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ON THE STRUCTURAL-MECHANICAL PROPERTIES OF PROTEIN FIBERS

As was shown ([1,2]), physico-chemical mechanics establishes a connection between the mechanical properties of the systems under study and the fine chemical features of their structure. The present work is devoted to an investigation of the structural-mechanical properties of individual protein (gelatin) fibers and of the change in these properties during the tanning process. Such fibers constitute a model of the structural elements of a complex protein microheterogeneous system—leather tissue. Studying the action of tanning reagents on the mechanical properties of such "model" protein fibers may provide a basis for further elucidation of the mechanism of the tanning process, which is of great practical importance.

Gelatin fibers are a more convenient object for investigation than native collagen fibers, since they have a constant cross-section along the entire length of the fiber and can be prepared in any length. We used fibers obtained by the method of A. V. Yudin and M. P. Kotov ([3]), from a 40% aqueous gelatin solution by salting out, by forcing it through spinnerets and spinning in a saturated solution of ammonium sulfate (at a draw ratio of 700%). The spun "raw" fibers, in the form of a strand consisting of 175 elementary fibers (the diameter of each 20 μ), were stored in the same solution $(NH_4)_2SO_4$ at room temperature.

The tanning of the fibers was carried out according to A. V. Yudin by treatment in the stretched state at 20° for 7 hours with a sulfate-glucose chromium-extract solution of 35% basicity, with the introduction of 1.34 moles of sodium formate per 1 g-atom Cr, at pH $\approx$ 4.9, with a Cr_2O_3 content of 40 g/l, at a liquor ratio of 5.

We investigated the kinetics of deformation (elongation) of a fiber under uniaxial stretching at a prescribed constant load (from 50 g to 5 kg) and the kinetics of the decrease in deformation after removal of the entire load.

Elongation was measured with an accuracy of 0.01 mm. The fibers were tested both in an air-dry state (after drying at room temperature) and in an extremely watered state (in a saturated solution of ammonium sulfate). Both very long-term and short-term experiments were carried out. Here we give the results of investigations with a loading and unloading duration of 60 min.

Fig. 1

Figure 1: Fig. 1

The character of the deformation curves (Fig. 1) shows that both raw and tanned fibers have almost the same yield limit $P_k \sim 10$ kg/mm^2, which corresponds to a load of 0.5-1.0 kg per specimen. Further, the conditionally instantaneous deformations ε_0, and consequently also the corresponding moduli $E = P/\varepsilon_0$ (≈ 600 kg/mm^2), are likewise practically identical in the dry state.

However, differences—moreover, quite considerable ones even in the air-dry state —are found in the fraction of deformation reversible after unloading,

$$\beta = \frac{\varepsilon_0 - \varepsilon_p}{\varepsilon_0} \cdot 100$$

(as a result of true elasticity and high elasticity), or, still more clearly, in the fraction of practically conditionally residual

deformation $\frac{\varepsilon_p}{\varepsilon_0} \cdot 100 = 100 - \beta$ after a sufficiently long time following unloading.

As we have shown, the values of these characteristics practically do not depend on the duration of loading, being determined, apparently, mainly by the rather rapid relaxation processes that occur during loading.

Fig. 1. Curves of the development and decay of deformation under loading and unloading of dry gelatin fibers. Black points—raw fibers, light points—tanned fibers. a—load 0.5, —1.0, —1.25 kgf.

Therefore, in what follows we confined ourselves to studying the decay of deformation upon unloading after conditionally instantaneous loading over a time sufficient for visual reading of the elongation that had arisen (~ 1 sec.).

The corresponding curves (Fig. 2) show that, at a load of 1.25 kgf, after 2 hours the fraction of deformation reversible in magnitude in the raw fiber is $\beta = 94\%$, and the fraction of residual deformation is 6%; in the tanned fiber, respectively, 98 and 2%.

All the rapidly decaying high-elastic deformation

$$\beta = \frac{\varepsilon_0 - \varepsilon'_p}{\varepsilon_0} \cdot 100,$$

where ε'_p is the deformation remaining after 30 min., amounts in raw fibers to 90%, and $100 - \beta = 10\%$; in tanned fibers $\beta = 95\%$, $100 - \beta = 5\%$.

