

Predictable building enveloping based on passive reactive functionalized TiO₂ glass foam

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Abstract. Foam glass PINOSKLO was enveloped with 1-4 layers of coating containing TiO₂ to study the thermal efficiency and the changes of the reflection spectrum in correlation with the number of layers. Time and temperature process parameters were controlled to have reliable results for all enveloped foam glass. The morpho-structural and optical properties of the enveloped foam glass were studied by X-ray diffraction (XRD), Fourier transform-infrared (FT-IR), Raman and ultraviolet-visible (UV-Vis) spectroscopy, scanning electron microscopy (SEM) and laser microscopy. We find that the thermal reflective heat-insulating property is significantly improved by TiO₂ coating enveloping so that the functionalized foam glass presents a reflectance with 78% higher for the four-layer enveloped foam glass when compared with non-layered glass foam. The enveloping foam glass with TiO₂ is an effective method to increase its thermal screen performance, reflecting a large part of the radiation. This makes TiO₂-enveloped foam glasses are efficient for thermal insulation of almost any part of a building like foundation, walls, interiors, or roofs, providing high resistance to light and temperature.

Keywords: passive insulation, active insulation, glass foam, heat control layering, reflective TiO₂

Introduction

In recent years, foam glass characterized by features such as ecological sanitary safety and cleanliness effect led to a global renaissance concerning new designs of insulation materials due to fire and ecology issues and due to the development of the continuous process which provides new and revolutionary energy solutions for residential construction, public and commercial buildings and industrial installations and local construction sector [1]. Cellular glass is an inorganic insulating material, with a closed cellular structure, light produced from glass waste with a texture like basalt shingles, but its weight is a fraction in comparison, so it is transported much more efficiently. Due to the appropriate technical and energetic properties such as lightweight, compression resistance, acts as a barrier against vapors, flame resistivity also not interacting with organic solvents and acids, also is an excellent sound insulation, often used in the construction of sound protection panels [2]. Compared to fibrous materials [3] that have needle-like dust which cause serious diseases after contact with the skin and respiratory system [4] and with polystyrene which is susceptible to the pathogenic disintegration of polymers to free radicals it is clear that

cellular glass does not injure and by its destruction presents the shape of crumbs - completely harmless glass honeycomb being an excellent option for any long time construction project.

Depending on the end use of the glass foam, the pore connection can be classified into two types with open pores or closed pores. To be applied as an acoustic absorber, it is necessary for the pore structure to be open. For thermal insulation the closed pore structure is beneficial, because the large amount of closed air in the pores ensures a perfect resistance to heat transfer, while it does not absorb moisture, being a product resistant to the action of frost-thaw [5].

In order to conserve energy, we proposed a reflective thermal insulation coating that can be used as a building material on the exterior wall. In our study in order to improve considerably the thermal insulation we choose titanium dioxide (TiO_2) because is the most efficient material and possesses a number of suitable properties. These properties are its high permittivity, refractive index and efficiency as well its low cost, chemical inertia, non-toxicity, photocatalytic activity, photostability and the ability to decompose a wide variety of organic compounds.

The use of solar reflective coatings characterized by high solar reflectance and infrared emission values have a great potential to reduce solar heat accumulation and cooling the loads of urban buildings, while improving indoor thermal conditions. For highly absorbent materials, such as a conventional black paint with solar reflectance of 0.05, the temperature rise compared to the air temperature can reach up to 50°C , while for a reflective solar material with solar reflectance of 0.8, such as a white paint, the temperature rise is limited to approx. 10°C [6]. Visible light represents 43% of the energy of the global solar radiation spectrum of air mass which is in 300-2500 nm, the rest reaches as near infrared radiation 700-2500 nm (NIR) and is 52% or ultraviolet (UV) radiation between 300-400 nm which is 5% [7]. Reflective properties of pigmented layers containing TiO_2 nanoparticles have been being a hot spot for research [8] because has the highest visible and near-infrared thermal reflection performance [9]. In this paper, we show how the thermal reflective heat-insulating property of foam-glass is significantly improved by enveloping with TiO_2 layers. This method is low cost, energy efficient and can be widely applied to envelope buildings.

