Determination of the solid phase concentration in the course of material solidification

O.Yu.Aktan

Physical Department, T.Shevchenko Kyiv National University,
2 Glushkov Ave, 03022 Kyiv, Ukraine

The solidification kinetics is considered. A method has been proposed to determine the solid phase concentration in the course of material solidification by measuring the shear modulus. As an example, the solid phase variation during the solidification of an aqueous gelatine solution has been determined which is used as the matrix of nanosystems are optical chemical sensors has been determined.

Исследуется кинетика процесса затвердевания. Предложен метод определения концентрации твёрдой фазы в процессе затвердевания путем измерения модуля сдвига. В качестве примера указанным способом определено изменение концентрации твёрдой фазы при затвердевании водного раствора желатина, который используется в качестве матрицы наносистем - оптических химических сенсоров.

A material being solidified is a two-phase system containing a soft phase and a solid one, the amount of the latter increasing in time in the course of solidification. The purpose of this work is to study the solidification process and to develop a control method therefor. It is the solid phase concentration in a solidifying material that is a macroscopic parameter characterizing the solidification process. Accordingly, the task is reduced to calculation of the solid phase concentration basing on experimental data.

A method has been proposed [1] to determine in experiment the shear modulus of a material in the course of its solidification. In this work being a continuation of the preceding study, it is shown how the solid phase concentration can be calculated using those data.

When determining the solid phase amount in a two-phase system, let the material under study be considered as an inhomogeneous continuum being a mixture of two isotropic phases. Thus, any characteristic of the inhomogeneous continuum measured in experiment is an averaging result over the areas exceeding considerably in size the area of heterogeneity. Such characteristics are referred to as "effective characteristics" or "mixture characteristics".

Let the following designations be introduced: G^*, K^*, ν^*, effective shear moduli, the volume modulus and Poisson ratio of a two-phase system, respectively; G_F and G_S, the shear moduli of solid and liquid phases, respectively; K_F and K_S, the volume moduli of solid and liquid phases, respectively; ν_F and ν_S, Poisson ratios of corresponding phases.

For calculation of effective constants of an inhomogeneous continuum, the elasticity theory of inhomogeneous media is used as a rule [2, 3]. The inhomogeneous continuum of a substance under study is a matrix with spherical inclusions. The matrix corresponds to the liquid phase, the inclusions, to the solid one. The average value of stress tensor $\langle \hat{\sigma} \rangle$ in a matrix is equated to the external stress tensor $\hat{\sigma}^0$ applied to the system at infinity. Inside of a spherical inclusion, the fields of stresses and strains are

homogeneous. The average stress $\langle \hat{\sigma} \rangle$ is determined as

$$\langle \hat{\sigma} \rangle = C_F \langle \hat{\sigma}(1) \rangle + C_S \langle \hat{\sigma}(2) \rangle, \qquad (1)$$

where C_F and C_S are solid and soft phase concentrations, respectively.

When calculating the effective elasticity constants for an inhomogeneous continuum, the elasticity theory problem is at first solved for the model being a single spherical inclusion of the single phase within a matrix having effective elastic properties. The solution hes the form

$$\langle \hat{\sigma}(1) \rangle = \hat{c}^* \hat{A}(1) \hat{\sigma}^0, \qquad (2)$$

where $\hat{c}^*$ the tensor of effective elastic constants. The formulas for the tensor $\hat{A}(1)$ are presented in [2].

Then, the problem of the elasticity theory is solved for a model representing a spherical inclusion of another phase within a matrix having effective elastic properties. This solution has the form

$$\langle \hat{\sigma}(2) \rangle = \hat{c}^* \hat{A}(2) \hat{\sigma}^0, \qquad (3)$$

where the tensor $\hat{A}(2)$ is defined by formulas presented in [2].

