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Abstract

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ON SHRINKAGE STRESS IN DISPERSE STRUCTURES

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The penetration of water into the interior of moistened bodies proceeds with a stress corresponding to the decrease in the surface free energy on the solid phase. The formation of adsorption-solvation layers is accompanied here by a certain reduction in the strength of the structure ($^{1-3}$). In the reverse direction, the mechanical action of capillary forces is manifested in the dynamics of drying, when, upon removal of hydration-adsorption moisture, the restored part of the free surface energy is used for the formation of secondary cohesion-adhesion bonds (^{4}), which fix shrinkage stresses.

The shrinkage stress F_σ (kg/cm^2) determined by us in drying systems ($^{5-7}$) must be regarded as a resultant quantity. It is the resultant of a series of stresses referred to the cross-sectional area S_0 of the particles of the disperse phase in the structure. Such a representation may be expressed by the equality

$$F_\sigma = \sigma L/S_0 + F_{\sigma_0} - F_s + F_k, \tag{1}$$

where $\sigma L/S_0$ is the compressive stress caused by the surface tension σ of the liquid along the perimeter L of the transverse section of the specimen; F_{σ_0} is the stress of capillary contraction as the sum of elementary capillary forces acting in the plane of the transverse section along the line of intersection of all menisci occurring there; $-F_s$ is the stress of the elastic resistance of the structure; F_k is the stress of cohesive and adhesive interaction at the points of secondary contacts.

Figure 1 shows a mechanical model of a porous disperse body in which the elements of the indicated stresses are combined.

The magnitude of the shrinkage stress changes during drying along the curve $F_\sigma(\tau)$ shown in Fig. 2. Its course in each of the four main regions reflects, in sum, the quantitative relations among the component stresses on the right-hand side of equality (1). The dotted branch of the curve shows a possible fall of F_σ as a result of relaxation processes in the structure and the disappearance of F_{σ_0} upon complete removal of the liquid phase. Figure 2 shows schematically the curves for the development of the component stresses F_{σ_0}, $-F_s$, and F_k. On

Figure 1 and Figure 2

Figure 1: Figure 1 and Figure 2

the basis of this representation, the entire drying process can be divided into the following four periods.

During **period I**, stresses arise only under the influence of the capillary pressure of the liquid that saturates the pores and has merged on the external surface into one continuous enveloping layer. Shrinkage during the drying of weakly structured systems proceeds with irreversible displacements of the particles. The other forces in this period are practically absent. Therefore

$$F_{\sigma}^{\mathrm{I}} = \sigma L / S_0. \tag{2}$$

II –the main period, during which, in drying, the entire magnitude F_{σ}, as well as its components F_{σ_0} and $-F_s$, arise, develop rapidly, and approach their maximum values. Let us note that the forces F_{σ_0},

arise from the moment when the common enveloping aqueous shell begins to split into separate concave menisci at the mouths of the pores on the surface of the drying system. The force F_{σ} is the quantity that leads up to the moment of complete evaporation of the liquid phase and the disappearance of its concave micromenisci. The rate of increase of F_{σ} is at first considerably greater than the rate of increase of F_s. This difference gradually decreases, and at the very end of this period (the transition of the ascending segment of the curve to a horizontal one) both rates

Fig. 1. Mechanical model of the action of molecular forces in drying systems: *a*—outer surface of the liquid enveloping layer with surface tension σ; *b*—element of the forces of capillary contraction, their sum per 1 cm^2 of cross section F_{σ_0}; *v* —element of the elastic force of the structure ($-F_s$); *g* and *d*—forces of secondary adhesion and cohesion bonds (F_k)

Fig. 2. Development of the shrinkage stress $F_{\sigma}(\tau)$ as the resultant component of the quantities composing it: F_{σ_0}—stress of capillary contraction; F_s—stress of the structure' s resistance; F_k—stress of cohesive and adhesive interaction at points of secondary contacts. *I*–*IV*—drying periods

become equal. The quantity F_k during this period still remains insignificant, especially in systems with very small and with very large moduli of elasticity; therefore it may be neglected:

$$F_{\sigma}^{\mathrm{II}} = F_{\sigma_0} - F_s. \tag{3}$$

Period III differs mainly in the horizontal course of the corresponding segment of the curve $F_{\sigma}(\tau)$, due to the fact that, while F_{σ_0} and F_s continue to increase,

Figure 3

Figure 2: Figure 3

Figure 4

Figure 3: Figure 4

the rates of their increase remain equal. The growth of the first quantity, and with it of the second, ends at the moment when the menisci of the evaporating liquid phase begin to disappear (transition to period IV). In this period the formation of secondary bonds is completed, entering into action with the stress F_k

$$F_\sigma^{\mathrm{III}} = F_{\sigma_0} - F_s + F_k. \tag{4}$$

At the end of period III the surface structure experiences the maximum stresses, critical for it. In rigid structures their defective

regions now become places of especially significant concentrations of tensile stresses and crack initiation.