Experimental part

Foam glass preparation and TiO_2 -enveloped foam glass

In this present study, we used foam glass PINOSKLO bought from Iridexplastic SRL company with following chemical-physical properties: Density: 110 - 160 kg / m^3 , Thermal conductivity: 0.045 - 0.054 W / m * K, Reaction to fire: Class A1, Compression strength: ≥ 700 kPa, Bending strength: 500 kPa, Water absorption: ≤ 0.5 kg / sqm . For experimental studies pieces of 10 mm \times 10 mm \times 4mm (length \times depth \times height) were cut in order envelope the foam glass with TiO_2 . TiO_2 powder was procured from Jalutex company and mixed with acrylic resin (1:1 weight ratio) while adding water. Acrylic resin, an economical, effective material was used as a

binder, while TiO₂ powder function was pigmentation effective and economical way for reflection of light.

Thermal investigation

The thermal properties of the glass enveloped with 1-4 layers of TiO₂ simulating real environmental conditions such as humidity and temperature for which the wrapped foam glass can be used as a building insulation material, were analyzed. Foam glass PINOSKLO with and without TiO₂ layering was fixed in turn in a polystyrene box, so that heat transfer is reduced to minimal between outside and inside. The upper surface of the samples was exposed to the Sol2A 94042A solar simulator from Oriel Instruments, Newport Corporation, with a stainless-steel surface as the lower support. The ambient temperature was kept constant at 23°C. The irradiation of the simulated solar radiation on the surface of the samples was approximately 895 W/m².

The temperature was measured constantly on the surface of the sample with the Infrared Ti110 infrared camera for two hours. K-type thermocouples connected to a 4-channel thermometer type TM -946 from Lutron Electronic were introduced 3cm inside the four-point foam glass pieces at equal distances from the sample height. Temperature recordings were made on the uncoated glass foam and after and enveloped with 1-4 TiO₂ layers.

Characterization

Structural characterization of powders has been carried out by X-ray diffraction (XRD) using a PANalytical X'Pert Pro MPD-type diffractometer with Cu-K α radiation ($\lambda_{\text{Cu}} = 1.54060 \text{ \AA}$). Optical properties such as Red, Green, and Blue (RGB) and the reflectance of glass foam and TiO₂ enveloped foam glass were recorded with a Meter-PCE-RGB 2 color from PCE Instruments UK Ltd. The reflectance was measured on the uncovered glass foam and also on each applied layer of the coating prior to the thermal experiments through an integrating sphere of 50 mm type ISP-50-8-R-GT connected to the UV-modular spectrophotometer VIS Jaz and LS-1 light source from Ocean Optics.

Olympus OLS 4000 LEXT was used to analyze surface texture and determine the roughness of foam glass after every layer of TiO₂ applied onto surface of foam glass. LEXT Olympus OLS 4000 LEXT was used to analyze surface texture. The laser confocal microscope can take high-resolution 3D images by acquiring successive images of the sample between two heights, then recombining the laser-recorded images and color images to produce a 3D projection. From this projection characteristics such as the surface roughness, area / volume ratio, film thickness and particle count are determined. Surface morphology (SEM) and elemental analysis (EDS) were investigated by scanning electron microscopy, Inspect S, FEI.

FT-IR spectrometer Vertex 70 (Bruker, Germany) using KBr pellet method in the wavenumber range of 400-4000 cm⁻¹, 128 scans and a resolution of 8 cm⁻¹ was used as characterization techniques for commercial glass foam and the obtained TiO₂ pigment in order to identify the main groups of their chemical composition. In addition, Raman spectra was obtained

with Multi Probe Imaging –MultiView 1000TM system from Nanonics Imaging, Israel on TiO₂ Pigment also on TiO₂ Layers applied to foam glass.

