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Physics Procedia 32 (2012) 239 – 244
Physics Procedia

Proceedings of IVC 2010

A Review of Vacuum Degradation Research and the Experimental Outgassing Research of the Core Material- PU Foam on Vacuum Insulation Panels

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Abstract

Vacuum Insulation Panels(VIPs) have been regarded as a super thermal insulation material with a thermal resistance of about 5-8 times higher than that of equally thick conventional polyurethane boards. In this paper, the researches on factors influencing interior pressure in VIPs, including gas and water vapor permeation through the barrier and outgassing of the core materials, were reviewed respectively. Following this, aiming at the outgassing from open cell PU foam, the specific outgassing rate of the core material is tested not only at room temperature but also at low and high temperatures by an orifice known-conductance method.

Keywords: Vacuum insulation panel; Vacuum degradation; PU foam; Outgassing

1. Introduction

The growing concerns over global energy crisis and the phasing out of polyurethane foams blown with CFC-11, which has high Ozone Depletion Potential(ODP), have pushed thermal insulation technology to improve its efficiency. VIPs consist of a filler material that is encapsulated by a thin, super-barrier film. The encapsulated system is then evacuated to a vacuum between 0.01 and 1mbar and sealed[1-3]. The actual vacuum required depends on the specific core material used and the desired thermal resistance of the finished panel. In addition, getters or dessicants are essential to absorb residual gases in order to maintain the vacuum level. Twenty-five percent of the energy consumption can be saved without an effective volume decrease of the refrigerators or freezers when VIPs are substituted for part of the polyurethane rigid foams as the insulation layer.

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doi:10.1016/j.phpro.2012.03.549

The thermal insulation performance of VIPs is greatly depending on the vacuum level. When interior pressure surpassing 1mbar, thermal conductivity of a VIP with core materials of foams or glass fibers will increase sharply. While regarding kernel of silica powders, the pressure at which thermal conductivity of a VIP starts to increase significantly will be postponed to about 10mbar for precipitated silica and 100mbar for fumed silica respectively, as shown in Figure 1[4].

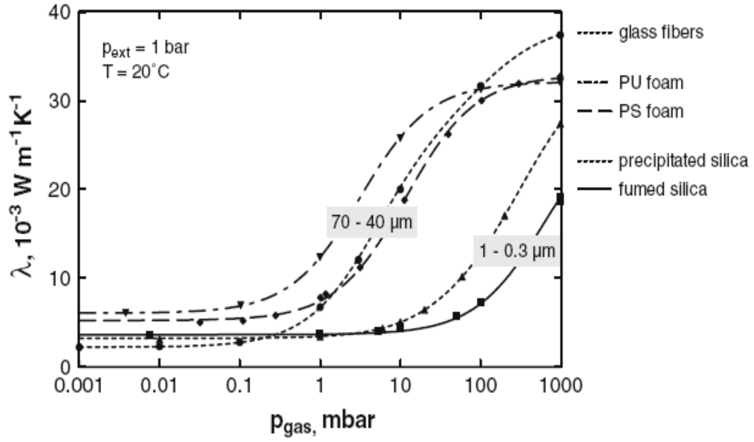


Figure 1. Thermal conductivity of fibers, powders and foams as a function of gas (air) pressure

During the service life, climatic conditions have a great influence on the degradation of VIPs. Firstly, permeation of dry atmospheric molecules(O_2, N_2, CO_2, etc.) through a more or less permeable barrier film surface or the edges and seams will contribute to the vacuum deterioration. Secondly, water vapor infusion will cause the total pressure increase[5]. Not only the pressure increase within the VIP but also the penetrated water vapor that is adsorbed by the core material will lead to a direct increase in the thermal conductivity of the evacuated porous core materials[6]. Thirdly, the degradation effect is also related with panel size and outgassing rate of the core material in a VIP. A review on vacuum degradation research will be focused in the first part of this paper.

