Dynamics of coalescence and spreading of liquid polymeric particles during coating formation

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Abstract. Processes of agglutination, coalescence and spreading of polymeric powder particles during coating formation are considered using methods of mathematical modeling. The relationships to evaluate time of particles agglutination, velocity of coalescence and spreading of material on the surface of a treated body are given. Recommendations on intensification of the given technological stages are presented.

Particles agglutination occurs in the deposition process of polymeric powder particles on a treated surface and after completion of this technological stage, in the following stage – coalescence, spreading, and finally, coating formation [1, 2]. Peculiarity of agglutination stage is that in the course of its implementation the certain connections are set between particles of the same materials in contact. In adhesion theory this case is called autohesion [3]. It is assumed that material of the particles in the contact region is not mixed; boundary surface of particles is retained.

In the next stage – coalescence stage of powder particles provided that their material is in the fluid (liquid) state the boundary surface of the particles unnoticeable. Over time, in the absence of external factors the two merging particles under the action of capillary forces form one particle close in shape to a sphere.

It should be noted that these two processes can occur, primarily, between softened particles of thermosetting materials as well as between fritted or melted thermoplastics particles.

1. Agglutination of polymeric powder particles

In order to mathematically describe the agglutination process of powder particles in an applied layer let us move from real porous medium of this layer to fictitious [4] and such that its voids are identical gaseous cavities of spherical shape uniformly distributed over the volume. It is easy to assure that in case of rhombohedral laying of spherical particles the diameter of these pores

\[ d_{11} = d_p \left( \frac{6 \sin^2 \theta \sqrt{1 + \cos \theta}}{(\pi (1 + \cos \theta)) - 1} \right)^{1/3}, \]

where \( d_p \) – particles diameter, \( \theta \) – angle characterizing the peculiarity of laying of particles (balls) (60° ≤ \( \theta \) ≤ 90°). Approximately

\[ d_{11} \sim d_p (1 - 0.22 \cos \theta). \]

Accordingly, the initial porosity of the medium...
Assuming for model (4) we obtain that for a time \( \tau \) parameters \( \sigma, \eta \) are close to their average values \( \sigma_0, \eta_0 \) we find:

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

where \( a_0 \) – initial equivalent radius of the spherical pores, \( m; K_0 = 3\mu r_0 / (4\eta_0) \).

Hence time of full agglutination of the polymeric powder particles (collapse of pores) will be:

\[
\tau_{\text{c1}} = a_0 / K_0.
\]

If at the initial time \( \tau = 0 \) laying of spherical particles of the applied layer of the powder with a radius \( r_p \) is rhombohedral, then \( a_0 = 0.5d_{\text{f1}} \) (see. (3)),

\[
\tau_{\text{c1}} \sim 1.33(1 - 0.22\cos 0.25)\eta_0 r_p / (\mu \sigma_0).
\]

Slightly different evaluation of the agglutination dynamics of polymeric powder particles can be obtained by considering an ideal model [4] of the layer instead of the named above fictitious model. At the initial time using the Kozeny formula we define the channel radius of an ideal porous medium by the formula:

\[
r_{\text{i10}} = 2m_0 r_p / (3(1 - m_0)),
\]

or by the relationship:

\[
r_{\text{i10}} \approx 2.83 \sqrt{k/m_0},
\]

where \( k \) – permeability coefficient of the applied layer of the medium [4, 5].

Further, assuming that dependence (4) where the bubble radius \( a \) is replaced by the channel cross-section radius \( r_{\text{i1}} \) acts in a circular cross-section of the pore channel we find:

\[
r_{\text{i1}} = r_{\text{i1}}(\tau) = r_{\text{i10}} - K_0 \tau.
\]

According to (6), (8) time of the full agglutination of the polymeric powder particles

\[
\tau_{\text{c1}} = r_{\text{i10}} / K_0 = 8m_0 \eta_0 r_0 / (9\mu \sigma_0 (1 - m_0)).
\]

Substituting dependence (3) in the equation (9), we approximately obtain:

\[
\tau_{\text{c1}} \sim 0.89(1 - 0.66\cos 0.25)\eta_0 r_p / (\mu \sigma_0).
\]

At an average value \( \cos 0.25 = 0.25 \) according to formula (5) time \( \tau_{\text{c1}} \sim 1.26\eta_0 r_0 / (\mu \sigma_0) \). It can be seen that usage of model of the ideal porous medium results in less time of full agglutination of particles than model of the fictitious medium. Probably, since its structure is more favorable for the agglutination of the material. In general, the time of full agglutination of powder particles can be decreased by reducing the particle size, changing their laying (decreasing angle \( \theta \)), reducing the polymeric material viscosity, increasing the surface tension coefficient at the polymer-gas interface.