Results and discussion

X-ray diffraction for cellular glass prepared for studies shows an amorphous structure of the material in Figure 1.a)

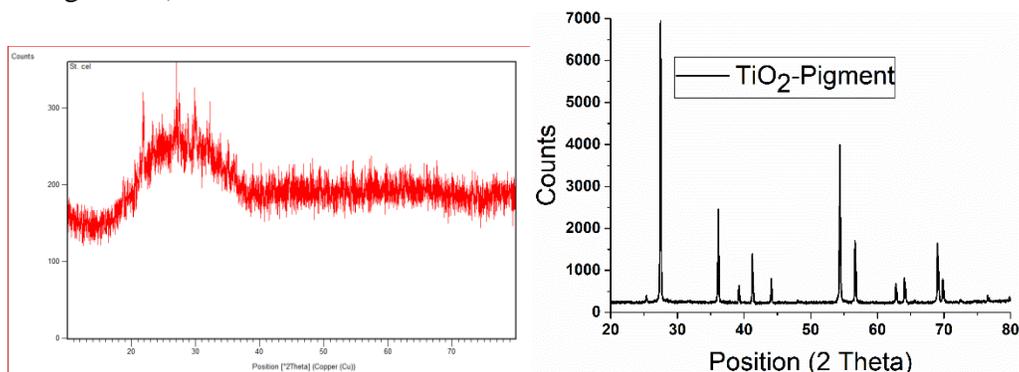


Figure 1. a) XRD diffraction patterns of the amorphous structure of the glass powder and b) TiO₂ powder used as pigment

XRD studies indicate that the materials synthesized were pure rutile TiO₂ phase and the crystal structures agree well with the corresponding reported JCPDS data (JCPDS powder diffraction data card no. 21-1276) while refined after ICDS 9015662. Line broadening of the diffraction peaks is an indication that the size of the synthesized material is in the nanometer range. The cell parameters were obtained to be:

a (Å)=4,5890

b (Å)=4,5890

c (Å)=2,9540

Alpha (°): 90,0000

Beta (°): 90,0000

Gamma (°): 90,0000

Crystal system: of TiO₂ is tetragonal, with space group: P42/mnm and space group number 136
Calculated density was 4,26 g/cm³ and Volume of cell 62,21 (10⁶ pm³).

Raman Spectroscopy

To complete the characterization of foam glass (Figure 2a) and TiO₂ pigment (Figure 2b), MicroRaman analysis were performed with a light source at 514 nm in accumulation mode and an exposure value of 10 seconds. Ceramics generally contains an excess of carbon in its structure, known as dispersed carbon phase, where the carbon atoms were not bonded to the polymeric network. Raman spectra for glass foam show two typical features of disordered graphitic forms, which verify the presence of free carbon [10] the D (disordered) band at ca. 1357 cm⁻¹ and the G

(graphite) band at around 1602 cm^{-1} . The spectral profile for foam glass showed a less intense band at 787 cm^{-1} , characteristic of SiC phase [11].

Dychalska, A. et al [12] observed in the Raman spectrum of the amorphous carbon phase (Fig. X) that it is composed of the two peaks: D which appears from the sp^2 hybridized carbon structure, and the second peak on 1602 cm^{-1} , called G -band and the physical properties of the amorphous carbon structure depend largely on the ratio of these two types of C-C bonds, peaks identified also in the Raman spectrum of cellular glass in figure 2 a) inset. Ferrari et al. [13] proposed in their study that bigger values than 90 cm^{-1} of full width of G band indicate that amorphous carbon in foam glass has a structure described as stage 1 in their three stage amorphization model.

Peak Type	Area Fit	Center Max	Maximum Height (I)	FWHM
Lorentz	1.253E7	1357.679	42212.058	283.682
Lorentz	5.186E6	1598.438	36442.538	103.136

Table 1. Deconvolution and extracted parameters for D and G peak

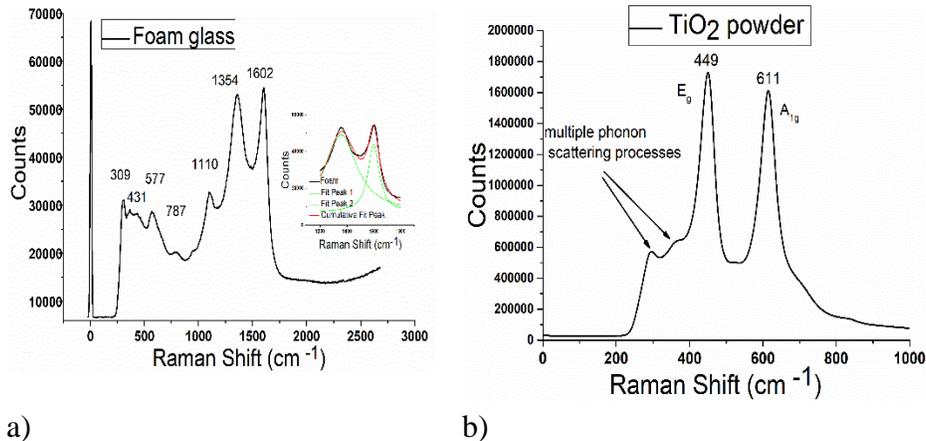


Figure 2.a) Raman spectra of the TiO_2 enveloped foam glass; Calculated deconvolution Raman spectra for 514 excitation wavelength for G and D peak of graphite b) Raman spectra for TiO_2 powder