The kinetics of deformation decay, as our experiments have shown, indeed provides a convenient and visual method for evaluating the structural-mechanical

Fig. 2. Kinetic curves of the decrease in deformation of dry gelatin fibers after a conditionally instantaneous load. A –tanned fiber, B –raw fiber, a –load 0.5, b –1.0, c –1.25 kgf

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properties of protein fibers and leather tissue, along with measurements of tensile strength and ultimate elongation under tension, taking the loading rate into account.

The method of unloading curves–the elastic aftereffect of the second kind (after unloading)–especially clearly characterizes the tanning process and the effectiveness of tanning agents in measurements in an aqueous medium.

In doing so, the following must be taken into account: all deformation in the protein spatial structure, beyond a small fraction of truly elastic deformation (developing at the speed of sound in the specimen, i.e., in no more than milliseconds),

is a highly elastic deformation, the "rapid" portion of which has time to develop fully during the first visual reading (1 sec.). Subsequently, only a small "slow" highly elastic deformation develops at comparatively low stresses. Only at appreciable stresses, exceeding the yield point (i.e., the lower strength limit), is there observed a noticeable development also of residual deformation as a result of gradually developing ruptures in the structure, which leads to a continuous increase in the true stress with the time spent under load.

Fig. 2. Kinetic curves of the decrease in deformation of dry gelatin fibers after a conditionally instantaneous load.
A –tanned fiber, *B* –raw fiber; *a* –load 0.5, *b* –1.0, *c* –1.25 kgf.

After unloading, the remaining undamaged elementary fibers, tending to contract, cause a gradual decrease in deformation. This decrease will be slowed at the greatest possible stresses near the breaking stress, owing to the fact that the entropic forces from the small number of unbroken fibrils will be insufficient to restore the initial length of the specimen.

At low stresses this decrease will also be slow, since the resistance of internal friction in a system of practically undamaged fibers is relatively very great.

The most rapid is the decrease in deformation after the action of stresses that are sufficiently high and of intermediate magnitude relative to the breaking stress: in Fig. 2 it is clearly seen that the tanned fiber shows a reduction in conditionally residual deformation by a factor of 2 compared with the raw fiber both after 30 min and after 2 hours at the greatest load; while at loads below the lower strength limit, i.e., the yield point, it gives the opposite effect compared with the raw fiber, namely:

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

Load in kgf	0.5	1.0	1.25
$100-\beta$ for tanned fibers	0	5	6
$100-\beta$ for raw fibers	9	10	2

Tanning, which, as is known, amounts to the blocking of polar groups in the protein molecule on the accessible inner surface of the primary fibers, can cause some decrease in strength in a dry (dried) fiber and, accordingly, in leather tissue ([5]).

With limiting moistening of the structure, however, the tanning effect is manifested especially clearly in the twofold decrease, after unloading (at $P = 0.75$ kgf), of the practically residual deformation, which is $100-\beta = 16\%$ for maximally moistened tanned fibers and 33% for raw fibers (Fig. 3).

The conditionally equilibrium highly elastic modulus on unloading over···

30 min; for maximally moistened tanned fibers $E_e = 100$ kg/mm^2, and for raw fibers $E_e = 42$ kg/mm^2.

The tensile strength (at a loading rate of 600 g/min) for raw fibers decreases, at maximum moistening, from 25 to 10 kg/mm^2 (by 60%), while for tanned fibers it decreases from 21 only to 15 kg/mm^2 (by 28%).

Fig. 3. Kinetic curves of the decay of deformation of gelatin fibers in a saturated ammonium sulfate solution after conventional instantaneous loading. Black points—tanned fibers; open points—raw fibers. *a*—load 0.25 kgf; *b*—0.5; *v* —0.75 kgf.

The permissible increase in temperature to 45° somewhat increases, after unloading, the fraction of reversible deformation owing to an acceleration of the decay of highly elastic deformation (Fig. 4). With such heating the fraction of practically residual deformation decreases still more, amounting to $100-\beta = 4\%$ for tanned fibers and 30% for raw fibers. This reveals still more sharply the effect of tanning in terms of increased high elasticity.

Fig. 4. Effect of elevated temperature on the kinetics of the decay of deformation of gelatin fibers in a saturated ammonium sulfate solution. Open points—raw fiber; black points—tanned fiber.

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