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COMPOSITE COATINGS WITH CERAMIC MICROSPHERES AS INSULATING MATERIALS FOR TRANSPORT MEANS

The paper presents the structure and the influence of the chemical composition and structure on the insulating properties of a polymer-ceramic microspheres hybrid composite used as insulating materials in infrastructure of transport and means of transport. The composite matrix is an acrylic resin and ceramic microspheres with the pressure of 13 Pa are the reinforcement. A content of about 44 microspheres in a 1 mm-thick coating has a major impact on the thermal insulating properties of the coating. The coefficient of heat conduction depends from the temperature and is lower at lower temperatures. This is the reason why these coatings are used as an insulator in technical means of transport requiring cooling (refrigerators and ice vehicles) and in the aviation industry to protect the interior of the plane against low temperatures during flights at high altitudes. Microscopic examinations were performed, the stereological features of the coating were examined and a equivalent model of the resistance of thermal transmittance through the coating have was developed. The equivalent coefficient of thermal conductivity of the composite, calculated on the basis of a formula taking into account the volume shares of the components and their thermal properties, is greater than the coefficient of ceramic spheres with their volume fraction amounting to 80%. This is caused by the fact that the formula does not take into account the stereological properties of spheres in the composite, i.e. the distribution pattern and number per unit of thickness of the coating.

Keywords: hybrid composite, structure, thermal conductivity, insulation, microspheres

KOMPOZYTOWE POWŁOKI Z MIKROSFERAMI CERAMICZNYMI JAKO MATERIAŁY IZOLACYJNE TECHNICZNYCH ŚRODKÓW TRANSPORTU

Przedstawiono budowę oraz wpływ składu chemicznego i struktury na właściwości izolacyjne hybrydowych kompozytów polimerowo-ceramicznych przeznaczonych do wytwarzania infrastruktury transportu i technicznych środków transportu. Osnową kompozytu jest żywica akrylowa, a ceramiczne mikrosfery z podciśnieniem 13 Pa stanowią zbrojenie. Zawartość około 44 mikrosfer w powłoce o grubości jednego milimetra wywiera istotny wpływ na cieplne właściwości izolacyjne. Współczynnik przewodności cieplnej zależy od temperatury i jest mniejszy przy niższych temperaturach. Jest to powodem stosowania tych powłok jako izolatora w technicznych środkach transportu towarów wymagających chłodzenia (pojazdy chłodnie i lodownie) oraz w lotnictwie do zabezpieczenie wnętrza samolotu przed niskimi temperaturami podczas lotów na dużych wysokościach. Wykonano badania mikroskopowe i cech stereologicznych powłok i opracowano model zastępczy oporu przekształcania ciepła przez powłokę. Obliczony z wzoru uwzględniającego udziały objętościowe składników i ich właściwości cieplne zastępczy współczynnik przewodzenia ciepła kompozytu jest większy niż współczynnik sfer ceramicznych przy ich udziale 80%. Powodem tego jest to, że wzór nie uwzględnia cech stereologicznych sfer w kompozycie, tj. sposobu rozlożenia i ilości przypadającej na jednostkę grubości powłoki.

Słowa kluczowe: kompozyty hybrydowe, struktura, przewodność cieplna, izolacja, mikrosfery

INTRODUCTION

Vehicles which are used for carrying fragile and perishable cargo require temperature stabilization at the level which would retard the biological processes occurring in the products. Generally food products are heat-releasing living organisms. In order to slow down the ripening process, the process of cooling is required [1]. To ensure the required quality of the transported food products and reduce the costs of transportation, vehicles equipped with refrigerators powered by an internal combustion engine are built. The insulation

materials which are used determine the effectiveness of the insulation and transportation costs.