TiO_2 exhibits characteristic stretching peaks for rutile at 449 , and 611 cm^{-1} that correspond to the symmetries of E_g , and A_{1g} [14]. In addition, another characteristic broad compound vibrational peak at 250 cm^{-1} arising from multiple phonons scattering processes is also clearly observed [15]. Our XRD and Raman analyses confirms the formation of pure phase rutile TiO_2 .

FT-IR characterization

In Figure 3, the FT-IR spectra of the TiO_2 powder used as a pigment for coating preparation a) and foam glass b) is represented.

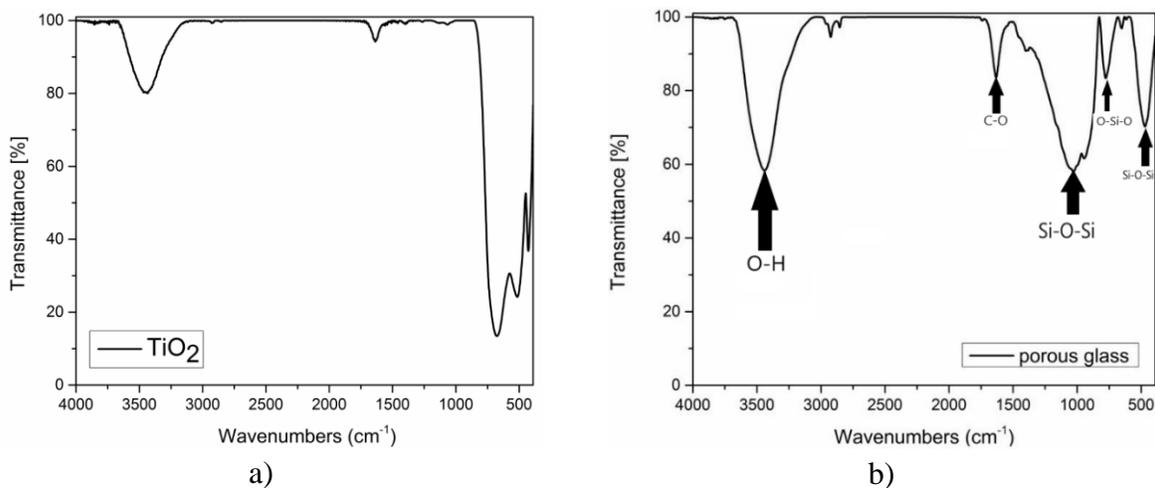
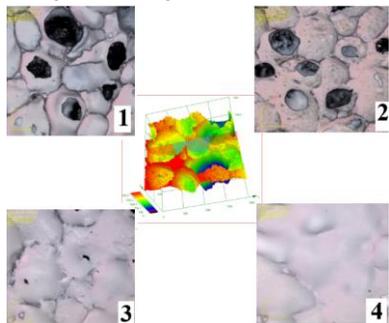


Figure 3.a) FT-IR spectra of the synthesized TiO₂ powder and b) foam glass

The FTIR spectra of nanoparticles only showed peaks corresponding to TiO₂. The peak observed at 590 cm⁻¹ is due to the vibration of the O-Ti-O bond. The peaks situated at 3500 and 1600 cm⁻¹ may be attributed to the OH groups of the adsorbed water. The Fourier transform infrared (FTIR) spectra of glass foam (Figure 9.b) that reveal information about metal oxygen in the material resulted mostly from tetrahedral SiO₄ groups. The main strong peak at 1050 cm⁻¹ and the shoulder peak at 1200 cm⁻¹ are the asymmetrical stretching of Si-O-Si bonds; the low frequency band between 400 and 500 cm⁻¹ is due to the rocking motion of O-Si-O bridges, whereas the corresponding bending mode is responsible for adsorption at 700–850 cm⁻¹[16]. As will be shown in more details by the EDX analysis later, the composition of glass foam consists mainly of SiO₂, Na₂O, Al₂O₃ and CaO but it may contain also graphite. It has to be mentioned that cations such as Na⁺, Ca²⁺ act as network modifiers, residing in sites interstitial to the tetrahedral network in the vicinity of the negatively charged non-bridging oxygens.

