

Mathematical modeling of binding material coalescence at the production of syntactic carbon foams

V L Fedyaev^{1,2}, E R Galimov¹, N Ya Galimova¹, V M Samoylov³ and M A Orlov⁴

¹IME - Subdivision of FIC KazanSC of RAS, Lobachevsky str. 2/3, Kazan, 420111 Tatarstan, Russia

²Kazan national research technical university named after A N Tupolev, K. Marx str. 10, Kazan, 420111 Tatarstan, Russia

³JSC NIIgrafit, Elektrodna str. 2, Moscow, 111524, Russia

⁴Bauman Moscow state technical university, Baumanskaya 2-ya str., building 1, house 5, Moscow, 105005 Russia

engelgalimov@yandex.ru

Abstract. The processes of agglutination and coalescence of a softened (liquefied) coating material of microspheres are considered both in the absence of an external influence and in its presence. The periodicity cell is singled out, the dynamics of the change in the form of the interface between the liquid and gas phases is described. The thermal and mechanical effects are marked out as external factors leading to shrinkage of the microspheres layer with coatings. Relationships for estimating the shrinkage of the periodicity cell and determining the influence of the named factors, viscosity, and surface tension on the porosity of the layer material are presented.

1. Introduction

Foams are one of the varieties of porous materials widely represented in nature and engineering. As in any porous structure, in the foam, you can mark out two main components: a solid framework (matrix, skeleton) and a liquid (usually gaseous) medium, located in the pores (cavities) formed by the framework material. In the extreme case, the situation in which there is no medium in the pores (vacuum) or its content (concentration) is so small that it can be neglected is possible. At the same time, cases in which both the liquid and gas (vapor) are in the pores are quite common. Foams according to one of the definitions are highly concentrated coarsely dispersed systems in which the dispersion medium is a solid material or liquid, and the dispersed phase – gas. The main distinguishing feature of foam is that it has a high porosity (its macroporosity is $m_s > 0.5$).

Depending on the conditions of production, foams can be divided into two types: natural and technical. In the surrounding nature, it is a marine foam, less often river foam often observed near the coastal edge; magma the streams of which erupt from the volcanoes.

2. Body text

In the solidified state the magma material is a pumice stone. Here, it is necessary to note one more difference of foam from porous materials itself: the foam framework material can be liquid (fluidal) and solid deformable. Perhaps, only by a long stretch of the imagination, the biological tissues of the lungs, the middle part of the human and animal bones, plant stems and etc. are foams. Undoubtedly, the conditions for their formation, operation and their properties are specific.



There are much more examples of foam materials used in everyday life at the implementation of technological processes, production and operation of various technical objects: fire extinguishing systems; flotation technologies for purification of liquid media, extracting of valuable components from them; sponges, heat-insulating and building materials (foam plastic, foam concrete, expanded clay, etc.); foam materials used for softening, damping the loads, etc.

Syntactic carbon foams have a special place among the foam materials. Firstly, this is due to the fact that carbon itself has unique performance properties secondly, the framework material of this foam consists of carbon serving as a binder for hollow microspheres of about 10-50 μm in size located in it. In turn, microsphere shells can be made of metal ceramics, carbon, and other materials. Thus, these foams are characterized by the above-mentioned macroporosity m_p (pore sizes of about 1 ÷ 5 mm) and microporosity m_g the micropore sizes are, of course, slightly smaller than the microsphere sizes.

By now, there are a number of production technologies of syntactic carbon foams [1]. This paper focuses on one of the technology stages in which the microspheres with a layer of the polymer coating are raw material. The main technological task of the implementation of this stage is the production of a monolithic polymer material containing to the extent possible uniformly distributed microspheres. Let us mark out two variants of the solution to this problem: due to particles agglutination when the coating material is softened and by coalescence of the liquefied layers of the coating.

Agglutination of particles containing microspheres

For a mathematical description of the agglutination process of the named particles in a bulk layer, let us move from a real macroporous medium to a fictitious one, whose voids are the gas spherical cavities of diameter d_s , distributed uniformly over the volume [2]. If the real layer of particles with the diameter d_p has the rhombohedral laying, then it is easy to make sure that the macropores diameter of the fictitious material is:

$$d_s = d_p \left(\left(6 \sin^2 \theta \sqrt{1 + \cos \theta} / (\pi (1 + \cos \theta)) \right) - 1 \right)^{1/3}, \quad (1)$$

where θ – the angle characterizing the laying peculiarities of spherical particles ($60^\circ \leq \theta \leq 90^\circ$). Approximately

$$d_s \approx (1 - 0.22 \cos \theta) d_p. \quad (2)$$

Hence the initial macroporosity of the medium

$$m_{s0} \approx 0.5 - 0.33 \cos \theta. \quad (3)$$

It should be noted that the given spherical macropores are only equivalent to cavities of a very complicated form of the original real bulk medium.