Substituting expressions (2) and (3) into (1) and taking into attention that $\hat{\sigma}^0 = \langle \hat{\sigma} \rangle$, we get

$$\langle \hat{\sigma} \rangle = \hat{c}^* [C_F \hat{A}(1) + C_S \hat{A}(2)] \langle \hat{\sigma} \rangle. \qquad (4)$$

Subsetting the stress tensor into the volume and deviator parts, we get from tensor equation (4) after substituting the $A(1)$ and $A(2)$ values under approximation $C_S = 1 - C_F$

$$\frac{C_F}{1 + \alpha^* \left(\dfrac{K_F}{K^*} - 1 \right)} + \frac{C_S}{1 + \alpha^* \left(\dfrac{K_S}{K^*} - 1 \right)} = 1, \quad (5)$$

$$\frac{C_F}{1 + \beta^* \left(\dfrac{G_F}{G^*} - 1 \right)} + \frac{C_S}{1 + \beta^* \left(\dfrac{G_S}{G^*} - 1 \right)} = 1, \quad (6)$$

where the following designations are taken:

$$\alpha^* = \frac{1 + \nu^*}{3(1 - \nu^*)}, \qquad (7)$$

$$\beta^* = \frac{2(4 - 5\nu^*)}{15(1 - \nu^*)}, \qquad (8)$$

$$\nu^* = \frac{3K^* - 2G^*}{6K^* + 2G^*}. \qquad (9)$$

It is known [4] that for the solid phase, $G_F \sim K_F$ and $K_S \sim K_F$. For the soft phase, let $G_S \ll K_S$, i.e., $G_S \ll G_F$ be taken.

In zero approximation for the small G_S/G_F parameter, the formula (5) takes the form

$$\frac{C_F}{1 + \beta^* \left(\dfrac{G_F}{G^*} - 1 \right)} + \frac{1 - C_F}{1 - \beta^*} = 1. \qquad (10)$$

For the soft phase Poisson ratio ν_S, it is possible to write a relation similar to (10):

$$\nu_S = \frac{3K_S - 2G_S}{6K_S + 2G_S}. \qquad (11)$$

Therefrom, $\nu_S \approx 0.5$.

The Poisson ratio ν^* for the mixture varies from ν_F to ν_S when the concentration C_F changes from 1 to zero. The lower limit of the solid phase Poisson ratio ν_F is about 0.33 [4]. The presented numerical estimations of ν_S and ν_F allow us to consider dependence of the mixture Poisson ratio on the solid phase concentration as a linear function

$$\nu^* = C_F \nu_F + 0.5(1 - C_F). \qquad (12)$$

Substituting the formula (12) into (8), we get

$$\beta^* = \frac{2(4 - 5(C_F \nu_F + 0.5(1 - C_F)))}{15(1 - (C_F \nu_F + 0.5(1 - C_F)))}. \qquad (13)$$

Then the formula (10) takes the form

$$\frac{C_F}{1 + \dfrac{2(4 - 5(C_F \nu_F + 0.5(1 - C_F)))}{15(1 - (C_F \nu_F + 0.5(1 - C_F)))} \left(\dfrac{G_F}{G^*} - 1 \right)} +$$
$$+ \frac{1 - C_F}{1 - \dfrac{2(4 - 5(C_F \nu_F + 0.5(1 - C_F)))}{15(1 - (C_F \nu_F + 0.5(1 - C_F)))}} = 1. (14)$$

The equation (14) is the $C_F(\nu_F, G_F, G^*)$ dependence. Thus, substituting the values of solid phase Poisson factor ν_F shear moduli of the mix and the solid phase G^* and G_F respectively, we will get the solid phase concentration in the two-phase system.

To check the procedure in experiment, let the experimental $G^*(t)$ dependence be
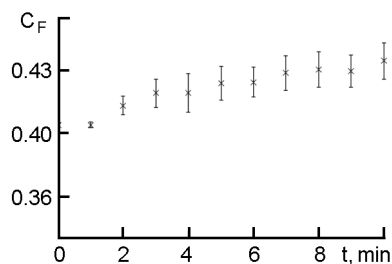
Fig. 1. Time dependence of solid phase concentration during gelatin solution solidification.