Surface Characterization

The surface analyzes were performed on the painted cellular glass represented in the Figure 4 for 1-4 layers of dye.; In Table 2 the rugosity for all 4 layers of paint is calculated.

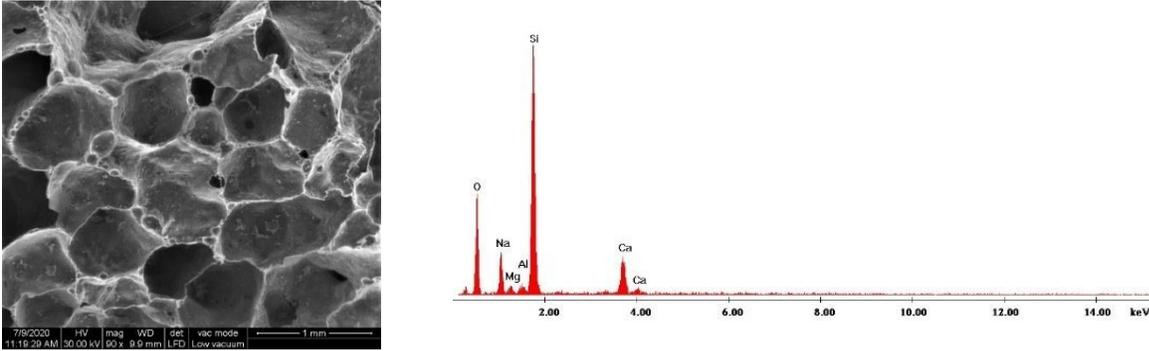


	Sq
1 Layer	26.925
2 Layers	13.927
3 Layers	6.143
4 Layers	3.942

Figure 4. Laser microscopy images of foam glass enveloped in 1-4 layers.

Table 2. The rugosity calculated for foam glass enveloped in 1-4 layers.

The scanning electronic microscopy image in Figure 5. a) reveals the glass foam surface with 1 mm pores of different sizes within its structure. It can be seen in the energy-dispersive X-ray recorded analysis in Figure 5 b) the elements contained in titanium dioxide foam glass :O, Na, Ca, Al, Mg and Si. We can also add graphite to its composition.



a) b)
Figure 5. a) Scanning electronic microscopy image and b) EDX of foam glass

Optical and Thermal characterization

To determine the reflectance spectra, the samples to be evaluated were analyzed in the absence of external light using the UV-VIS Jaz spectrophotometer, portable provided by Ocean Optics, which offered the possibility of applying a portable integrating sphere to record reflectance on the cellular glass surface connected with fiber optics one side to the spectrophotometer and the other to a halogen light source (LS-1 from Ocean Optics). The reflectance was recorded on the entire surface of the glass in 10 different points to determine the reflectance measurements accurately and reproducibly, the results were averaged. The UV-VIS spectra for cellular glass painted with 1-4 layers of TiO₂ were recorded in several areas on the surface. The average of the values is presented in Figure 6.

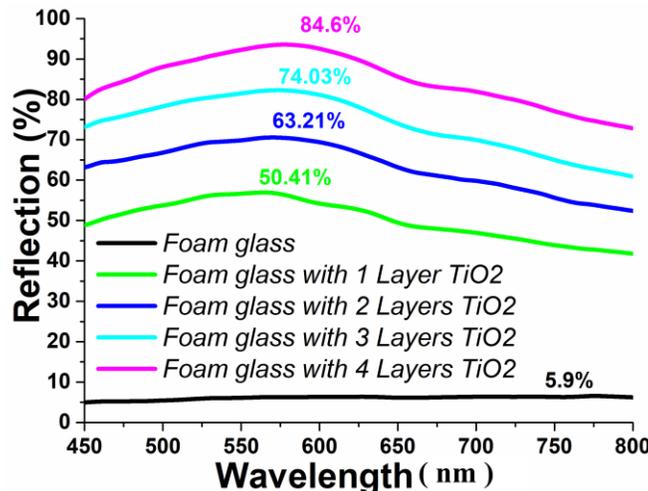


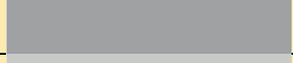
Figure 6. UV-VIS spectra for cellular glass and painted with 1-4 layers of TiO₂ dye.

