INVESTIGATION OF THE PROCESS OF FORMATION OF THE MECHANICAL PROPERTIES OF POLYMER COATINGS AND OF INTERNAL STRESSES IN THEM

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Abstract

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INVESTIGATION OF THE PROCESS OF FORMATION OF THE MECHANICAL PROPERTIES OF POLYMER COATINGS AND OF INTERNAL STRESSES IN THEM

(Presented by Academician P. A. Rebinder on 13 VII 1961)

In works (1) it was shown that the magnitude of the internal stresses arising in polymer coatings applied to solid substrates does not depend on the nature of these substrates. This indicates that the principal cause of the occurrence of internal stresses in a coating is the shrinkage processes taking place in it during formation. The role of the substrate, adhesively bonded to the coating, consists in preventing the free contraction of the coating during its hardening. Therefore, by studying the kinetics of formation of the mechanical properties of polymer films and the shrinkage phenomena occurring in them during hardening, it is possible to calculate the internal stresses that arise in a coating applied to a solid substrate. We have carried out an attempt at such a calculation using gelatin films as an example.

Let us suppose that a polymer coating dried from moisture content U_0 to moisture content U has an instantaneous deformation modulus E_1 and an equilibrium modulus of high-elastic deformation E_2. As a result of shrinkage phenomena that occurred in the coating during its drying time t, internal normal stresses σ arose in it. Let us subject such a coating to further drying for a time Δt. During this time the moisture content of the coating will decrease by ΔU, and the linear shrinkage will increase by $\Delta\varepsilon_y$:

$$\Delta\varepsilon_y = \alpha\Delta U, \tag{1}$$

where α is the coefficient of linear shrinkage.

The increase in linear shrinkage by $\Delta\varepsilon_y$ will cause an increase in internal stresses by $\Delta\sigma$, determined by the relation

$$\Delta\sigma = \left(\Delta\varepsilon_y - \Delta\varepsilon_v\right) E_k, \tag{2}$$

where $\Delta\varepsilon_v$ is the magnitude of the residual deformation that arose in the film during the time Δt under the action of internal stresses, and E_k is the apparent

Figure 1

Figure 1: Figure 1

modulus of elasticity of the coating.

Assuming that the coating at the stage of formation is a Bingham body, the development of high-elastic deformation in which is described by the Kelvin-Voigt model (2), E_k and $\Delta\varepsilon_v$ can be expressed by the equations:

$$E_k = \frac{1}{\dfrac{1}{E_1} + \dfrac{1}{E_2}\left(1 - e^{-\Delta t/\theta}\right)}; \tag{3}$$

$$\Delta\varepsilon = \frac{\sigma - \sigma_0}{2\eta}\,\Delta t, \tag{4}$$

where θ is the stress-relaxation period; σ_0 is the yield limit of the coating; η is the viscosity of the coating.

Combining (2), (3), and (4), we obtain an equation determining the increase in internal stresses in the polymer coating:

$$\Delta\sigma = \left(\Delta\varepsilon_y - \frac{\sigma - \sigma_0}{2\eta}\,\Delta t\right) \frac{1}{\dfrac{1}{E_1} + \dfrac{1}{E_2}\left(1 - e^{-\Delta t/\theta}\right)}. \tag{5}$$

With very slow drying of the coating (as $\Delta t \to \infty$), the entire shrinkage $\Delta\varepsilon_y$ is realized in the form of viscous flow, as a result of which at any stage of coating hardening $\Delta\sigma$ becomes zero. In the case of instantaneous drying (as $\Delta t \to 0$), $\Delta\sigma$ reaches a limiting value equal to:

$$\Delta\sigma_{\mathrm{p}} = \Delta\varepsilon_y E_1. \tag{6}$$

Fig. 1. Change in the relative shrinkage ε_y, the modulus of elasticity of instantaneous deformation E_1, and the apparent modulus E_k as functions of the moisture content of gelatin

During the formation of real films, which proceeds at a finite rate, $\Delta\sigma$ has an intermediate value between 0 and σ_{p}.

Integrating equation (6) from the initial moisture content to the final one, we obtain the limiting stresses that would arise in the film if viscous flow and relaxation were absent in it. Integration of equation (5), however, makes it possible to find the actual stresses in a film forming at a finite rate.

Figure 2

Figure 2: Figure 2

Integration of equations (5) and (6), which we carried out by a numerical method, requires knowledge of the dependence of the shrinkage $\Delta\varepsilon_y$, the modulus of instantaneous deformation E_1, and the apparent modulus E_k of gelatin jellies on their moisture content. To obtain these dependences, a study was made of the mechanical properties of jellies of various concentrations and of the shrinkage phenomena accompanying the process of their drying. Fig. 1 shows the dependence of the relative linear shrinkage ε_y of jellies on their moisture content U. As U decreases, the shrinkage increases (especially at the initial stage of drying), and for air-dry specimens containing 14-13% water it reaches a value of about 2.

