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RESEARCH ARTICLE

Moisture Behavior of Thermal Insulation Coating Consisted of Vacuum-Hollow Nano-Ceramic Microspheres

Dávid Bozsaky[1]

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Abstract

Nanotechnology-based thermal insulation materials have appeared in building industry in the last two decades. Among them thermal insulating coatings consisted of vacuum-hollow nano-ceramic microspheres are the subjects of most professional discussion. Most studies about these coatings focus only on examination of thermodynamic properties, because there is still no consensus in academic circles about thermodynamic processes inside nano-ceramic coatings. These professional discussions distract attention from other unknown but also important material properties, like behavior by contact with moisture. This paper summarizes the results of moisture behavior tests with nano-ceramic thermal insulation coatings which were conducted to determine the time trend of water absorption, as well as volume, mass and thermal insulation quality changes caused by increasing moisture content. Analyzing the results mathematical connections were found to describe the relation between water content, dimensional and thermal conductivity changes.

Keywords

nano-ceramics, thermal insulation coatings, moisture behavior

1 Department of Architecture and Building Construction
Faculty of Architecture, Civil Engineering and Transport Sciences
Széchenyi István University
H-9026 Győr, Egyetem tér 1, Hungary
* Corresponding author, email: bozsaky@gmail.com

1 Introduction

Regulations about thermal insulation quality of buildings became extremely rigorous in the 21st century because building and construction industry is a prime consumer of world's material and energy resources which accounts nearly for 40% of usage [1][2]. These requirements are often very difficult to accomplish with traditional insulating methods because excessive structural thickness is required to achieve appropriate thermal insulating effect an environmental impact of building structures [3][4][5]. One of the principal topics of sustainable construction is to minimize or eliminate the negative effect on environment, what became a point of interest of civil engineers, architects, designers and researchers [6]. Therefore; they are forced to use high-performance thermal insulation materials to provide adequate thermal insulating effect with a relatively low structural thickness [7][8].

Use of nanotechnology-based thermal insulation materials offers an alternative solution for this problem [9]. Among nanotechnology-based thermal insulation materials thermal insulation coatings consisted of vacuum-hollow nano-ceramic microspheres receive the most criticism in academic circles. Particularly their thermal insulation quality, because of the contradictory technical data that could be found in special literature and in producers' handouts about thermodynamic properties of thermal insulation coatings consisted of vacuum-hollow nano-ceramic microspheres. Wide ranges of theories have been set up about the thermodynamic process inside the nanostructure of thermal insulation coatings. Various data can be found about their thermal conductivity that was measured by several researchers with different methods. This paper does not try to summarize the current results of thermodynamic tests about nano-ceramic coatings because it focuses on hydrotechnical research. The summary of these studies can be found in previous articles [10][11].

Most research papers and studies are exhausted with thermodynamic experiments and they do not pay attention to other important but also unknown properties of nano-ceramic coatings. They also do not specifically deal with hydrotechnical properties even though effects of moisture are always cardinal issues for thermal insulation materials [12][13][14][15][16][17]. Most important materials characteristics of moisture behavior are water absorption, moisture-induced deformities and effects of moisture on thermal insulation quality. Unfortunately only a few experiments have been carried out formerly, which have only investigated short-term water absorption. Relative humidity was varied from 25% to 90% at 293 K for 2 hours. The samples were wettedfor 2 and 4 hours as well. Sorption and desorption as well as kinetic curves were presented [18]. However; these experiments did not provide complete information about the moisture resistance of nano-ceramic coatings.

2 Nano-Ceramic Coatings

Synthetizing of nano-ceramic microspheres was developed in 1984 by S. Komarneni and R. Roy. This process called 'sol-gel' and enabled researchers to test properties of nano-ceramics [19]. To produce nano-ceramics at a more efficient way this process was replaced by microwave sintering in the 2000s [5].

Most paint-on insulation products contain microscopic vacuum-hollow ceramic microspheres with a diameter of 20–120 μm and with a cellular wall thickness of 50–200 nm. Nano-ceramic coatings are made of melted glass or ceramics on high gas-pressure and high temperature (1500 °C). After cooling down, the pressure ends, leaving vacuum inside the microspheres. A mixture of synthetic rubber and other polymers is used as binding materials. Its main components are styrene (20%) and acryl latex (80%). Styrene enhances mechanical strength and acryl latex makes nano-ceramic coating resistant against weather conditions and provides flexibility. Other additives (e.g., biocides, anti-fouling and antifungal materials) make the final product durable and mold-proofed [10][20].

