Determination of thermal conductivity of moist rigid polymer foams

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Abstract. A geometric model of the polymer foam structure was verified taking into account the moisture content of the material and the degree of wetness of the pore surface. Mathematical relations were developed to determine the moisture value at which transition from partial to full wetting of the pore surface occurs and vice versa. A mathematical description of the heat transport process was carried out in the model structure of moist foam taking into account the diffusion of water vapour in the pore space and the nature of wetting of the pore surface. The influence of material porosity, its moisture and water vapour diffusion within the effective porosity on the effective thermal conductivity of the material was determined by calculation. A comparison between the calculation results and experimental data shows their sufficient compatibility.

1 Introduction

Rigid polymer foams are widely used in various industrial sectors, including the construction industry in which they are mainly used as an effective thermal insulation in buildings and engineering structures. The general characteristics of the complicated heat transfer process in polymer foams are reflected in the effective thermal conductivity coefficient used to determine the thermal properties of building envelopes.

It is obvious that the thermal conductivity of polymer foams depends on the thermal characteristics of both the solid polymeric material and the substance present inside the pores, which in moist foams consists of a vapour-gas mixture and water. When determining the thermal conductivity coefficient of such a porous substance, the effect of moisture diffusion caused by the movement of water vapour transfer in the direction of the heat flow and the accompanying phase changes of moisture (evaporation in the warmer zone and condensation in the cooler one) should be considered [1, 2, 3, 4]. At the same time condensation of the diffusing water vapour may cause a significant increase in the thermal conductivity of moist materials, especially in the case of highly porous polymeric foams.

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Application of the known methods for calculating the effective thermal conductivity of moist porous materials produces results that differ significantly. It requires determination of certain empirical coefficients. When the influence of water vapour diffusion on heat transport is assessed with the use of the existing methods, the resistance of the porous material to the diffusion of water vapour is not taken into account. In addition, the characteristics of wetting of the pore surface with liquid (partial or full) are not taken into account. And the transition from partial to total wetting of the pore surface is associated with a step increase in the effective thermal conductivity of materials. The properties indicated impose certain restrictions on the application of these methods.

This paper proposes a method for calculating the effective thermal conductivity of highly porous ($P > 0.85$), moist polymeric foams that does not require empirical coefficients. The method takes into account the resistance of the porous material to the diffusion of water vapour. Conditions were determined for transition from partial to total wetting of the pore surface with liquid.

2 A model of the structure of a moist polymer foam and calculation relations

Visualization of various types of foamed polymeric structures, presented in a series of works [4, 5, 6, 7] shows that the rigid polymer skeleton consists of polyhedral cells (bars and membranes) with walls mainly in the form of tetrahedrons, pentagons and hexagons. The main part of the polymer is located inside straight bars with a practically constant cross-section, with a slight increase in thickness in the nodes usually caused by the connection of four bars. Depending on the type and technology used for foaming the polymer, the content of open cells varies in a very wide range and can reach 98% [4].

Fig. 1. The eighth part of the unit cell

The thermal degradation of polymer occurs as a result of interaction with the surrounding environment, causing a reduction in the number of closed cells [8]. This allows us to state that the structure of used rigid polymer foams consists mainly of open cells, which should be compared with a structure with mutually interpenetrating, geometrically equivalent components. For this type of structure the widely used method of transition to the unit cell can be applied. In the works [9, 10], the analysis of the results of numerical modelling shows that for dry, highly porous polymer foams, the form of cells and the cross-section shape of the bars have a weak influence on thermal conductivity. Cells with a regular structure in the form of cubes, dodecahedrons and tetrakaidecahedrons (Kelvin cells) were considered in the above mentioned works. The volume distribution of the polymer between the rods and cell nodes and the node form do not have a significant

influence on the thermal conductivity of highly porous polymer foams either. Therefore, the simplest cells in the form of a cube and bars with a constant, square cross-section can be adopted as unit cells. The symmetry of the unit cell in two mutually perpendicular directions makes it possible to describe the researched process in 1/2, 1/4 and 1/8 of the cell. The eighth part of the unit cell is shown in Fig. 1.

To assess the distribution of liquid moisture in a cubic unit cell, the moisture level ψ and the contact angle θ formed at the boundaries of the solid, liquid and gas phases have to be considered. As an example, Fig. 2 shows an eighth part of the unit cell containing the insulated liquid inclusions at a contact angle of 45° . As the moisture level increases, the dimension x (Fig. 2) will increase and at $x = L - \Delta$, the isolated liquid inclusions will rise until they join in the porous space. Then, the porous space should be regarded as a binary system with interpenetrating components. For this reason, when calculating the thermal conductivity of a porous space, it is necessary to know its moisture limit level at which transition from a binary system with isolated inclusions to a system with interpenetrating components takes place and vice versa.