In parallel with the study of shrinkage, the deformation properties of the jellies were investigated. For this purpose, specimens dried to various moisture contents were subjected to stepwise loading (as in (3)). Fig. 2 shows the curves of change in deformation of the specimens during loading, holding under load, and after unloading. From the magnitude of the deformation ε_1, the modulus of instantaneous deformation E_1 was calculated and its dependence on the moisture content of the specimens was plotted. Fig. 1 shows such a dependence, from which it is seen that a decrease in moisture content from 90 to 30% does produce a considerable increase in E_1 (by a factor of 180), but its value still remains low (about 70 kgf/cm^2). With a further decrease in moisture content, the modulus increases sharply, and for air-dry gelatin it reaches a value of 4.2-4.5 $\cdot$ 10^4 kgf/cm^2. Specimens dried at 70-80° to constant weight have a modulus of the order of $9 \cdot 10^4$ kgf/cm^2.

Fig. 2. Deformation curves of gelatin jellies of different moisture content (*a*—18.9%, *b*—17.2%, *v*—13.6%)

Having the dependences $\varepsilon_y = f(U)$ and $E_1 = f(U)$, one can calculate the limiting stresses $\sigma_{\mathrm{p}} = f(U)$ arising in a gelatin film during its formation. Fig. 3 gives the dependence $\sigma_{\mathrm{p}} = f(U)$. As can be seen, in the moisture-content interval from 90 to 30%, σ_{p} remains low (about 7 kgf/cm^2),

which is quite natural, since E_1 remains small in this humidity interval. A sharp increase in σ_{p} occurs below a humidity of 20%, which is caused by the transition of the jelly from a highly elastic state to a glassy one. For air-dry specimens, σ_{p} reaches values on the order of 500 kg/cm^2.

From the deformation curves of gelatin jellies (Fig. 2), the apparent modulus E_{k} was determined. Fig. 1 shows the dependence of E_{k} on the humidity of the specimens U. For jellies containing from 90 to 40% water, the highly elastic deformation is approximately 25-30% of the instantaneous deformation, as a result of which the difference between E_{k} and E_1 is comparatively small. At the same time, the value of the limiting stresses σ_{p}, which should arise in the

Fig. 3

Figure 3: Fig. 3

coating at this stage of curing, proves to be higher than the yield point σ_0. Therefore, flow develops intensively in the coating, leading in practice to the complete removal of internal stresses.

Fig. 3. Change in the limiting σ_p and actual σ internal stresses as a function of coating humidity

The stresses (σ) also remain low in the humidity interval from 40 to 20%, since in jellies of this concentration considerable highly elastic deformations develop, leading to a sharp decrease in the apparent modulus E_k in comparison with E_1. Finally, in the humidity interval of 20% and below, the jellies pass from the highly elastic to the glassy state. Viscous flow almost completely disappears, while the highly elastic deformation, developing mainly at the initial stage of load application, amounts to an insignificant fraction of the instantaneous deformation (not more than 20% at a specimen humidity of 17% and not more than 10% at a humidity of 13%).

In Fig. 3 the curve σ represents the dependence of internal stresses on humidity, calculated from the apparent modulus and shrinkage. These stresses should be close to the actual stresses arising in the coating during formation. For air-dry specimens these stresses are approximately 350-400 kg/cm^2. Direct experiments on the study of internal stresses in gelatin films ([1]) showed that the magnitude of the internal stresses is 270-300 kg/cm^2. If the planar stressed state is taken into account, the agreement of σ will be still better. The satisfactory agreement of the data presented shows that the mechanism of the occurrence of internal stresses at the stage of formation of polymer coatings is essentially exhausted by the development of shrinkage-relaxation processes.

Equation (5) and the experimental data make it possible to draw two important conclusions concerning the influence of the concentration of the solution from which the coating is obtained, and of the coating thickness, on the magnitude of the stresses in it. The lower the concentration of the solution from which the coating is applied, the greater the shrinkage it undergoes during drying. Therefore, with a decrease in the solution concentration, the stresses in the coating ought to increase. However, since over the entire concentration range up to the transition to the glassy state only very insignificant stresses can arise in the coatings, the concentration of the initial solution cannot exert any substantial influence on the value of σ in the formed coatings. This conclusion is well confirmed by direct experiments on the study of σ in gelatin films ([1]). The film thickness does not enter directly into equation (5). But with an increase in coating thickness, the time Δt during which the coating is at each stage increases.

stage of drying. Therefore, as the thickness of the coating increases, the internal stresses in it should generally decrease. Thus, for example, in coatings of plasticized gelatin, in which high-elastic deformation and viscous flow persist up to the air-dry state, the internal stresses do indeed decrease as the coating thickness increases (Table 1).

Table 1

Coating thickness, mm	0.04	0.05	0.10	0.20	0.26	0.3	0.5	0.75
σ, kg/cm^2:								
pure gelatin	280	270	270	280	–	–	–	–
plasticized gelatin	80	60	55	40	30	–	–	–
polyester varnish	–	–	3.3	3.4	2.8	3.0	3.0	3.0

In coatings of pure gelatin, the formation of internal stresses occurs almost completely in the process of gelation, as a result of which the role of viscous flow and relaxation is sharply reduced. Consequently, the value of σ in such coatings does not change with changes in thickness (Table 1). A similar picture should also be observed for polymerizing coatings for which the polymerization time does not depend on the coating thickness. This is confirmed by experiments on the study of internal stresses in coatings of cold-curing polyester varnish, the results of which are given in Table 1.

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