Nano-ceramic coatings are typically used for exterior and interior wall insulation, but they are also suitable for pipe insulation and protection against fire and corrosion. They can be easily transmitted to hard-to-reach places [10][20][21].

3 Former Experiments

In 2014–2017 series of thermodynamic test were conducted in the Laboratory of Building Materials and Building Physics at Széchenyi István University (Győr, Hungary). The average thermal conductivity in air-dry condition was 0.0690 W/mK [10][11]. Other experiments showed that thermal insulating quality of nano-ceramic coatings could be caused by their high surface heat transfer resistance. Test results also evinced that thermal insulating ability of nano-ceramic coatings prevails otherwise on different kind of surfaces. Insulation effect depends not only on the thickness of the air gap but also on the material of the insulated surface. Presumably the same material quality, composition and application technology may not be suitable for insulating different kind of surfaces [10][11].

In parallel with the examination of thermal insulating quality, only Experiment 1 was conducted in 2014 in order to analyze the effects of moisture content on materials characteristics. Results were published, but further research focused on thermal insulation quality, therefore; there has been no progress in this research topic for a long time. In Experiment 1 dimensions, mass and density of the samples were measured according to EN 822:2013, EN 823:2013 and EN 1602:2013 standards. Then thermal conductivity was measured according to EN 12667:2001.

After this procedure samples were dried to constant weight in a standard drier cabinet. Dimensions, mass, density and thermal conductivity were measured at certain intervals and in the end in air-dry condition.

Analyzing the connection of thermal conductivity and moisture content it was proved that the difference between thermal conductivity in air-dry condition and with a water content of 12% m/m is unnoticeable (each has 0.0690 W/mK value). Passing this limit a linear relationship was found between thermal conductivity and moisture content. It is declarable that thermal conductivity is directly proportional to moisture content after a limit of 12% m/m (Fig. 1). This moisture content can be termed as natural water content, which has no effect on thermal conductivity. This attribute is very similar to natural thermal insulation products (wood wool, fiberwood, cornstalk insulation blocks etc.) even though liquid nano-ceramic insulation coatings are not nearly natural, organic materials [10][11].

4 New Research Directions

Following the successfully closure of Experiment 1, main focus of further laboratory tests was determining thermodynamic properties of nano-ceramic coatings. Many results and conclusions were born on this subject and they were published in 2015-2017. Recognizing the same importance of moisture behaviour, in parallel with thermodynamic tests, hydrotechnical studies have also begun in the Laboratory of Building Materials and Building Physics at Széchenyi István University (Győr, Hungary).

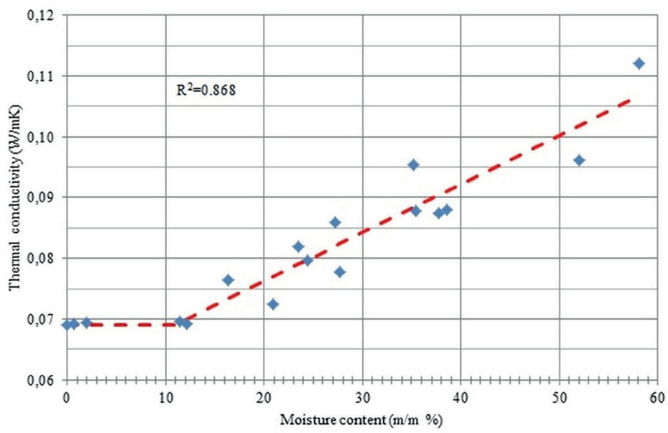

Fig. 1 Relation between moisture content and thermal conductivity in Experiment 1 [10][11]

In order to thermal conductivity to be measureable with reliable accuracy directly according to EN 12667:2001 samples with a minimum thickness of 20 mm were necessary. Therefore; a total number of 9 (3 × 3) samples were made for these measurements with an area of 300 × 300 mm with 3 different thicknesses (25, 30 and 35 mm). The fresh liquid nano-ceramic mixture was sprayed into wood frames and left for solidifying. After two days the samples were solid enough to take out from the formwork and they were suitable for laboratory tests [10][11]. Samples were prepared by the manufacturing company that provided only approximate data about the raw material. The composition is patented and manufacturers generally do not give completely accurate details about the product. It could be definitely stated that the examined coating was outside façade insulation. Wide limits (20–50 m/m %) were given about the ratio of the binder material, but certainly it neared the lower limit because coating was sprayed on the surface of samples and low ratio of binder material is ideal for spray technology.

