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

V L Fedyaev¹,², 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, Elektrodnaya 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 $m_p > 0.5$).

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 microparticles of about 10-50 μm in size located in it. In turn, microparticle 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 microparticle 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 microparticles 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 microparticles. 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 microparticles**

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:

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

where \( \theta \) – the angle characterizing the laying peculiarities of spherical particles (60° ≤ \( \theta \) ≤ 90°). Approximately

\[
d_s \approx (1-0.22 \cos \theta)d_p.
\]

Hence the initial macroporosity of the medium

\[
m_{i0} \approx 0.5-0.33 \cos \theta.
\]

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 \( \tau \) we use the equation:

\[
da / d\tau = -3 \kappa \sigma / (4\eta),
\]

where \( \eta \) – the viscosity of the polymer coating material, \( \sigma \) – the surface tension coefficient at the interphase boundary, \( \kappa \) – 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 \( \tau \) the values of \( \eta, \sigma \) are close to their average values \( \bar{\eta}, \bar{\sigma} \), we obtain:

\[
a = a(\tau) = a_0 - K_0 \tau,
\]

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

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

\[
\tau_{ag} = a_0 / K_0.
\]

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
\[ \tau_w \approx 1.33\left(1-0.22\cos \theta\right)\eta pr / \left(\kappa \sigma\right). \]

As follows from this formula the smaller is the particle size \( r_p \), the average viscosity of the polymer material \( \eta \) and the greater is the average surface tension \( \sigma \), the smaller will be the time of particles agglutination. This is completely consistent with the existing physical representations. As for the parameter \( \kappa \), 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 \( \eta = \eta(T) \), \( \sigma = \sigma(T) \), \( \bar{p}_s = \bar{p}_s(T) \), \( \kappa = \kappa(T) \).

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 \( p_s \) in the pore space at that moment, there are two possible variants of the coalescence process of the particles. If the pressure \( p_s \) 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 Kozeni formula will be:

\[ r_{0\circ} = 2m_{so} r_p / \left(3\left(1-m_{so}\right)\right). \]

Another estimate of the radius \( r_{so} \) is possible [2, 4]:

\[ r_{so} \approx 2.83 \sqrt{k_s / m_{so}}, \]

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:

\[ r_s = r_s(T) = r_{0\circ} - K_{so} \tau. \]

Hence the time of complete coalescence of the polymer material particles

\[ \tau_w = r_{so} / K_{so} = 8m_{so} \eta r_p / \left(9K_s \sigma \left(1-m_{so}\right)\right). \]

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

\[ \tau_w \approx 0.89\left(1-0.66\cos \theta\right)^2 \eta r_p / \left(\kappa \sigma\right). \]

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 \( p_{so} \) 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 sings 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
According to the Laplace formula on a given spherical surface
\[ p_{s0} - p_{c0} = 2\sigma / r_{s0}. \] (12)
Here \( p_{s0} \) 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
\[ p_s = R M_s T / V_s. \] (13)
where \( R \) – gas constant, \( M_s \) – the mass gas 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 \( r_s \):
\[ 4\pi p_s r_s^3 + 2\sigma r_s^2 = 3RM_s T. \] (14)

Obviously, the change of radius \( r_s \) is small, so we write \( r_s = (1 + \varepsilon_s) r_{s0} \) where \( \varepsilon \) is a small quantity. After a series of transformations and discarding of small quantities for estimating \( \varepsilon_s \) we find the relation:
\[ \varepsilon_s \approx 0.25 \left( (3RM_s T / r_{s0}^3) - 2(2\pi p_c / \sigma / r_{s0}) \right) / (3\pi p_s / \sigma / r_{s0}). \] (15)
It can be seen from (15) that with increasing the temperature \( T \) and other parameters being constant \( \varepsilon_s \) and hence the radius \( r_s \) increase. Conversely, when surface tension coefficient \( \sigma \) and pressure \( p_s \) increase, the parameter \( \varepsilon_s \) 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].

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