Fig. 2. Qualitative dependence of the effective solid phase concentration on the effective shear modulus.

used describing the solidification process of aqueous gelatin solution (Fig. 1) and presented in the previous work [1]. The selection of this object was caused by that circumstance that the object indicated widely is used as the matrix of nanosystems are optical chemical sensors, intended for the analysis of liquid media [5]. To calculate the amount of solid phase from the measured shear modulus value, it is necessary to know the solid phase elastic characteristics v_F and G_F. The solid phase is a gel in this case. According to [6], the Poisson factor of the gel v_F makes 0.47. The G_F value was determined from the known formula of the elasticity theory [2]

$$G_F = \frac{3K_F(1 - 2v_F)}{2(1 + v_F)}. \qquad (15)$$

The gel belongs to the class of so-called water-like materials. For such materials, the bulk modulus K_F is assumed to be equal to that of water ($2.25 \cdot 10^9$ N/m^2) [7]. The calculated G_F value has found to be $1.4 \cdot 10^8$ n/m^2.

In Fig. 1, the dependence of gel (solid phase)concentration calculated using (14) is presented. The zero time moment in Fig. 1 corresponds to the measurement onset. It is seen from the Figure that the system contained some gel at the start of the measurements. This fact can be explained as follows. The gelatin was dissolved at 70°C. Then the solution was cooled continuously down to 25°C being the starting measurement temperature. The gel formation is known to onset at 40°C [8, 9]. Thus, the tube was filled with gelatin solution containing a certain amount of gel. In spite of this, the measured shear modulus remains at first zero as is seen from the $G(t)$ curve in [1]. That is to say, the $G(C_F)$ dependence has the form shown in Fig. 2.
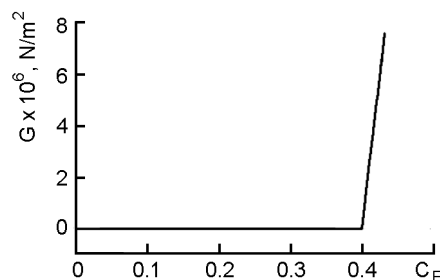
Basically, the design procedure offered in given article, allows to define quantity of a firm phase at any a parity of liquid and firm phases. For this purpose it is necessary to measure effective shift the module at any parity of these phases. Such measurements can be executed only I use, a technique [1]. Other techniques allow to spend such measurements only for small concentration of this or that phase.

The character of that dependence allows us to conclude that a percolation transition [10] related to the shear modulus occurs at $C_F = 0.4$. The dramatic increase of the shear modulus in the percolation transition point is associated to the formation of the solid phase cluster having the diameter equal to the tube transversal dimension. In fact, when the solid phase aggregates are smaller than the tube diameter, the presence thereof does not contribute essentially to the shear modulus, since it is the soft phase that is in contact with the tube walls. Only when the solid phase aggregates become equal to the tube diameter, the experiment "reveals" the solid phase.

The percolation transition in a three-dimensional system is known to take place when the concentration of the corresponding phase is 0.15 of the total volume. For a two-dimensional system, this transition should be observed at the corresponding concentration equal to 0.45 of the total volume. In our case, the system under investigation is cylindric [1] with the cylinder length exceeding its radius by a factor of 20. That is why it is just the radius that is critical dimension for percolation. Taking into account the experimental errors, the obtained critical concentration 0.4 is in agreement with the theoretical one (0.45).

The testing has shown that the procedure proposed can be used to determine the solid phase amount in a solidifying material. The procedure provides the solid phase amount

deermination in the later stages of solidification that is impossible at the existing techniques using, e.g., viscosimetry and light scattering [11, 12] that allows to study the solidification process at low solid phase concentrations only.

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Визначення концентрації твердої фази у процесі твердіння матеріалу

О.Ю. Актан

Досліджено кінетику процесу твердіння. Запропоновано метод визначення концентрації твердої фази у процесі твердіння шляхом вимірювання модуля зсуву. Як приклад, вказаним способом визначено зміну концентрації твердої фази при твердінні водного розчину желатину, який використовується як матриця наносистем - оптичних хімічних сенсорів.