These tests were conducted in two phases. In first step (Experiment 2) experiments concentrated to determine the end point of moisture absorption and to monitor the time trend of water absorption and concurrently occurring volume and weight changes. In the next step (Experiment 3) main focus was to determine the time of fully dehydration, and to monitor the evolution of material consistency, the time trend of mass, volume and the concurrently occurring thermal conductivity changes caused by moisture content changes.

4.1 Experiment 2

During Experiment 2 samples were placed into a water tank to conduct long-term water absorption test with full immersion according to EN 12087:2013. As required by this standard, water absorption should be determined as a percentage by volume (V/V %) or by weight (m/w %) after 28 days of water immersion compared to air-dry condition [22]. However; the date of saturation was unknown, and it was also important to document the evolution of water absorption process in time. Therefore; contrary to the regulations water absorption was determined not only after 28 days but at several intervals before and after it. Dimensional changes were also observed. The width (a), length (b), thickness (v), and mass (m) of the samples were measured after each period of time by which it was possible to calculate dimensional changes – width (Δa), length (Δb), thickness (Δv), volume (ΔV), density ($\Delta \rho$) – and water absorption (W). Results showed that water absorption of nano-ceramic coating after 28 days is 28.81 m/m %, but samples did not at all became fully saturated after 28 days. Therefore; Experiment 2 was continued until samples reached a constant weight. The last three weights were recorded on days 685, 729 and 846, during which there was no apparent increase in water absorption.

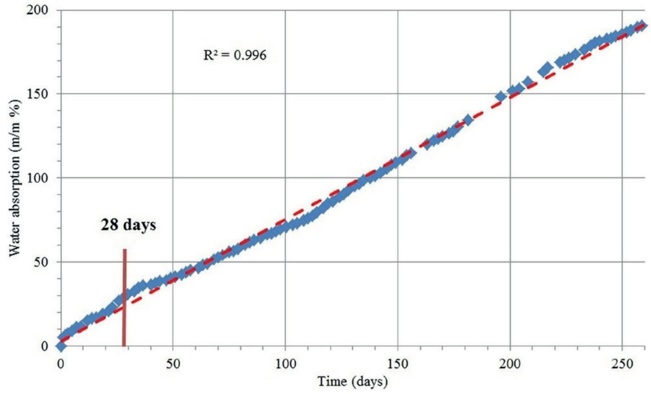

Fig. 2 Time trend of water absorption (1–260 days)

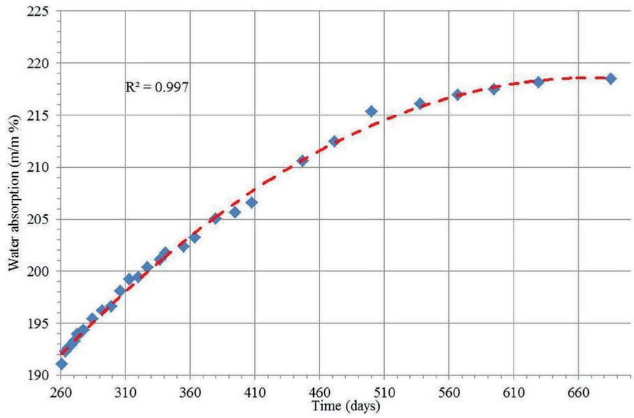

Fig. 3 Time trend of water absorption (after 260 days)

It was also found that water absorption of nano-ceramic coating is 6% in the first 24 hours. Examining the further development of water absorption it can be concluded that after the first day evolution of water absorption continues along a linear function (Fig. 2).

Using nonlinear regression it has been proved that water absorption after the 260$^{\text{th}}$ day increases according to a second degree function (Fig. 3) and the specific equation was defined:

$$W = -1{,}51 \times 10^{-6} t^2 + 2{,}06 \times 10^{-3} t + 1{,}49. \qquad (1)$$

In Eq. (1) W means water absorption in m/m % and t means time in days. The function was perfectly matched to measurement results (R^2 = 0.997). Deriving this real-valued function, it was possible to determine the global maximum point which is equivalent with the volume of water absorption endpoint. This value was calculated to be 218.85 m/m %, which occurs after 680 days. This is considered to be the theoretical full saturated condition.

