability (although quite hard it shatters easily).

Fig. 3. Space shuttle insulation tiles made of aerogel

The aerogel is not new, it was discovered in 1931 [12, 13]. The real development of this technology took place in 1960s and 1970s during the cold war and „space race". It is literally a „space technology" and has been used to manufacture insulation tiles for the space shuttles (Fig. 3).

As with many other „space technologies", the aerogel eventually „descended to the earth". In the last decade aerogel based products got a good foothold in the specialty insulation market. Aspen Aerogels, GreenTech, Cabots and ThermaBlok already offer on commercial basis modified aerogel products. They claim good thermal conductivity < 14 mW/(deg · m), good fire resistance, easy handling and a bit more „down to Earth" prices.

The secret of aerogel's impressive thermal conductivity lies in its nano-size open cell morphology. This is what the new generation of PIR foam may aim at. Nano-size structure will provide excellent thermal resistance. Open cell (most probable fibrous) morphology ensures good dimensional stability, even at extremely low density. The air as the fill gas inside will satisfy the most discerned ecologists. In the absence of highly flammable hydrocarbons as the blowing agents, the PIR polymeric matrix will be able to perform to its best in any fire situation. Focusing straight away on using PIR polymeric matrix for this new generation nanofoams may provide interesting solutions for a wide range of applications.

RECENT DEVELOPMENT IN THE AREA OF POLYMERIC NANOFOAM PRODUCTS

The work on nano-porous polymeric foams has already started.

NASA's Glenn Research Center has developed new technologies to enhance the original silica aerogel and make the material more commercially attractive. They used different polymers (including isocyanates and polyureas), to reinforce silica aerogel [14, 15].

In the PUR industry Bayer scientists research a POSME (principle of supercritical microemulsion) technique, in which carbon dioxide and liquid PUR raw materials with special surfactants are mixed under high pressure [16].

The technology exploiting supercritical CO_2 is used to make aerogels using other polymers as well: syndiotactic polystyrene, poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) [17, 18], resorcinol-formaldehyde polymers [19], polyimide [20, 21], epoxies [22], polyacrylates, polyurea, etc. [23].

Using supercritical CO_2, still makes the technology expensive and difficult, so the possible applications of these materials are at the moment restricted to highly effective sorption materials, extreme weather clothing, cryogenic and very high temperature vessels, offshore pipe insulation, architectural day-lighting, filters, etc.

However Cabot based in Germany, claim to have developed a commercially viable continuous process that allows production of aerogel materials under ambient conditions. Their material has λ values 9—12 mW/(deg · m) and density 30—100 kg/m^3. It is hydrophobic and translucent. Svenska Aerogel AB also announced having low cost, ambient temperature and low pressure aerogel technology.

Is there a cheap and easy technology, which will allow PIR to enter its new nano-chapter and match the aerogel's insulation performance?

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