Following [3] to describe the dynamics of the change of the equivalent radius of the spherical pore $a = a(\tau)$ over time τ we use the equation:

$$da/d\tau = -3\kappa\sigma/(4\eta), \quad (4)$$

where η – the viscosity of the polymer coating material, σ – the surface tension coefficient at the interphase boundary, κ – correction coefficient taking into account the influence of the external factors on the particles agglutination process.

Integrating the equation (4) under the condition that at the initial time the radius $a = a_0$ for a time τ the values of η , σ are close to their average values $\bar{\eta}$, $\bar{\sigma}$, we obtain:

$$a = a(\tau) = a_0 - K_0 \tau, \quad (5)$$

where $K_0 = 3\kappa\bar{\sigma}/4\bar{\eta}$.

It can be seen from (5) that the time for complete agglutination of particles containing the microspheres ($a = 0$) will be:

$$\tau_{sc} = a_0/K_0.$$

In the case when at the initial time $\tau = 0$ the laying of spherical particles of the bulk layer with radius r_p is such that $\theta = 90^\circ$, $a_0 = 0.5d_s$ (see (1)) we have

$$\tau_{sc} \approx 1.33(1 - 0.22 \cos \theta) \bar{\eta} r_p / (\kappa \bar{\sigma}).$$

As follows from this formula the smaller is the particle size r_p , the average viscosity of the polymer material $\bar{\eta}$ and the greater is the average surface tension $\bar{\sigma}$, the smaller will be the time of particles agglutination. This is completely consistent with the existing physical representations. As for the parameter κ , it can be assumed that it depends on the pressure ratio $\bar{p} = p_c / p_s$, where p_s , p_c – the pressure in the threshold space and softened polymer material of the microsphere coating layer, respectively.

In particular

$$\kappa = k \cdot \bar{p}.$$

Here k – the empirical coefficient the pressures p_s , p_c characterize the external impact on the medium.

It must also be kept in mind that along the process under consideration the temperature T of the porous medium can change accordingly $\bar{\eta} = \bar{\eta}(T)$, $\bar{\sigma} = \bar{\sigma}(T)$, $\bar{p}_n = \bar{p}_n(T)$, $\kappa = \kappa(T)$.

If the change of the given quantities is relatively small during the allotted time, then the above relationships are applicable with a certain accuracy degree.

Coalescence of the particles with the liquefied layer of the coating

At the moment of contact of the spherical surfaces of the liquefied surface layers of particles, we select the periodicity cell enclosed between six planes passing through the centers of neighboring particles. This cell includes eight spherical segments and a gas cavity bounded by eight spherical surfaces six sections of the secant planes.

Immediately after the neighboring spherical segments come in contact, depending on magnitude of the pressure p_{s0} in the pore space at that moment, there are two possible variants of the coalescence process of the particles. If the pressure p_{s0} is small the gas in the macrocavities is discharged the interphase surface remains convex the pore space will have a complicated formula. In this situation for a mathematical description of the particles coalescence, it is convenient to use the model of an ideal (tubular) porous medium [2]. At the initial time the channels radius of the named medium according to the Kozeny formula will be:

$$r_{s0} = 2m_{s0} r_p / (3(1 - m_{s0})). \quad (6)$$

Another estimate of the radius r_{s0} is possible [2, 4]:

$$r_{s0} \approx 2.83 \sqrt{k_s / m_{s0}}, \quad (7)$$

where k_s – permeability coefficient of the bulk layer.

Further assuming that the dependence analogous to (4) operates in the circular cross-section of the pore channel where the sphere radius a is substituted by the current radius r_s of the channel cross-section, we find:

$$r_s = r_s(\tau) = r_{s0} - K_0 \tau. \quad (8)$$

Hence the time of complete coalescence of the polymer material particles

$$\tau_{sc} = r_{s0} / K_0 = 8m_{s0} \bar{\eta} r_p / (9\kappa \bar{\sigma} (1 - m_{s0})). \quad (9)$$

Substituting the dependence (3) in the relationship (9), we approximately get:

$$\tau_{sc} \approx 0.89(1 - 0.66 \cos \theta)^2 \bar{\eta} r_p / (\kappa \bar{\sigma}). \quad (10)$$

Comparing the formula for the agglutination time and (10), we make sure that the time for complete coalescence of particles is generally less than time for their agglutination.