Besides the review, the quantitative effect of the outgassing of the core material will be studied in the second part of the paper. The vacuum inside VIPs will be influenced by the degassing of the core material after putting it into vacuum conditions. Recently, the outgassing rate of many materials under vacuum has been measured. Not only outgassing of stainless steel, which is often used under vacuum conditions, was measured, but also other metals and nonmetals were researched including alloys, stacked laminations, CPVC, textile materials, polyethylene sheet, plastics, etc[7-9]. WEI-HAN TAO[10] discussed the influence of drying temperature and time of open cell foam on the thermal conductivity of VIPs and got the conclusion that baking pretreatment of the 100% open cell foam have an obvious influence on the thermal performance of VIPs. Outgassing measurement was also carried out at room temperature on a bankable stainless steel bench equipped with a quadrupole mass spectrometer in order to develop effective getters used in VIPs by Paolo Manini[11]. The source and quantity of the gas contributions causing the pressure to increase due to outgassing of the core material in the VIP has been obtained by Richard[12]. Not only the core material of polymer staggered beam but also the envelope surface outgassing phenomenon were studied with the pressure rise method by Jae-Sung Kwon[13], with the gas load conclusion of 1.11×10^{-9} and 5.66×10^{-10} Pa・L/s for the core material and polyethylene envelope respectively.

2. Review of vacuum degradation research on VIPs

2.1Recent experimental researches on gas and vapor permeation through barrier films

There are two types of barrier films used to resist the permeation of gases and water vapor into VIPs. One is metal foils(AF) consisting of a central aluminium barrier layer, laminated between an outer PET layer for scratch resistance and an inner PE sealing layer, and the other is metallized films(MF) made from up to three layers of aluminium coated PET films and an inner PE sealing layer[14,15]. The anti-permeation performance of barrier films has been investigated deeply and comprehensively in Germany and Switzerland. The rate of pressure rise and mass increase in VIPs with different foils and panel sizes were tested under specified conditions of different temperatures and relative humidities by Schwab etc[16]. It can be concluded that the air and vapor transmission rates of the foil covers depend on temperature, relative humidity, foil type and panel size. The higher the temperature and humidity, the lager pressure increase occurs in VIP, which can be contributed to the concentration difference and the transmission ability of gas and vapor. It is interesting that if the panel circumference L is doubled, approximately one half of the rate of pressure increase occurs. The author indicated that the pressure increase is mainly caused by the length-related gas transmission rate[16]. The influence of moisture on thermal conductivity also has been investigated. The increase is about 0.5×10^{-3} W/(mK) per mass% of water. For typical middle European climate, a maximum moisture content of about 6 mass% can be expected, which corresponds to a maximum increase of thermal conductivity of about 3×10^{-3} W/(mK) for VIPs with fumed silica kernels[17,18]. Martin etc.[19], from a real construction perspective, gave an overview of the requirements for and the behaviours of VIPs integrated into building components and constructions according to the results of predecessors.

Brunner[20] focused on the deterioration of the barrier function of two different MF laminates with defects in the laminates visualized by means of focused ion beam etching. Simmler and Brunner[21] did an experiment for VIP used in a real terrace building on a hill side to investigate the aging mechanism and results for different temperature and humidity induced deteriorations. A larger temperature and humidity range were adopted than that of Schwab's in order to evaluate the more practical applications. The trends of all factors are as same as Schwab's. There is a new discovery when using a cyclic condition (8h at 80℃/80% R.H. and 4h at 25℃/50% R.H.), in which pressure and moisture content increase rate are more severe than a constant 80℃/80% R.H.. This may arise either from shear strain or by cyclic condensation of water on the ‘‘cold’’ VIP surfaces being delayed in temperature–humidity rise periods.

2.2 Recent models to predict pressure increase and resultant increase in thermal conductivity of VIP

A linear increase in pressure in VIP was got on the assumption of a constant climatic conditions and pressure difference across VIP[17]. Based on the total gas transmission rate, which includes the surface-related(gases permeate through the surface of barrier film) and length-related(gases permeate through the sealings) transmission rate, the pressure –related gas transmission rate, called permeance, was got. Through that, accompanied by ideal gas equation, the pressure increase with time was obtained. The change of water content with time can be calculated based on sorption isotherm of different cores[16]. Then, the total thermal conductivity, which consists of the thermal conductivity of the core in the evacuated and dry state, gaseous thermal conductivity at a certain gas pressure caused by gas permeation and thermal conductivity induced by water content, can be calculated. A dynamic thermal model to predict the internal pressure in VIP was also developed on the basis of experimental results for different temperature and humidity induced deteriorations of MF and AF barrier films[21,22]. In the model, the influences of temperature and humidity on the pressure increase were described by Arrhenius function and sorption isotherm respectively. With the model, the thermal conductivity of VIP over time of 25 years was calculated with some measured data.