The total reflectivity is increasing with addition of layers over the evaluated range of 400-800 nm which contain VIS and a part of NIR spectra. Table 2 lists the reflectance for red (R), green (G) and blue (B) spectral regions. The RGB was recorded at 10 bytes and transformed in 8 bytes in order to calculate the reflectance:

	R	G	B	Max reflected R	Max reflected G	Max reflected B
Layer 1	656,25	669,9	673,2	0.6433	0.656	0.66
Layer 2	825	835	832	0.808	0.818	0.815
Layer 3	889	898	898	0.871	0.88	0.8803
Layer 4	986	940	926	0.966	0.921	0.907
FG	78	74	67	0.076	0.072	0.065

Table 2. The RGB transformation from 10 bytes to 8 bytes and calculated the reflectance

Also, the change and intensification of the color at each applied layer were investigated using the red-green-blue chromatic model (RVA), a model that allows color simulation using values recorded in the range 0 ÷ 1023. Below are the RVA (RGB) values as an average of 20 recorded values and the simulated color before and after each coat of paint.

Layer	Red	Green	Blue	Simulated colour
0	72,15	68,65	62,2	
1	640,45	647,75	656,9	
2	803,9	810,75	805,3	
3	909,25	916,25	902,4	
4	1002,55	1001,75	987,15	

In order to evaluate the thermal effect given by the functionalized coating layers the upper surface of the cell glass was exposed for 2 hours to the solar simulator (ORIEL SOL-2A). The temperature of the samples was monitored on the irradiated surface and inside them at 4 points located at equal distances on the height of the samples as seen in Figure 7. The measurement of thermal performance was performed for the uncoated glass as well as for each layer of paint applied.



Figure 7. Image of foam glass with 4 points where temperature was measured

In Figure 8 the surface temperatures measured for all the samples exposed to the radiation are presented. The ambient temperature was recorded as 23°C. Uncoated cellular glass that is dark in color showed a significantly enhanced surface temperature. A nearly stable surface temperature of about 76°C is reached after 2h of illumination. Adding TiO₂ layers continuously reduces the final surface temperature. For four layers of TiO₂ the heating of the foam glass is reduced to about 50°C. This reduction demonstrates that enveloping foam glass with TiO₂ is an effective method to increase its thermal screen performance, reflecting a large part of the radiation.