Thanks to their properties composite materials have significantly contributed to the changes in machine and plant construction, for example by reducing the dimensions and increasing the durability of the parts. For some time composites have been used as insulating materials of the "next generation" [2, 3]. The best example is the space industry, which uses liquefied gases. The development of hydrogen powered vehicles

would definitely increase the interest in composite insulation materials in the automotive industry. Liquefied gas is delivered to the newly launched LNG terminal in Świnoujście by special huge capacity vessels, the storage rooms of which require effective cryogenic insulation. Cryogenic tanks require new, innovative insulation materials characterized by low thermal conductivity and density [4]. Some of the requirements of cryogenic insulation materials can be ensured by composite coatings with a plastic matrix, modified by expanded perlite ($\lambda = 0.001 \text{ W/(mK)}$ at 170 K) or ceramic microspheres (soda lime borosilicate glass) ($\lambda = 0.0007 \text{ W/(mK)}$ at 170 K) or silicon aerogels ($\lambda = 0.003 \text{ W/(mK)}$ at 170 K) [5]. At higher temperatures these materials exhibit much poorer thermal properties than perlite ($\lambda = 0.042 \text{ W/(mK)}$) [6]. The way they expand as well as the particle size have a significant impact on the thermal properties [7].

Composites with a plastic matrix filled with ceramic spheres have already found their application in the construction of cars and planes where they function as insulators and reduce the weight of some aircraft components by about 5% and cars up to 30% [8]. Polyester or polyurethane resin composites containing expanded polymer spheres with a diameter of 20 to 80 μm and a wall thickness ranging from 0.1 to 0.2 μm are also known to be applied in the insulation of car chassis (as filler additives). The thermal conductivity for coatings with 42%_v microspheres and no mineral filler determined according to test method EN 12664 was lower than 0.071 W/(mK) [9].

Composite insulating materials are also used as insulation in commercial transport for the insulation of pipes carrying hot technological liquids such as hot water of 80 to 120°C.

THERMODYNAMIC BASES

The main objective of applying composite insulating materials is to stop the heat stream at the barrier i.e., the insulation. In commercial conditions heat transfer usually takes place between two media, in this case liquids such as a heating working agent placed in the pipeline (steam or water at the temperature of T_1) which unintentionally gives heat away to the air surrounding the pipeline of temperature T_2 . In order to reduce heat loss, the walls of pipelines should be insulated and the selection of insulating material should be focused on the greatest possible thermal resistance, determined from the relationship:

$$R = \frac{1}{F_1 \alpha_1} + \sum_{i=1}^n R_{\lambda,i} + \frac{1}{F_2 \alpha_2} \quad (1)$$

$$R_{\lambda,i} = \frac{g_i}{F \lambda_i} \quad (2)$$

where: R - total thermal resistance of the multilayer barrier; α_1 - coefficient of heat penetration from medium 1 into the barrier material [W/(m²K)]; α_2 - coeffi-

cient of heat penetration from the barrier material into medium 2 [W/(m²K)]; F_1 - surface area of the barrier from the side of heat stream penetration [m²]; F_2 - surface area of the barrier from the side of heat penetration from the barrier to medium 2 [m²]; $R_{\lambda,i}$ - thermal resistance on the barrier, in a homogeneous composite is the sum of the thermal resistances of the matrix layer and reinforcing phase (n barriers), $R_{\lambda} = \sum R_{\lambda,i}$; g - barrier thickness [m]; F - barrier surface area [m²]; for the reinforcing phase it is the surface area of a hemisphere with an average diameter.

The above formulae show that the thermal resistance of the composite material consisting of a matrix and particles (spheres) as the reinforcing phase depends on the number (n) of the particles constituting the barriers and on their thermal properties.

Heat conduction through the composite material can be considered as the conductivity in multiphase material consisting of a matrix and reinforcing phase. The composite coating can be replaced with a serial model, where the heat stream flows perpendicular to the interface of the material phase. The thermal conductivity coefficient of the composite material can be calculated, in a simplified way, from the dependence which arises from the rule of mixtures:

$$\frac{1}{\lambda_c} = \frac{V_m}{\lambda_m} + \frac{V_{RP}}{\lambda_{RP}} \quad (3)$$

where: λ_c - thermal conductivity coefficient of composite [W/(mK)]; λ_m - thermal conductivity coefficient of the matrix, for acrylic resin $\lambda = 0.20 \text{ [W/(mK)]}$ [10]; λ_{RP} - thermal conductivity coefficient of RP, for spheres $\lambda = 0.055 \text{ W/(mK)}$ at temp. 21°C [11, 12]; V_m - volume fraction of matrix material, 20% acrylic resin with additives; V_{RP} - volume fraction of reinforcing phase, 80% spheres.