Fig. 2. The distribution characteristics of the isolated liquid inclusion inside the unit cell at the contact angle $\theta=45^\circ$

The volumetric moisture of pores ψ_p is related to the liquid volume V_w and the pore volume V_p according to the relation $\psi_p = V_w/V_p$ and to the volumetric moisture of material ψ and its porosity P according to the relation $\psi_p = \psi / P$. It results from Fig. 2 that $V_w = 3 \cdot x^2 \cdot \Delta/2 + x^3/6V$. The pore volume is $V_p = (L - \Delta)^3 + 3 \cdot \Delta \cdot (L - \Delta)^2$. Assuming that $x = L - \Delta$, after simple transformations we obtain the threshold volumetric moisture of the pores at the contact angle $\theta=45^\circ$

$$\psi'_p = \frac{1+8 \cdot c}{6 \cdot (1+2 \cdot c)}; c = \Delta/L. \quad (1)$$

Similarly, at the contact angle $\theta=90^\circ$, we obtain:

$$\psi'_p = \frac{\pi \cdot (1+3.5 \cdot c)}{6 \cdot (1+2 \cdot c)}. \quad (2)$$

At the contact angle $\theta=0^\circ$, the searched value of moisture is calculated from the formula:

$$\psi'_p = \frac{(4-\pi) \cdot (1+14 \cdot c)}{20 \cdot (1+2 \cdot c)}. \quad (3)$$

From the formulas (1), (2) and (3) it is possible to determine the dependence between the pore moisture ψ'_p and the contact angle θ for different values of the relative size of the unit cell bars $c = \Delta/L$. The indicated dependence is shown in Fig. 3.

Fig. 3. The dependence of the pore boundary moisture ψ_p' on the contact angle θ calculated for different values of the relative size of unit cell bars c

The relative size of bars is calculated using the formula [11]:

$$c = 0.5 + \sin \left[\frac{\arcsin(2 \cdot m_i - 1)}{3} \right], \quad (4)$$

where m_i – the concentration of the i -th component ($i = 1, 2$), for which the value c is determined. In order to determine the effective thermal conductivity of a three-component structure consisting of a solid skeleton, liquid and vapour-gas mixture, the theory of generalized conductivity was applied [12]. At the beginning, the effective thermal conductivity of the pore substance λ_{subP} consisting of a vapour-gas mixture (component 1) and water (component 2) with known concentrations of m_1 and m_2 , the thermal conductivity λ_1 and λ_2 ($\lambda_1 = \lambda_{va}$ and $\lambda_2 = \lambda_w$) was determined. If the cell surface is only partially wet, then the dependence for the structure with isolated inclusions is used [12]:

$$\lambda = \lambda_1 \frac{v - (v-1)(1 - m_2^{2/3})m_2^{1/3}}{v - (v-1)m_2^{1/3}}, \quad (5)$$

where $\lambda = \lambda_{subP}$, m_2 – the volumetric concentration of water inclusions, $v = \lambda_2/\lambda_1$. In this case, the structure components are not geometrically equivalent, and the continuous component is always taken first, with the concentration of m_1 .

If the liquid continuously wets the cell surface, then the formula for the structure with interpenetrating components should be applied [12]:

$$\lambda = \lambda_1 [c^2 + v(1 - c)^2 + 2vc(1 - c)(vc + 1 - c)^{-1}], \quad (6)$$

where $\lambda = \lambda_{subP}$, $v = \lambda_2/\lambda_1$. The components of this structure are geometrically equivalent and it does not matter in the calculations which of the two components will be adopted first. After determining the thermal conductivity of the pore substance using the formula (6), the effective thermal conductivity of the material consisting of a hard polymer skeleton and a pore substance is determined.

The thermal conductivity of the vapour mixture λ_{va} is determined as a sum of the thermal conductivity of the vapour λ_v and air λ_a . The thermal conductivity of water vapour λ_v caused by its transport by diffusion in the pore space is determined from the equation [3, 12]:

$$\lambda_v = \frac{D}{\mu} \cdot \frac{M}{R \cdot T} \cdot \frac{p_{va}}{p_{va} - p_v} \cdot \frac{dp_v}{dt} \cdot q_t, \quad (7)$$

where: D - coefficient of water vapour diffusion in stationary air, m^2/s ; μ - coefficient of resistance to vapour diffusion in the pore space; M - molecular weight of water vapour,

kg/mol; R - universal gas constant, J/(mol · K); T - temperature of water vapour, K; p_{va} - total vapour and air pressure, Pa; p_v - partial pressure of saturated steam, Pa; t - temperature, °C; q_t - specific heat of evaporation at the temperature T , J/kg.

The relation formulated in 1938 by Schirmer is widely used to determine the coefficient D [3, 13]:

$$D = \frac{2.305 \cdot 10^{-5} \cdot p_0}{p_{va}} \cdot \left(\frac{T}{273} \right)^{1.81}, \quad p_0 = 101323 \text{ Pa} \quad (8)$$

The derivative dp_v/dt can be determined from literature data or from the formula [3]:

$$\frac{dp_v}{dt} = \frac{2.44314 \cdot 10^6}{(234,175+t)^2} \cdot \exp\left(\frac{17,08085 \cdot t}{234,175+t}\right).$$