Analysing the functions of Fig. 2 and Fig. 3 it could be concluded that water absorption is completely permanent until the 260$^{\text{th}}$ day. In the next 260 days (until the 520$^{\text{th}}$ day) significantly increasing water absorption is expected. Samples are nearly saturated to constant weight on the 520$^{\text{th}}$ day but they require additional 160 days to be fully saturated. This extremely low saturation process could be explained by the nanostructure of the material. Water can infiltrate excessively slow into nanopores; therefore saturation process is considerably prolonged compared to conventional thermal insulation materials.

4.2 Experiment 3

After finishing Experiment 2 samples were placed into a drier cabinet and they left to dry out to constant weight under normal laboratory circumstances (23±2 °C, 50±5% relative humidity). Dimensions, mass, density and thermal conductivity were also measured in certain intervals.

Thermal conductivity of nano-ceramic coatings was measured directly with a standard Taurus TCA 300 heat flow meter on samples with a thickness of 20 to 35 mm. Heat flow is induced by electrical heating using a resistor heater having a direct thermal contact with the surface of the sample [23]. Each sample was tested 3 times. It is well-known that the accuracy of Taurus TCA heat flow meter is up to 5% and these results might be fluctuations in measurement limits. However, in fact, in 87% there were no deviation between 3 test results of an individual sample, and in 13% the difference was only ± 0.0002 W/mK which means really 0.1–0.3% accuracy.

Results were basic data to monitor changes in moisture content and release as well as dimensional, consistence and thermal conductivity changes. Linear and nonlinear regression methods were used for determining the mathematical relationship between different variables. Using nonlinear regression it was found that dimensional (volume) and mass changes could be described by logarithmic mathematical functions (Fig. 4 and Fig. 5).

Time trend of mass changes could be described by Eq. (2) and time trend of volume changes by Eq. (3):

$$m = -396.2\ln(t) + 4498.5 \tag{2}$$

$$V = -206.5\ln(t) + 4720.1 \tag{3}$$

In Eq. (2) and Eq. (3) m means mass in gram, V means volume in cm^3 and t means time in hours. Both equations matched perfectly to measurement results because in case of Eq. (2) $R^2 = 0.991$ and in case of Eq. (3) $R^2 = 0.989$.

It could be observed that mass and volume changes are extremely intensive in the first 10 days (240 hours). After 10 days drying process slows down rapidly but changes are also relatively high until the 100th day (2400 hours). After 100 days the slope of the function decreases considerably and dehydration until constant weight occurs on the 225th day (5400 hours).

Analysing the relation between moisture content and thermal conductivity a linear function was found to describe the relation between them. A linear mathematical relationship was also found between moisture and thermal conductivity changes based on the values measured in air-dry condition (Fig. 6 and Fig. 7).

It can be stated that increasing moisture content significantly and permanently decreases thermal insulation quality of nano-ceramic coatings. It could also be shown that increasing