After inserting $V_m = 0.2$ and $V_{RP} = 0.8$ and the thermal conductivity values of the matrix ($\lambda_m = 0.2$) and RP ($\lambda_{RP} = 0.055$), we obtain the approximate coefficient of thermal conductivity of the composite $\lambda_c = 0.064 \text{ W/(mK)}$. The calculated thermal conductivity coefficient reported in literature is smaller and equals $\lambda = 0.0012 \div 0.0016$ [13]. The divergence results from the fact that equation (3) does not take into account the way the components are distributed in the composite coating (stereological parameters). Similar problems are known in sintered composites with a ceramic matrix [14] and epoxy resin reinforced with fibers [7]. For analytical and computational calculation of the effective thermal conductivity of the composite some other formulas can be used e.g. the exponential model [7, 15, 16] but they are subject with some inaccuracy as well. The results are affected among others by the stereological parameters of the reinforcing phase [7]. Therefore, in practice formula (1) should be used. However, heat penetration coefficients (α) are difficult to determine which creates problems applying the formula.

MATERIAL FOR RESEARCH

A water-soluble composite material with an acrylic resin matrix recently introduced on the market, ($\lambda = 0.19 \div 0.20 \text{ W/(mK)}$) modified with ceramic microspheres made of borosilicate glass ($\lambda = 0.055 \text{ W/(mK)}$ at 0°C) together with other additives, was used in the research. The diameter of the microspheres ranged from $30 \div 115 \mu\text{m}$ [9, 11]. To prevent damage of the microspheres (crush stresses $\sim 3 \text{ MPa}$ [11, 12]) the coating was applied with a brush on the samples of vehicle body sheet and the steel pipe used for hot water transport. The coatings were applied and dried according to the instructions for 24 hours in air at 20°C to remove the excess water. The samples used to determine thermal properties as well as for microscopy tests ($\phi = 12 \text{ mm} \times 1 \text{ mm}$) were made in a paper form, which increased water evaporation. Additionally, the samples from pipe coating decomposed after thermal tests at temperature up to 100°C were used. A view of the coating surface is shown in Figure 1a and samples for microscopic examination in Figure 1b. In order to verify the structure of the coating after drying, the samples were broken and microscopic examinations were performed.

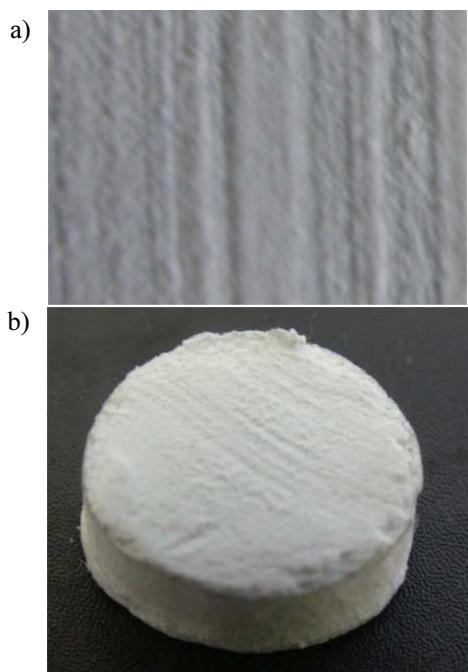


Fig. 1. View from surface of composite insulating coating on sheet sample of car body (a - macrophotograph x10) and sample used for SEM examinations (b)

Rys. 1. Widok z powierzchni powłoki kompozytowej nałożonej na blachę karoserijną (a - makrofotografia, x10) i próbki użytej do badań mikroskopowych (b)

RESEARCH RESULTS

Microscopic tests of the surface and side walls of the coating as well as the coating fracture were performed. In addition, the decomposed portion taken from the pipe was examined. The results are shown in Figures 2-4.