2. Coalescence and spreading of material of polymeric particles
The coalescence process of the polymeric powder particles is typical, in our opinion, for the particles the material of which is in slow-flowing state or close to it, for example, in a plastic state. In this case with respect to the processes occurring in the applied powder layers we will assume that particles coalescence is the stage that follows the agglutination when as a result of heating of material up to a certain temperature \( T_i < T_f \) \( (T_f \) – limiting temperature, probably, decomposition temperature of the polymeric material) the surface tension, viscosity decrease and its fluidity increases.

Considering a layer of liquid polymeric particles on the body surface we can identify, firstly, a layer of particles in contact with the body; secondly, layer of particles in contact with the ambient gaseous medium and, finally, a plurality of particles located in the inner region of the layer. For the latter it is typical that each of them is surrounded by other particles.

It should be expected that coalescence processes of liquid particles in the selected areas of the applied layer will be slightly different from each other. The near-border particles, their coalescence will of course be under a certain influence of both the solid body and ambient gaseous medium (air).

Let us consider further as the most interesting from a practical point of view coalescence of polymeric powder particles that are located on the surface of a treated body. Considering the regularities of spreading liquid on the solid surface \([6-8]\) we adopt the following assumptions as the initial ones. Let us assume that liquid and gas media are incompressible; process of deformation, form changing of particles, pores is slow (quasi-stationary), isothermal; pressure in material of particles \( p_p \) does not change over time \( (p_p = const) \) however in both opened and closed pores pressure \( p_g \) can change. Loads from side of the overlying layers of particles, mass forces are not taken into account, movement of the media in the vertical to the body surface section, passing through the mass centers of the selected neighbouring polymeric particles is plane-parallel (two-dimensional).

Fig. 1 shows the possible change over time of periodicity cell initially representing a half circle of the spherical particle cross-section with radius \( r_p \), in case of wettable solid body surface.

Here \( AB \) – upper limit of the cell, \( A'B' \) – its middle position, \( h_k = h_k(\tau) \) – cell height, \( PQ \) – interface between polymeric material and gas medium of the cavity, \( BQ (PP') \) – conventional border between the considered cell and cell of the neighbouring particle symmetric to it, \( \theta \) – limiting wetting angle. We emphasize that the border \( PQ \) close to the arc of a circle is equivalent to the real border that has a more complex shape (fig. 2).

Thus the problem is to define the changing over time radius of the curvature border \( PQ \) \( R = R(\tau) \), height \( h_k = h_k(\tau) \), ordinate of point \( Q \ y_Q = y_Q(\tau) \), distance from point \( P \) to the coordinates origin \( x_p = x_p(\tau) \). Following dependencies are used to solve it. According to the Laplace’s formula on the interphase boundary \( PQ \)

\[
R = \sigma / \Delta p ,
\]

where \( \Delta p = p_g - p_p \) – pressure difference in the gas \( (p_g) \) and material of the particles \( (p_p) \).

At the point \( P \) on the solid body surface equilibrium condition of the interface between the liquid and gaseous phase (Young’s equation) is as follows:

\[
\cos \theta = \Delta \sigma_s / \sigma
\]

where \( \Delta \sigma_s = \sigma_{sg} - \sigma_{sl} \) – jump of the surface tensions on a solid body; \( \sigma_{sl}, \sigma_{sg} \) – surface tension on the interface between solid body – liquid, solid body – gas, respectively.

Due to the fact that at coalescence of adjacent particles the tangent \( EQ \) (fig. 3) must be parallel to the axis \( OX \) center of the circle \( C \) is located on the line \( DQ \) we get:

\[
\theta = \pi - \gamma ,
\]

where angle \( \pi / 2 \leq \gamma \leq \pi \).
Figure 1. Dynamics of coalescence of liquid particles of polymeric powder on the wetted surface.