Some numerical models were also developed to predict the degradation of barrier films. The pinhole theory introduced by Decker[23] was the basis of numerical models. A three dimensional diffusion problem was modeled through standard Finite Element Analysis software[24]. Focused on the oxygen transmission rate (OTR), the model provides an approximate OTR for barriers that have an OTR below the current limits of testing, as well as an alternate barrier construction design direction. A promising application of VIPs in buildings with extruded polystyrene (EPS) foam as protective layer was analyzed both numerically and experimentally[25]. It is indicated that the integration of VIP with EPS foam as protective layer in construction can greatly decrease insulation thickness by 3.5 times compared with the traditional insulating material with a thermal conductivity of 0.036W/(mK). In addition, the protective foam added can reduces the edge effect of the VIPs caused by the aluminum layers within their barrier envelope.

3. Experimental research on the specific outgassing rate of open cell PU foam used in VIPs

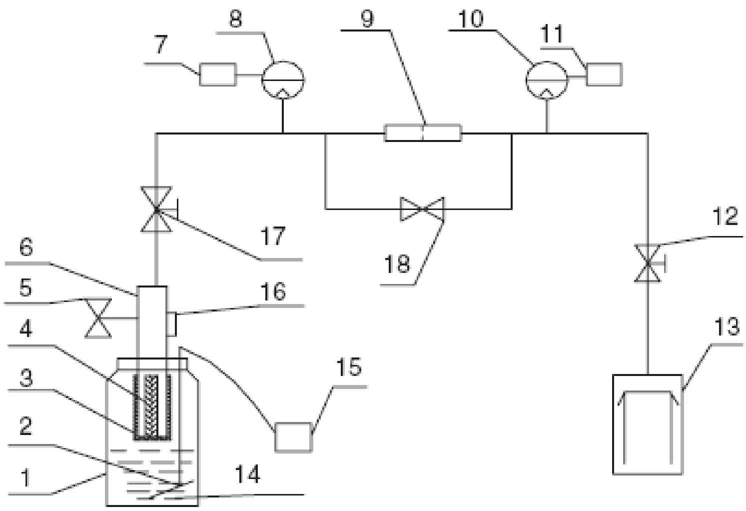
3.1 Materials and experimental apparatus

There are some special characteristics for the PU foam used as the core material to meet the stringent requirements for VIPs, such as a low thermal conductivity, a high open-cell content, a high compressive strength, ect. The foam used in the study was prepared by a blend polyol, which is a mixture of two types of polyethers with different OH value, combined with appropriate amount of surfactant, open-cell agent, multiple catalysis, blowing agent and foam stabilising agent[26]. The reactants were mixed at room temperature, and the mixing speed and times were 1500 r/min and 8 – 10 s, respectively. Then the reacting mixtures were poured directly into stainless steel boxes (40℃) and allowed to rise freely, then demolded after 5 min. The properties of the foam panels were measured after the foams were aged at 70℃ for 24 h (Table 1).

Table 1. Properties of the foam sample

property	value
Open cell content/%	≥95
Cell size /μm	150～200
Density/kg • m^{-3}	55～65
Thermal conductivity/W • $(m • K)^{-1}$	≤0.010
Compressive strength /MPa	0.2-0.3

There are a few outgassing measurement methods such as throughput method, pressure rise method, total mass loss method and gas collecting method. The throughput method was adopted in this study to overcome difficulties of readsorption of the pressure rise method and the disadvantage that can not be used conveniently to dynamically analyze of total mass loss method and gas collecting method [7,27]. In the experimental system, as shown in Figure1,



1: Dewar, 2: heater, 3: heating jacket, 4: sample, 5,17: flapper value,
6: sample chamber, 7,11: vacuum ionization gauge, 8,10: ionization gauge, 9: orifice,
12: high vacuum value, 13: vacuum pump, 14: liquid nitrogen, 15: transformer,
16: thermal couple interface, 18: diaphragm valve.

Figure 2. Experimental equipment

a baking or cooling stainless steel chamber with wall thickness of 0.3mm and length of 400mm is connected with vacuum pumping unit by an orifice with a diameter of 5mm. There are two vacuum gauges located on the upstream side and down stream side of the orifice respectively. A heating tape is wrapped on the out surface of the sample chamber to get high temperature measurement condition . A low temperature can be obtained by putting the sample chamber in gas phase in a Dewar, which contains liquid nitrogen. At low temperatures, the temperature was controlled by the evaporation rate of liquid nitrogen, which was controlled by the power of the electrical heater in the liquid nitrogen. Before outgassing test of the foam core, the test apparatus was baked at 200℃ for 24 hours to minimize outgassing from stainless steel chamber and gauges. After the pretreatment, a blank experiment was performed to evaluate the background outgassing rate, which proved to be neglectable compared with that from nonmetal foam materials in the results.