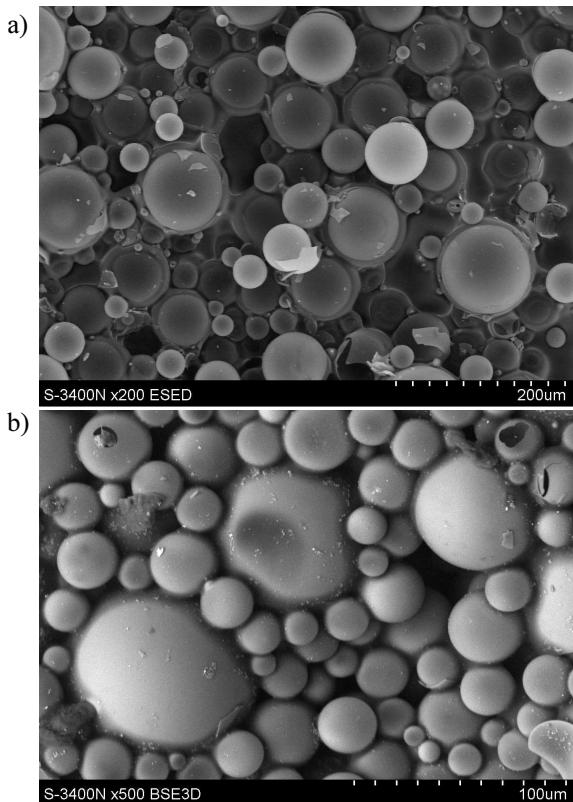


Fig. 2. Ceramic microspheres before use placed on conducting tape (a) and in coating with acrylic matrix (b), SEM

Rys. 2. Ceramiczne mikrosfery przed użyciem naklejone na taśmę przewodzącą (a) i w powłoce z osnową akrylową (b), SEM

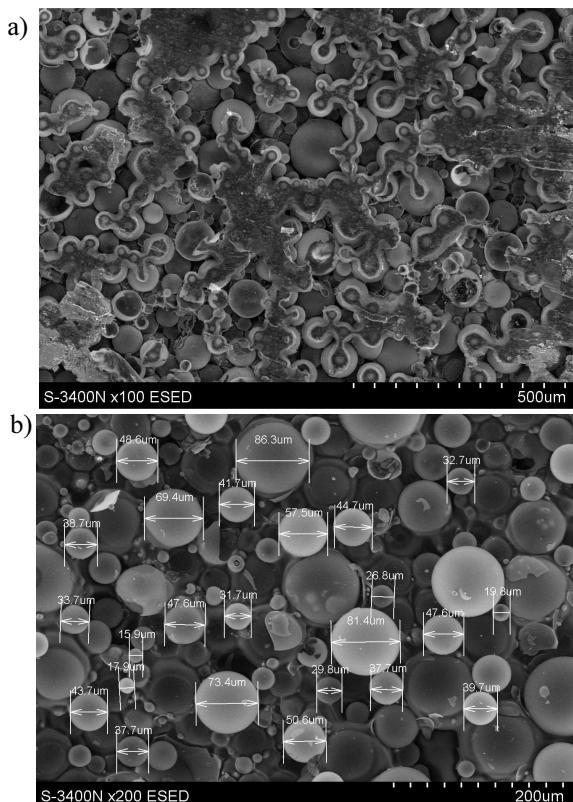


Fig. 3. Surface of coating after loosening from insulated pipe (a) and measurement of stereological parameters of spheres (b)

Rys. 3. Powierzchnia powłoki po odspojeniu od izolowanej rury (a) i pomiar cech stereologicznych sfer (b)