In the case when the pressure p_{s0} in the pore space is increased after the contact of the neighboring spherical segments near the points of contact the polymer layer material is closed down under the action of capillary forces, the sections with curvature inverse to the curvature of the original spherical surfaces are formed. Obviously, the interphase boundary with the curvature of unlike signs will be unstable and in a relatively short period of time will take a form close to spherical one. It is easy to verify that its radius

$$r_{s0} = r_p \sqrt[3]{(6/\pi) - 1}. \quad (11)$$

According to the Laplace formula on a given spherical surface

$$p_{s0} - p_{c0} = 2\sigma/r_{s0}. \quad (12)$$

Here p_{c0} is the pressure in the liquid material of the coating layer by the time when the external factors start acting.

Since the radius r_{s0} of the spherical cavity located in the center of the selected periodicity cell is smaller than its transverse dimensions these cavities are closed (bubbles) the gas pressure in them during the processing step can, in general, be changed only by heating or cooling the porous medium. In the absence of phase transitions at the interface boundary according to the Clapeyron-Mendeleev law the pressure in the cavity is

$$p_s = RM_s T / V_s, \quad (13)$$

where R – gas constant, M_s – the gas mass in the cavity, V_s – its volume.

In (12) replacing the values of p_{s0} , p_{c0} , r_{s0} by the current values of p_s , p_c , r_s , substituting the pressure p_s (13) we get the equation to find the cavity radius r_s :

$$4\pi p_c r_s^3 + 2\sigma r_s^2 = 3RM_s T. \quad (14)$$

Obviously, the change of radius r_s is small, so we write $r_s = (1 + \varepsilon_s) r_{s0}$ where ε is a small quantity. After a series of transformations and discarding of small quantities for estimating ε_s we find the relation:

$$\varepsilon_s \approx 0.25 \left((3RM_s T / r_{s0}^3) - 2(2\pi p_c + \sigma / r_{s0}) \right) / (3\pi p_c + \sigma / r_{s0}). \quad (15)$$

It can be seen from (15) that with increasing the temperature T and other parameters being constant ε_s and hence the radius r_s increase. Conversely, when surface tension coefficient σ and pressure p_c increase, the parameter ε_s decreases.

3. Conclusions

Thus, the relationships to determine the time of complete agglutination and coalescence of the microsphere coating polymer material and to estimate the influence of initial particle sizes, their laying, material viscosity, and surface tension at the interphase boundary on these processes are obtained. The dependence characterizing the change of the gas cavity dimensions in the periodicity cell at the particles coalescence in the course of the heating (cooling) of the porous medium and the influence of mechanical loads on it is established. These relationships and dependencies can be useful when choosing the rational technological modes of production of the articles made of syntactic carbon foams and in other cases [4-10].

References

- [1] Fedyaev V L, Galimov E R, Samoylov V M, Danilov E A and Orlov M A 2016 Production of thermally conductive carbon foams and their application in automobile transport *Proceedings of the International Scientific and technical conference "Innovative Engineering Technologies, Equipment and Materials – 2016"* part 2 pp. 211 – 214
- [2] Polubarinova – Kochina P Ya 1977 *Theory of ground water motion* (Moscow: Publishing house Nauka)
- [3] Yakovlev A D 1987 *Powder paints* (Leningrad, Publishing house Khimiya)
- [4] Belov S V 1981 *Porous metals in mechanical engineering* (Moscow: Publishing house Mashinostroenie)
- [5] Kashapov N F, Luchkin G S and Luchkin A G 2010 *Vacuum technologies for the application of functional coatings* "Vestnik" of Kazan State Technological University No 2 pp 340-34
- [6] Kashapov N F, Luchkin G S and Tagirov R F 2010 *Vacuum test bench for the application of functional coatings* "Vestnik" of Kazan State Technological University No 2 pp 346-52
- [7] Mazo A B 1996 *Mathematical modeling of processes of hot metal processing* (Kazan Math. Soc.) p 209

- [8] Adamson A 1979 Physical chemistry of surfaces (Moscow: Mir)
- [9] Betchelor Dzh 1973 *Introduction to fluid dynamics* (Moscow: Mir)
- [10] Galimov E R, Fedyaev V L, Galimova N Ya, Takhaviev M S and Siraev A R 2017 *Mathematical modeling of processes occurring during deposition of sprayed particles of polymeric powder* Journal of Physics : Conf. Series vol 789 **012007**