3 Calculation experiment and its results

The calculation experiment aims to assess the effect of the moisture ψ and the porosity of polyurethane foam P on its thermal conductivity λ at 20°C. The thermal conductivity of the polymer was assumed to be 0.25 W/(m·K). This value of thermal conductivity is typical of polyurethanes. Thermal conductivity was adopted as 0.596 W/(m·K) for water and 0.0257 W/(m·K) for air. The specific heat of evaporation at the temperature $t=20^\circ\text{C}$ equals $q_t=2.38 \cdot 10^6$ J/kg. The other parameters necessary to perform calculations were determined using the formulas presented in this work. In the calculations the moisture ψ changed from 0.01 to 0.20 m³/m³, and the porosity P from 0.85 to 0.99. In this case, the so-called effective porosity $P-\psi$ varied from 0.65 to 0.98, and the total concentration of polymer and water varied from 0.02 to 0.35. In addition, the calculation was also made for a completely dry material $\psi=0$, which made it possible to explain the effect of the influence of moisture and water vapour diffusion on the thermal conductivity of high-porous materials. The results of the calculations are shown in Fig. 4 together with the experimental data for phenolic foam taken from the work [4].

Fig. 4. The dependence of the effective thermal conductivity of polyurethane foam on the total concentration of polymer and water $1 + \psi \cdot P$

These results reflect the mutual influence of the moisture ψ , the porosity P and the diffusion of water vapour within the effective porosity $P-\psi$ on the effective thermal conductivity of the material. Fig. 4 shows that all dependencies obtained at different values of real moisture ($\psi \leq 0.2$) can be described adequately precisely with one relation. It should be emphasized that this relation simultaneously corresponds to the empirical dependence of

the effective thermal conductivity of different dry thermal insulation materials from their apparent density, determined by different authors [4, 14].

The proposed method of calculating λ pretty well describes the experimental data marked with triangles obtained for phenolic foams [4]. As is known, the λ of the phenolic polymer is smaller than the polyurethane polymer and amounts to about 0.19W/(m·K). If this value is used in the calculations, then the computational curve will descend even lower and the experimental data marked with triangles will be predicted even more closely.

It should be noted that the actual experimental evaluation of the thermal conductivity of wet materials is very difficult. In the works [4, 12] it was experimentally determined that the thermal conductivity of the same material with fixed moisture can change significantly (even several times). In the first place, this can be explained by the characteristics of the liquid distribution in the sample volume (uniform or uneven), the characteristics of the pore surface wetting (partial or total), the λ measurement method (stationary or non-stationary), etc. Special investigations should be performed to clarify the indicated circumstances.

Summary

The geometric model of the polymer structure was verified. A mathematical description of heat and water vapour transfer in a rigid polymer foam was formulated with the use of the theory of generalized thermal conductivity. This description takes into account the influence of water vapour diffusion in the pore space and the resistance of this space to the diffusion. Dependences enabling calculation of the threshold value of moisture at which there is transition from partial to full wetting of the pore surface and vice versa were formulated. The influence of material porosity, humidity and water vapour diffusion within the effective porosity on the effective thermal conductivity of the material was determined by calculation. A comparison between computational results and data shows their sufficient compatibility.

References

1. O. Krischer, W. Kast, *Die wissenschaftlichen Grundlagen der Trocknungstechnik* (Springer-Verlag, Heidelberg, 1992)
2. A. Missenard, *Conductivité thermique des solides, liquides, gaz et de leurs mélanges* (Éditions Eyrolles, Paris, 1985)
3. F. Ochs, W. Heidemann, H. Müller-Steinhagen, *Int. J. Heat Mass Transf.* **51**, 14 (2008)
4. V. V. Gur'ev, V. S. Žoludov, V. G. Petrov-Denisov, *Teplovaâ izolaciâ v promyšlennosti. Teoriâ i rasčet* (Strojizdat, Moscow, 2003)
5. M. Shi, X. Li, Y. Chen, *Sci. China Ser. E-Tech. Sci.* **4**, 8 (2006)
6. J. Randrianalisoa, D. Baillis, C. L. Martin, R. Dendievel, *Int. J. Heat Mass Transf.* **98**, 10 (2015)
7. D. Baillis, R. Coquard, S. Cunsolo, *J. Mater. Sci.* **52**, 22 (2017)
8. A. Alsabry, V. Nikitsin, B. Backiel-Brzozowska, V. Kofanov, *Int. J. Appl. Mech. Eng.* **23**, 4 (2018)
9. L.R. Glicksman, *Heat transfer in foams*. In: N.C Hilyard., A. Cunningham (eds) *Low density cellular plastics* (Springer, Dordrecht, 1994)
10. R. Coquard, D. Baillis, *ACTA MATER* **57**, 14 (2009)
11. V. Nikitsin, B. Backiel-Brzozowska, *Int. J. Heat Mass Transf.* **56**, 5 (2013)
12. G. N. Dul'nev, V. V. Novikov, *Transfer processes in inhomogeneous media* (Energoatomizdat, Moscow, 1991)

13. G.A Scheffler., R. Plagge, Int. J. Heat Mass Transf. **53**, 11 (2010)
14. F. Dominguez-Munoz, B. Anderson, J.M. Cejudo-Lopez, A. Cariello-Anders, ENERG BUILDINGS **42**, 11 (2010)