Figure 2. Approximate shape of the interface between liquid medium and gas at particles coalescence.

Figure 3. Part of the periodicity cell with an equivalent interface.

The condition of liquid conservation in the cross section $OPQBA$ in the process of particles coalescence is represented by the dependence:

$$S_p = S_{OBQ} + S_{QB} - S_c = 0.5 \pi r_p^2 + r_p h_k - 0.5(r_p - x_p)(y_Q - R) - 0.5 \gamma R^2.$$  \hspace{1cm} (14)

Finally, from the triangle $PDC$ (fig. 3) it follows that

$$y_Q = R + \sqrt{R^2 - (r_p^2 - x_p^2)}.$$  \hspace{1cm} (15)

Since it is assumed that at coalescence, shifting of the points $P$ and $Q$ the line $PQ$ remains an arc limiting wetting angle $\theta$ must change over time $\theta = \theta(\tau)$, accordingly, $\zeta = \cos \theta = \zeta(\tau)$. Indeed [8] since limiting wetting angle depends on the properties of liquid, solid medium, structure of the body surface, presence of adsorbed vapors and surface-active substances on it, as well as on temperature, mass forces, velocity of movement of the interface between the liquid and gaseous media.
along the body, it is quite possible that when shifting the point $P$ the value of angle $\theta$ will be changing. Considering this fact we can write:

$$
\zeta = \zeta(x_p) = (x_p + R - 1) / R,
$$

(16)

where $x_p = x_p / r_p$, $R = R / r_p$. Further taking into account

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we find:

$$
(x_p = x_p(\tau) = 1 - \delta_s R),
$$

(17)

where $\delta_s = 1 - \Delta \sigma / \sigma$.

In accordance with Ошибка! Источник ссылки не найден., the dimensionless radius of curvature

$$
R = \tilde{R}(\tau) = 1 / ((1 - \tilde{p}) / \tilde{p}_g) \approx (1 + \tilde{p}) / \tilde{p}_g - 1 / \tilde{p}_g.
$$

(18)

Here $\tilde{p} = \tilde{p}_p / \tilde{p}_g$ – ratio of pressures $p_p$ and $p_g$ ($\tilde{p} \approx 1$); $\tilde{p}_p = r_p p_p / \sigma$, $\tilde{p}_g = p_g(\tau) = r_p p_g / \sigma$ – dimensionless pressure in the material of particles of a gas cavity, respectively.

Taking into account (17) the dimensionless coordinate of the point $Q$ (see Ошибка! Источник ссылки не найден.) is given by the formula:

$$
\tilde{y}_Q = y_Q / r_p = \tilde{R}(1 + \sqrt{1 + 2 \delta_s (1 - 2 / \tilde{R})} / 2).
$$

(19)

If the value $\delta_s (1 - 2 / \tilde{R})$ is small then approximately

$$
\tilde{y}_Q \approx \tilde{R}(2 - 0.5\delta_s (1 - 2 / \tilde{R})).
$$

Passing in (14) to the dimensionless variables, we get the evaluation of the height of the periodicity cell:

$$
\tilde{h}_k = \tilde{h}_k(\tau) = h_k / r_p \approx 0.5 \pi + 0.5(1 - \tilde{x}_p)(\tilde{y}_Q - \tilde{R}) + 1.2 \tilde{R}^2 \square
$$

~0.5\pi + 0.5\delta_s \tilde{R}^2 (1 - 0.5\delta_s (1 - 2 / \tilde{R})) + 1.2 \tilde{R}^2.

(20)

In this case for the sake of simplicity, the angle $\gamma$ is replaced by its average value of 2.355.

In the limit when $\tilde{R} \to 0$ accordingly $\tilde{y}_Q \to 0$ (see Ошибка! Источник ссылки не найден.), $\tilde{x}_p \to 1$, height $\tilde{h}_k = 0.5 \pi$ and area of the rectangle $OPBA$ is equal to $S_p$.

