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Abstract

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THE INFLUENCE OF TANNING AGENTS ON THE STRUCTURE OF GELATIN SOLUTIONS

The action on protein substances (for example, collagen fibers) of tanning (organic and mineral) compounds is, as is well known, one of the types of protein denaturation. The mechanism of this process, which in a number of cases is interpreted as a spatial structural rearrangement with the formation of bridging bonds, is still far from clear.

Fig. 1. 1 —rheological curves for a solution of ordinary gelatin at 25 and 40°, and, for comparison, 2 —flow curves for water

Fig. 2. 1 —rheological curves for a gelatin solution with formalin (pH 9) at 25 and 40°, and, for comparison, 2 —curves for pure gelatin solutions from Fig. 1

In this work, the influence of typical tanning agents on the structural features of gelatin solutions was investigated by measurements of the effective viscosity at various small pressure differences from 0.25 to 2 cm water column in a horizontal capillary viscometer with a tube radius $r = 0.5$ mm and length $l = 100$ mm. The pressure was precisely regulated by a manostat with a micromanometer. The temperature of the viscometer was kept constant by means of an ultrathermostat to $\pm 0.1^\circ$. Viscosity measurements at 25° were carried out in order to determine the influence of the tanning process on the intrinsic structural viscosity of gelatin. At the higher temperature (40°), the tanning process proceeds with a considerably smaller initial structuring.

A 3% aqueous gelatin solution was studied: a 6% solution of photographic gelatin at 40° was diluted twofold with water or with a solution of the tanning agent, likewise preheated to 40°. For measurements at 25°, the solutions were slowly cooled.

The shear stress at the walls of the capillary was calculated from the pressure difference at its ends Δp as $P_s = \Delta p \cdot r/2l$.

The mean linear outflow velocity $\bar{v} = Q/\pi r^2$, where the volume flow rate of the liquid $Q = v/\tau$ $\text{cm}^3 \cdot \text{sec}^{-1}$. Q can be calculated by the Poiseuille formula $\eta = \pi r^4 \Delta p \cdot \tau / 8vl$, whence $v/\tau = \pi r^4 \Delta p / 8l\eta$; then the effective velocity gradient is $\bar{v}/r = Q/\pi r^3 = \pi r^4 \Delta p / 8l\eta\pi r^3$, or $\bar{v}/r = \Delta p \cdot r/8l\eta = P_s/4\eta$, where P_s is the shear stress at the inner surface of the capillary, $\eta = \dfrac{P_s}{4\bar{v}/r}$ is the effective viscosity of the solution.

From the experimental data of the rheological curves (Figs. 1 and 2), the values of η_m were calculated—the lowest effective viscosity of the limitingly destroyed structure at sufficiently high velocity gradients, at which the value of η no longer changed over a wide interval of further increase of $\bar{v}/r$, and η_0—the conventional greatest limiting viscosity of the practically undestroyed structure. The values of η_0 were certainly underestimated, since measurements in the region of very small P_s cannot be carried out by the outflow method.

Table 1

Solution	25° η_0	25° η_m	25° $(\eta_0 - \eta_m) \cdot 100$	40° η_0	40° η_m	40° $(\eta_0 - \eta_m) \cdot 100$
Gelatin	4.7	3.1	153	2.6	1.5	110
Gelatin + tannin	9.7	2.7	704	2.9	1.4	159
Gelatin + chromium sulfate, 0% basicity	7.7	4.5	320	4.6	1.7	285
Gelatin + chromium sulfate, 30% basicity	11.6	4.1	754	4.6	1.7	285
Gelatin + formalin	13.5	6.2	730	7.2	2.9	437

The results obtained (Table 1) show that the action of tanning agents is always expressed in the development of a spatial structure, i.e., in an increase of the greatest limiting viscosity η_0, especially at 25°, i.e., under conditions of an already structured gelatin solution.

This becomes especially clear when comparing the values $\eta_0 - \eta_m$, which make it possible to estimate the degree of structuring caused by the tanning agent, in comparison with $\eta_0 - \eta_m$ for a solution of gelatin alone.

It is characteristic, however, that the value of the lowest viscosity η_m of the limitingly destroyed structure under the influence of the tanning agent increases only insignificantly in chrome tanning, even decreases in tannin tanning, and only in formalin tanning increases twofold, and moreover equally at 25 and 40°.

From this it follows that the addition of formalin promotes globulization and, over and above increasing the structural viscosity η_0, causes an increase in the structureless viscosity η_m as a consequence of the effect of volume increase during globulization.

On the other hand, it is understandable that denaturation, i.e., a certain hydrophobization of the hydrophilic polymer (in tannin tanning), after destruction of the structure under conditions of the lowest structureless viscosity η_m, causes even a certain decrease in viscosity in comparison with a pure gelatin solution without tanning agent.

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