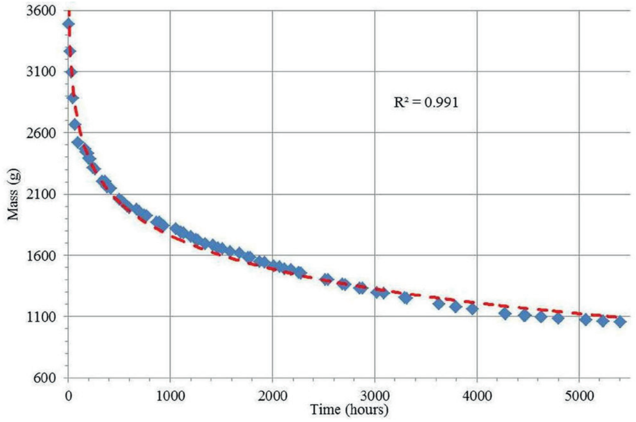

Fig. 4 Time trend of mass changes

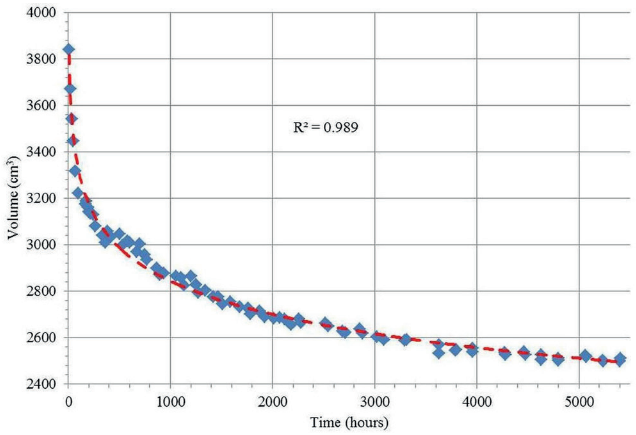

Fig. 5 Time trend of volume changes

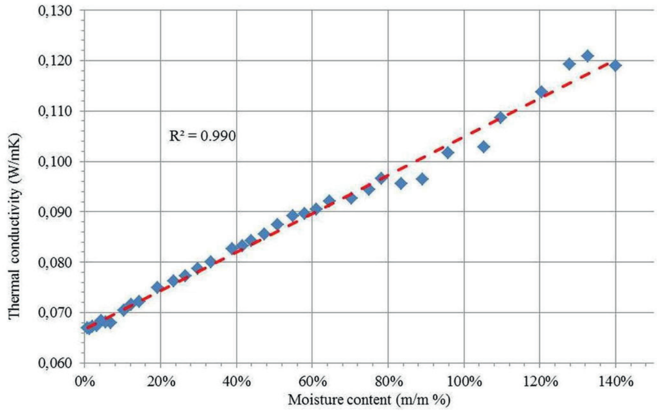

Fig. 6 Relation between moisture content and thermal conductivity

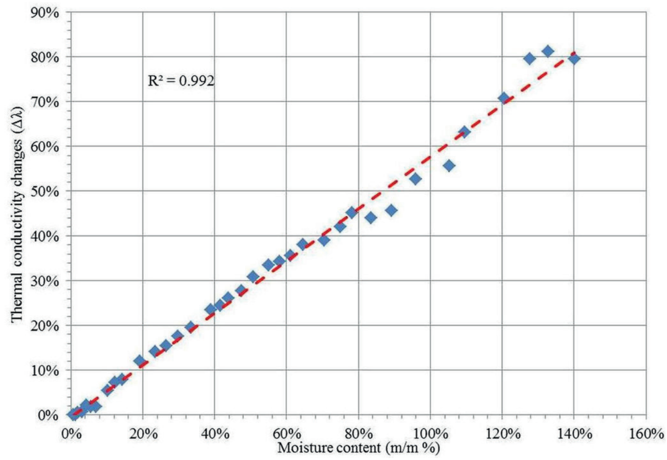

Fig. 7 Relation between moisture content and thermal conductivity changes

moisture content could double thermal conductivity (140% moisture content causes 80% increase of thermal conductivity). However; it should also be added that due to the extremely slow water absorption, only a sufficiently long-time moisture effect can cause high degradation of thermal insulation quality. In order to reach 140% moisture content nano-ceramic coating 190 days full immersion (Fig. 2). This incident does not occur in normal architectural practise.

Furthermore; it was also determined that after one cycle of drying-saturating-drying the material to constant weight, it does not lose its original consistence and thermal insulation quality.

5 Conclusions

Former laboratory experiments in the Laboratory of Building Materials and Building Physics at Széchenyi István University (Győr, Hungary) were conducted to clearly determine and describe the thermodynamic process inside nano-ceramic coatings. Laboratory tests showed that nano-ceramic thermal insulation coatings probably do not have an extremely low thermal conductivity that was described by the available documents of producers and distributors. The hypothesis was also partially seemed to be proven that insulating effect of nano-ceramic coatings comes from a relatively high surface heat transfer resistance.

Recent research has examined the effects of moisture on different material properties. Main focus was the time trend and limit of water absorption and the parallel thermal insulation quality changes caused by the increasing moisture content.

It has been proved that water absorption endpoint does not occur in 28 days compared to conventional thermal insulation materials, however; this process is much longer. Water absorption limit was determined at 218.85 m/m % and it was calculated to be on the 680^{th} day. A mathematical relationship was also found to describe the time trend of water absorption. It was found that water absorption follows a linear function in the first 260 days, after 260 days it turns to a second degree function. It has been also demonstrated that both mass changes and volume changes occurring in parallel to the increasing moisture content are following logarithmic functions.

Analyzing the relation between moisture content and thermal insulation quality it was found that the increase of moisture content is directly proportional to the increase of thermal conductivity. It was also found that there is a moisture content limit (12 m/m %) which has a negligible impact on thermal insulation quality. This material property is very similar to the phenomenon known as natural moisture content of organic materials.

Beside of further studying the thermal insulation ability of nano-ceramic coatings in built-in state, investigating the durability, weather and fire resistance also offers additional research opportunities.

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