3.2 The influence of temperature and baking pre-treatment on the specific outgassing rate

In order to investigate the temperature influence on outgassing of the PU foam, outgassing experiments at -25, 5, 30, 45, and 70℃ were performed respectively, and the results are shown in Figure 3. It can be seen that the specific outgassing rate decreases with decreasing temperature. The desorption ability of gases on the surface of the sample is enhanced due to high temperature, and this will lead to a decreasing gas concentration on the surface. As a result, diffusion rate of gases in the bulk will increase because of the increasing gas concentration gradient. Additional thermal energy of gases in the sample caused by high temperature will accelerate gas diffusion from the bulk too. All these make the obvious outgassing rate at high temperature higher than that at low temperature.

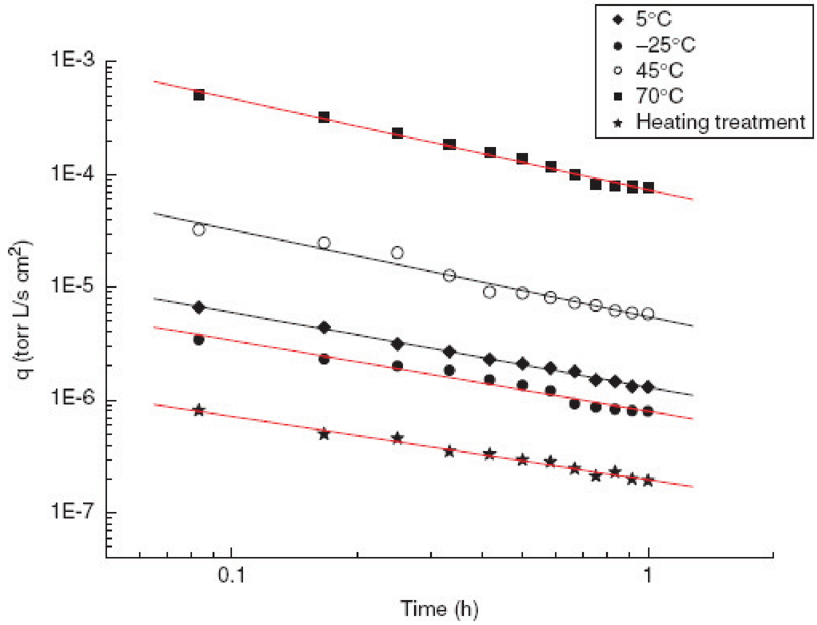


Figure 3. Specific outgassing rate at different temperatures

A temperature-adjustable oven was used to bake the sample to account for the baking pre-treatment effect of the sample outgassing in vacuum condition. The weight of this PU foam became constant after baking at 120℃ for 15min. Compared with the literature [10], the baking time to obtain constant weight of a foam is a little longer. This is because of the different formulation and manufacturing process. In order to get a long-term good performance of a VIP, baking is needed before it is sealed in the vacuum bag made of barrier materials. As can be seen in Figure 3, the specific outgassing rate of the baked foam is obviously less than that of unbaked foam at room temperature. This indicate that a baking pretreatment under a certain temperature within an appropriate time is necessary before the sealing of the sample.

4. Conclusions

VIPs have been regarded as one of the most super heat insulation material used in buildings, refrigerators, freezers and water heaters etc. Most studies focus on how to maintain the appropriate vacuum inside the panel to provide a better thermal performance and a long service life. Lab scale experiments, analytical and numerical measures have been simultaneously used to get the basic data of gas and water vapour permeation through barrier films in order to enhance the film's anti-permeation ability while decreasing the thermal bridge effect. Recently more and more researchers pay attention to outgssing from the core material and high efficient getters. In this paper, specific outgssing rate of the open cell PU foam was studied experimentally, in which a wider temperature range and baking effect were studied in order to provide basic datas to meet the requirements of different application fields. The experimental outgassing research can help to determine the optimal quantity of getters inserted into VIPs and improve the core material microstructures.

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