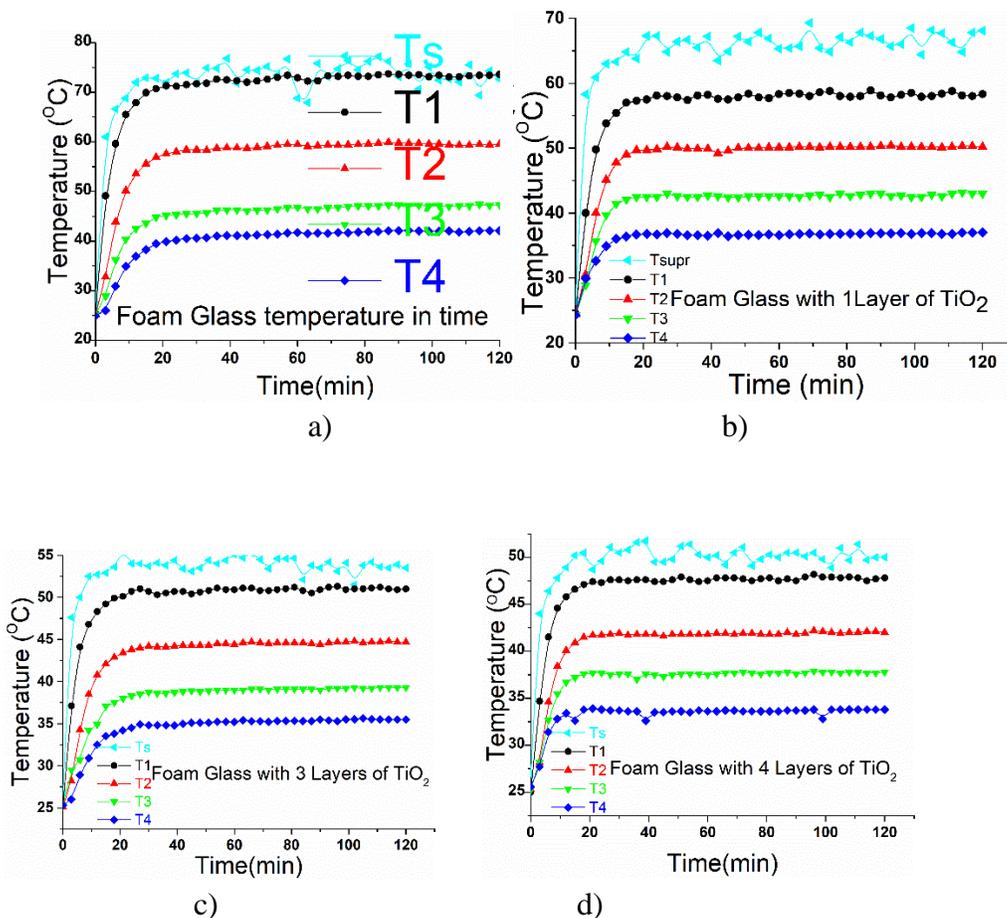


Figure 8. The surface temperature change and in the four monitored areas (T1, T2, T3, T4) for each layer of TiO₂ paint ((a) -foam glass with no coating; (b) - layer 1; (c) layer 2; (d) layer 3; (e) layer 4))

The values of temperatures T1, T2, T3, T4 and respectively the surface temperature, decrease after the application of the paint by approximately:

- 20.5%, 16.7%, 8.5% 10.8% and 10.7% for the first layer
- 24.7%, 21.7%, 14.9%, 14.28% and 19.7% for the second layer
- 30.14%, 25%, 17%, 16.7% and 27.6% for the third layer
- 34.24%, 34.25%, 16.6, 19.7% and 32.7% for the fourth layer

The temperature of the surface exposed to sunlight is influenced by solar reflectance and the infrared emission of the surface. We observed that painting the roof surface of foam glass with solar reflective paint is a very effective way to reduce thermal discomfort by 20% with only one layer of TiO₂. The research results show that the surface temperatures measured for samples exposed to the solar simulator decreased with numbers of layers and proved that the solar reflectance of layers directly affects the thermal performance of dyed surfaces, evidencing that with increasing number of layers the reflectance increases and the temperature decreases. The coating reduces the surface temperature also called a cold coating applied to the surfaces of a building has several potential benefits, such as reducing the energy required for cooling, improved thermal comfort and mitigating the effect of urban heat island.