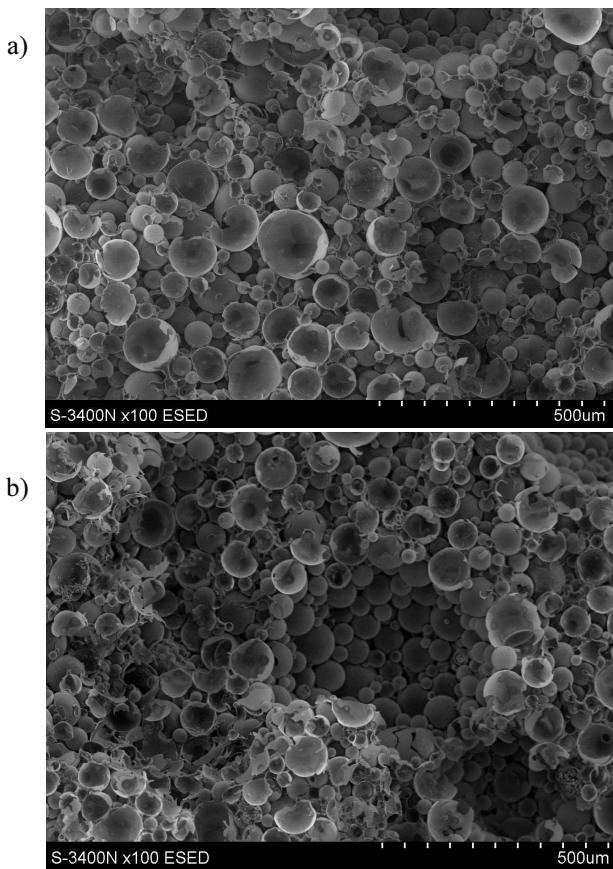


Fig. 4. Fracture surface of multilayer insulating composite coating correctly prepared (a) and including gas bubbles (b)

Rys. 4. Powierzchnia przelomu wielowarstwowej, izolacyjnej powłoki kompozytowej wykonanej prawidłowo (a) i zawierającej pęcherze gazowe (b)

Figure 5a shows the microstructure of the composite side surface of the insulating coating with a thickness of 0.5 mm deposited on the body sheet of a vehicle used to transport goods at low temperatures.

Cross-section A-A indicates a location with hardly any spheres, while cross-section B-B denotes a location with a large number of spheres. Figure 5b shows the equivalent diagram of a multilayer barrier, the dimensions of which correspond to the tested coating.

The stereological parameters i.e., the average thickness of the acrylic layer which binds the spheres were measured upon micrographs of the side walls of the coatings. The measurements were performed by applying lines every 10 mm on the surface of the photograph by measuring the lengths of each section per matrix material (odd numbers in Figure 5 A-A cross-section and even numbers cross-section B-B) and the sphere material (even numbers in Figure 5 cross-section A-A).

Measurement of the average diameter of the microspheres was performed using the software of the scanning microscope (3 images). An example is shown in Figure 3b. The average thickness of the acrylic layer between the spheres is $g_{av} = 7.4 \mu\text{m}$ with a standard deviation of $\sigma_g = 6.8 \mu\text{m}$. The minimum layer thickness was $2.5 \mu\text{m}$ and the maximum $50 \mu\text{m}$. The average diameter of the sphere measured on the micrographs

(3 images x 80 spheres) was $d_{av} = 15 \mu\text{m}$ ($\sigma_d = 5.96 \mu\text{m}$) with minimum $d_{min} = 4 \mu\text{m}$ and maximum $d_{max} = 86.3 \mu\text{m}$.

After taking into account d_{av} and g_{av} the average number of spheres per 1 mm of coating thickness $N_{sr} = 44.4 \text{ mm}^{-1}$ was determined. This is essential for computing of the equivalent thermal resistance (R) of the coating.

The diffusivity of the tested samples was $a = 0.128 \text{ mm}^2/\text{s}$ and the specific heat $cp = 4.423 \text{ J}/(\text{kgK})$ at the temperature of 80°C and $1.73 \text{ J}/(\text{kgK})$ at the temperature of -20°C [17].

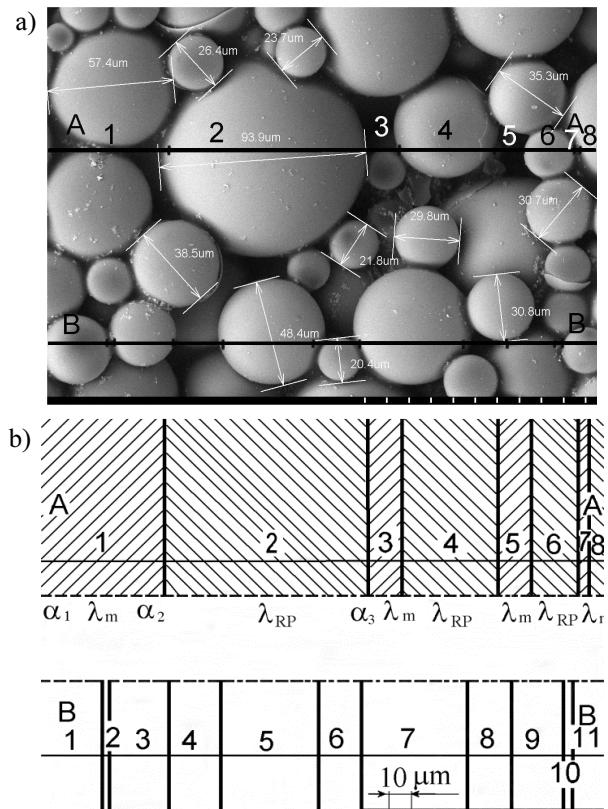


Fig. 5. Side surface of composite coating side (a) with thickness of $250 \mu\text{m}$ and model of barrier for heat flux (b)