In **period IV** the stress of capillary contraction F_{σ_0} disappears together with the liquid phase. At the same time, the compensating stresses of the secondary cohesion–adhesion bonds F_k, which arose under the compressive action of capillary forces, correspondingly come into action. The forces F_k fix the shrinkage deformations of the structure and its internal stresses F_s in the dry state, and

$$F_\sigma^{\mathrm{IV}} = F_k - F_s. \tag{5}$$

If the resultant of F_{σ_0} and F_k at any moment of period IV is equal to $F_{\sigma_0\,\max}$ and $F_{k\,\max}$, i.e. $F_{\sigma_0} + F_k = F_{\sigma_0\,\max} = F_{k\,\max}$, then no relaxation of the shrinkage stress occurs at the end of drying, and equilibrium between them is preserved.

Thus, period III may gradually pass into period IV with preservation of the horizontal course of the final section of the curve $F_\sigma(\tau)$.

Fig. 3. Dependence of shrinkage stress on time. A—leather after tanning, B—leather after liming; a—experimental curve, b—theoretical curve

Fig. 4. Theoretical dependence of shrinkage stress on time and its components; y—total shrinkage stress F_σ; y_1—forces of elastic resistance of the structure F_s; y_2—forces of capillary contraction F_{σ_0}

The mutual inverse replacement of the stress F_k by the stress F_{σ_0}, with excess compensation, can be observed during deformations of silica gel in the process of its capillary-condensation humidification. A substantial shrinkage is then detected under the influence of capillary forces on the surface of the menisci that arise.

In the case $F_{k\,\max} < F_{\sigma_0\,\max}$, during period IV relaxation takes place—a decrease in the determined value F_σ. Under such conditions, freely drying rigid systems, after ordinary shrinkage, exhibit expansion, which at first sight seems incomprehensible, since at this time the loss of (adsorption) moisture still continues. The expansion at the end of drying is due to the action of internal stresses, $-F_s$, tending to return the compressed structure to its initial state.

It is natural to express the S-shaped curve $F_\sigma(\tau)$ in Fig. 2 for the period (τ_0, τ_1) by a power function—an algebraic polynomial. In view of the fact that the experimental curve $F_\sigma(\tau)$ in Fig. 2 has an inflection point, the approximating polynomial must be no lower than third degree:

$$F_\sigma = a(\tau - \tau_0)^3 + b(\tau - \tau_0)^2 + c(\tau - \tau_0) + d. \tag{6}$$

From Fig. 2 it is seen that the curve $F_\sigma(\tau)$ passes through point A and is tangent to the abscissa axis at this point. Therefore the coefficients c and d in formula (4) must be equal to zero. Thus, equation (6) takes the form

$$F_\sigma = a(\tau - \tau_0)^3 + b(\tau - \tau_0)^2. \tag{7}$$

The next characteristic point of this curve will be the greatest value of the stresses B. The choice of the coefficients a and b is made so that the approximating curve passes through point B and, in addition, the derivative of function (7) at the indicated point becomes zero. If the coordinates of point B are denoted by τ_1 and $F_{\sigma m}$, then the coefficients a and b are expressed through them as follows:

$$a = -2F_{\sigma m}/(\tau_1 - \tau_0)^3, \qquad b = 3F_{\sigma m}/(\tau_1 - \tau_0)^2. \tag{8}$$

Consequently, there is a possibility of characterizing certain physicochemical and mechanical properties of various materials by a two-parameter family of curves.

From Fig. 3 a quite satisfactory agreement between the theoretical and experimental curves is seen. An important merit of the approximation presented, besides its simplicity, is also that the properties of various materials are determined by two independent parameters, the meaning of which admits a physical interpretation.

Indeed, in period II (Fig. 2) the most essential, as was indicated above, are two forces F_{σ_0} and $-F_s$, which increase with time while retaining different signs. Function (7) can be regarded as the sum of two components

$$y_1 = a(\tau - \tau_0)^3, \qquad y_2 = b(\tau - \tau_0)^2. \tag{9}$$

The graphs of these functions are given in Fig. 4. The quantity y_2 could be interpreted as the force of capillary contraction F_{σ_0}, and the curve y_1, correspondingly, as the force of elastic resistance of the structure $-F_s$. From the model presented in Fig. 1 it follows that the dependence of these forces on time and on moisture corresponds to the form of the curves. Therefore the coefficient b in equation (8) reflects the action of the forces of capillary contraction F_{σ_0}, and the coefficient a reflects the forces of elastic resistance of the structure $-F_s$.

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Note: Figure translations are in progress. See original paper for figures.