It should be noted that in the proposed model of powder particles coalescence, spreading of polymeric material on the body surface the main reason of particles transformation is the change of gas pressure $p_g$ in the pores over time. In turn the change of pressure $p_g$ is possible in the following cases. If the pores are open and connected with an external environment then pressure $p_g$ changes in accordance with the changes of the external pressure $p_a = p_a(\tau)$. In the case of closed (dead-end) pores the pressure $p_g$ will change by the action of external loads on the particles trying to change the pores size when heating or cooling of powder particles. Despite the fact that we are not taking into account the direct influence of external factors on the considered particles we will assume that their influence has effect indirectly through the pressure $p_g$ change.

For further analysis of the obtained solutions let us assume that the dimensionless gas pressure in the pores depends on time linearly:

$$
\tilde{p}_g = \tilde{w}_0 + \tilde{w}_1 \tau.
$$

If $\tilde{p}_g$ changes over time relatively small then the radius of curvature

$$
\tilde{R} = \tilde{R}(\tau) \sim (1 - k_p \tau) / \tilde{w}_0 (k_p = \tilde{w}_1 / \tilde{w}_0),
$$

(21)

decreases over time according to the law which is close to the linear one.
Further considering that when the angle $\theta$ changes from $\pi/2$ to 0 parameter $\delta_s$ decreases from 1 to 0, we can write:

$$\delta_s = \delta_s(\tau) = 1 - \tau / \tau_p,$$

(22)

where $\tau_p$ – characteristic time of spreading of polymeric material on the body surface, for example, time during which the point $P$ reaches the position $D$.

Taking into account dependencies (21), (22), we define the velocity of spreading of material of particles (velocity of point $P$ movement):

$$v_p = v_p(\tau) = dx_p / dt = \dot{\mathbf{w}}_p(\mathbf{w}_{p0} - 2\dot{\tau}).$$

(23)

Here $\mathbf{w}_p = r_p k_p / \mathbf{w}_0$, $\mathbf{w}_{p0} = 1 + 1 / (\tau_p k_p)$, $\dot{\tau} = \tau / \tau_p$.

From formula (23) it follows that at the beginning of the spreading ($\tau \sim 0$) point $P$ velocity $v_{p0} > 0$. By the end of shifting of the point $P$ it reaches the position $D$, when time $\tau = \tau_*$, the polymeric material completely wetted the body surface, the condition $v_{p1} \geq 0$ must be satisfied. Hence it follows that

$$\tau_p k_p \leq 1 / (2\tau_* - 1).$$

(24)

At fixed time $\tau_*$, initial dimensionless gas pressure $\mathbf{w}_0$ from relationship (24) we find that the parameter $\mathbf{w}_1$ characterizing the intensity of the increase of gas pressure in the cavity must satisfy the condition:

$$\mathbf{w}_1 \leq \mathbf{w}_0 / (\tau_p (2\tau_* - 1)) = r_p p_{g0} / ((\sigma \tau_p) (2\tau_* - 1)),$$

(25)

where $p_{g0}$ – gas pressure at $\tau = 0$. If this condition is not satisfied the pressure in the cavity increases at a higher rate, then by the time $\tau = \tau_*$ the cavity will not close, gas bubbles are formed on the surface of a treated body. On the other hand when parameters $\mathbf{w}_0, \mathbf{w}_1$ are specified the time $\tau_*$ is defined from the equation $x_p(\tau = \tau_*) = r_p^*$:

$$\tau_* = 1 / k_p = \mathbf{w}_0 / \mathbf{w}_1.$$

(26)

Therefore, time of spreading of the polymeric material and hence the stages of particles coalescence can be decreased by lowering the initial gas pressure $p_{g0}$, increasing the intensity of increase of $p_g$. It is also necessary to keep in mind that according to (23) over time $\tau$ velocity of spreading $v_p$ decreases. Slowing down the movement of the point $P$ along the surface of the solid body is, apparently, caused by counteraction of the gaseous medium, pressure of which in the cavity of pores increases over time.

In conclusion we note that for intensification of impregnation of capillary-porous bodies by the liquid at which the movement processes of liquid media in the pores are very similar to those considered in this paper, the following techniques are used [9-11]: vacuumization of the bodies before immersion to the liquid, increasing the pressure after the loading, replacement of air that fills the pores on the gases easily soluble in liquid.

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