Rys. 5. Powierzchnia boczna powłoki kompozytowej (a) o grubości $250 \mu\text{m}$ i model przegrody dla przepływu strumienia ciepła (b)

DISCUSSION OF RESULTS

On the basis of the performed microscopic tests upon the composite coating, it is possible to observe that its structure is practically correct on its surface (Fig. 2b) and on the bottom pipe side (Fig. 3a) with small pores which were most probably formed by the collected steam (Fig. 4b). Some spheres supplied by the manufacturers are damaged (Fig. 2a). The manufacturer allows up to 10% of such spheres [12]. The large standard deviation of the average thickness of the acrylic matrix layer which binds the ceramic spheres is the result of a conscious choice of spheres with varying diameters in order to fill up the coating thickness with these spheres. Spheres of smaller diameter ($d_{min} = 4 \mu\text{m}$)

are located in the spaces between the large spheres ($d_{max} = 86.3 \mu m$). For this reason, it was possible by the heat flux penetration to obtain more spheres ($\lambda = 0.055 \text{ W/(mK)}$) than matrix material ($\lambda = 0.20 \text{ W/(mK)}$).

The heat flux penetrating the composite barrier is stopped (the case of section A-A, Fig. 5) by the resistance of:

- penetration from the surrounding liquid, most frequently hot water or steam, into the matrix material (α_1);
- matrix conductivity ($R_{\lambda m}$);
- heat penetration from the matrix material into sphere material (α_2);
- conductivity of the sphere material ($R_{\lambda s}$);
- penetration from the sphere into the material filling up a sphere (α_3);
- conductivity inside the material filling up a sphere (R_{ARP});
- penetration from inside the sphere material into the sphere wall (the α_3 - thickness of the sphere wall is not indicated in Fig. 5);
- conductivity of the sphere material ($R_{\lambda s}$);
- penetration from the sphere material into the matrix material (α_4);
- conductivity of the matrix material (λm);
- penetration from the matrix material into the liquid on the other side of the barrier (α_5), most frequently air surrounding heat pipelines.

The structure and heat properties of coatings are strongly dependent on their manufacturing technology and application. In order to estimate the insulation properties of composite coatings it is possible to use stereology. The average diameter of microspheres can be read from the product card supplied by the manufacturer, while the average thickness of the matrix material layer can be measured or determined on micrographs.

In order to calculate the heat conductivity coefficient of composite coating it is necessary to determine the coefficient of heat penetration from the environment into the coating and from the coating into the environment.

On the basis of the image presented in Figure 3a, it can be claimed that acrylic resin adheres properly to the pipe surface and wets the sphere interface, which is clear evidence of correct application of the coating upon the tested pipeline.

SUMMARY

The use of the simplified formula - resulting from the rule of mixtures - which take into account only the volume fraction and heat properties of the components for computing the equivalent coefficient of heat conductivity for composite coatings is not adequate. This formula takes into account only the volume fractions and heat properties but does not look at the way the reinforcing phase material is distributed in the form of

a large number of microspheres posing resistance to heat flow. Therefore, in order to determine the real heat resistance of the coatings, further investigations will be carried out which seem essential to define the coefficient of heat penetration.

The low thermal conductivity of the investigated composite coatings, according to the literature ($\lambda = 0.0016 \text{ W/(mK)}$), requires equipment for direct measurement of λ with a measuring range lower than the given level (0.001 W/(mK)). Such special devices are used for examining cold insulation (cryogenic materials) not for insulating materials used as thermal barriers at elevated or higher temperatures up to 100°C (hot insulation).

A decrease in thermal conductivity of polymer materials due to the addition of a number of ceramic spheres can reduce the dimensions of cooled or refrigerated rooms in means of transport because of the lower thermal conductivity than existing materials, according to the producer's data.

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