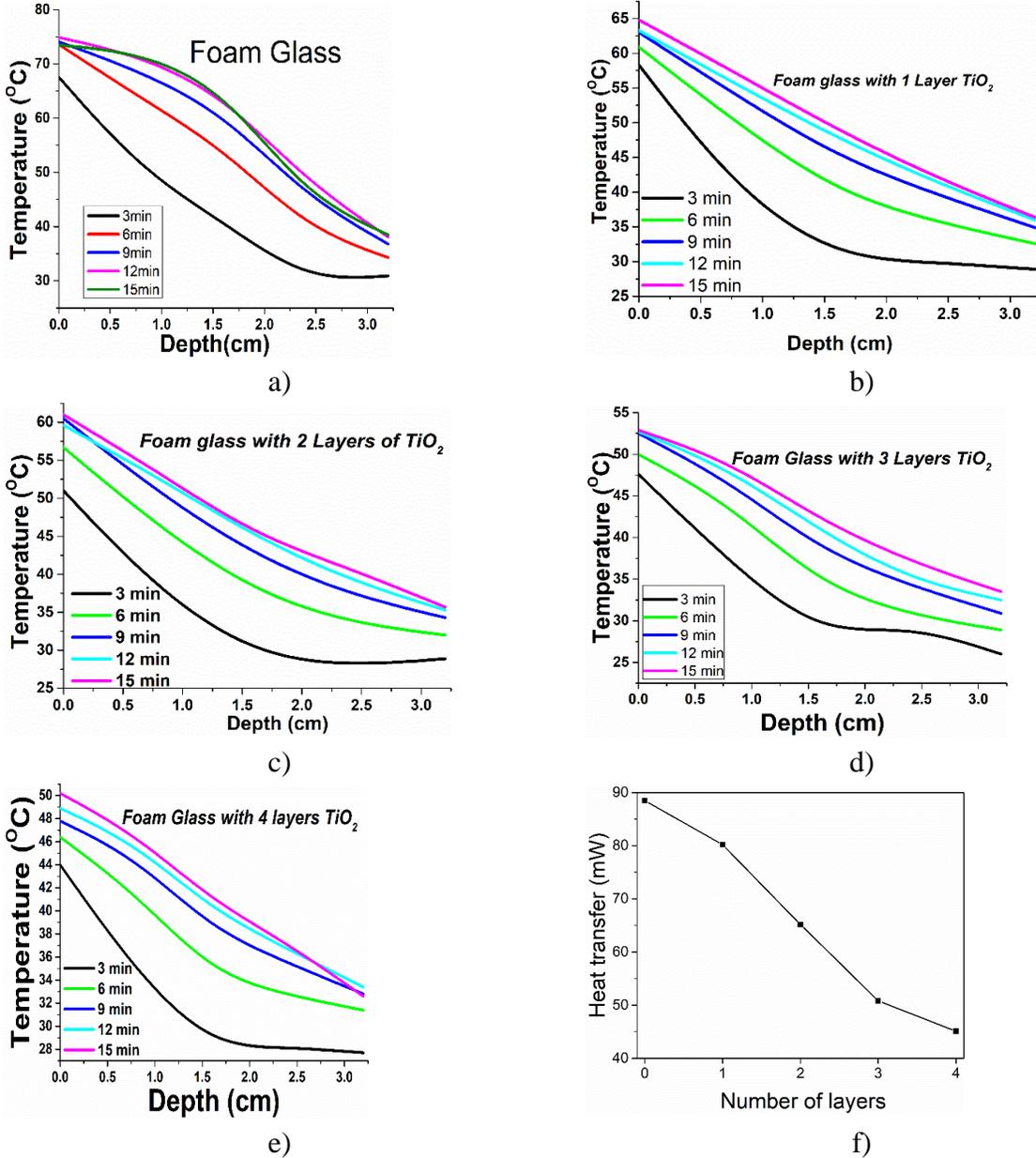


Figure 9. Temperature change with Depth for Foam Glass a) and foam glass with 1 b) --4 layers d) in time 3 min-15 min f) Calculated heat transfer.

The heat transfer formula used in figure 9 f) was:

$$q = k \cdot A \cdot \frac{dT}{s}, \text{ where}$$

q - heat transfer (W)

k - thermal conductivity of material - W/(m °C), (thermal conductivity of the glass foam was 0.054 W/m*K)

A - heat transfer area (m²)

dT - temperature gradient across a certain thickness –s (°C)

s – thickness (m)

The decrease of temperature (as presented above) both at the surface and inside the glass foam insulation was caused by the reflective white coating containing TiO₂ pigment. Therefore, each applied layer of the coating led to a lower absorption of the heat of the artificial solar radiation.

In Figure 9.f), the heat transfer of the insulating material calculated after applying each layer of the coating is presented. Heat transfer was determined considering the surface temperature and the temperature measured in 3 cm depth. As it was expected the heat transfer across the insulating material decreases as number of coating layers increases which is explained by the visible light and infrared reflective properties of the TiO₂-based coating.

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Conclusions

This study demonstrated the effect of using reflective materials on improving thermal comfort conditions for buildings. Structural characterization by X-ray diffraction reveals the amorphous nature of foam glass, and the presence of rutile structure for TiO₂.

Improving the thermal properties of the existing building with a solar reflective layer is one of the most important strategies in building modernization in many cases, logical and practical solutions to reduce energy consumption for buildings. The heat transfer is reduced to half from almost 90 mW in the case of uncoated foam glass to around 45 mW for the 4 layers of TiO₂ enveloped foam glass.

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