Journal of Engineering Physics and Thermophysics, Vol. 76, No. 3, 2003

INFLUENCE OF THE MOLECULAR-MASS DISTRIBUTION OF GELATINS MODIFIED WITH A LIKI-1 TANNING AGENT ON THE RHEOLOGICAL PARAMETERS OF INTERPHASE ADSORPTION LAYERS AT THE INTERFASE OF AN AQUEOUS SOLUTION OF GELATIN–METAXYLENE

M. A. Sakvarelidze,[a] S. M. Levachev,[b] A. E. Kharlov,[b] V. N. Izmailova,[b*] and G. P. Yampol'skaya[b]

UDC 541.182.02+547.96.541.183

The influence of the interaction of gelatin with a protected formaldehyde tanning agent on the rheological parameters of interphase adsorption layers formed at the interface of a 0.1% aqueous solution of gelatin–metaxylene has been investigated as a function of the mass-molecular distribution of initial gelatins. It has been shown that the chemical modification of gelatin with tanning agents weakens the process of gel formation in the interphase layer directly with the depth of the tanning process. This dependence is the most pronounced for gelatin with a high content of fractions with a molecular mass of more than 285 kDa.

Introduction. It is known that gelatin is widely used in the food, chemical, biochemical, and pharmacology industries and in medicine. Gelatin is the main component in the production of cinema-photographic materials.

An important parameter influencing the properties of photographic materials is the molecular-mass distribution of gelatins, which in turn depends on the source of the gelatin, the technology of production, and the ratio between the types of collagens in tissues [1].

The main components of gelatins are α-, β-, and γ-polypeptide chains; the last two components are chemically cross-linked α-chains.

Polypeptide chains differing in their molecular-mass distribution carry different charges and reveal dissimilar capacities for reducing three-spiral collagenic domains. The reactivity of the polypeptide chains of gelatin depends on the conformational-configurational state of the chain, which manifests itself in the processes of oxidation and chemical modification.

Gelatin used in the photographic industry as a film-forming polymer is modified with substances of different nature for the purpose of improving the physicomechanical and photographic properties of films [2]. Of great practical importance is the possibility of controlling the strength properties of the structures formed by the modified gelatins in the volume and at the interphase boundaries [3, 4].

In [5], the influence of the molecular-mass distribution of gelatins on the processes of tanning has been investigated by high-efficiency liquid chromatography and gel electrophoresis. The highest reactivity of the α-chains was established. In the process of tanning, the content of α-chains decreases and the content of γ-chains and higher-molecular-weight components increases. At a low content of α-chains in gelatin and a high content of their fragments, the process of tanning selectively depends on the nature of the tanning agent.

In [6], the peculiarities of formation of interphase adsorption layers by tanned gelatins have been investigated. It was revealed that virtually all the parameters of the interphase adsorption layers are decreased in this case.

The aim of the present work is to investigate the influence of the molecular-mass distribution of gelatins and their modification in the process of tanning with the use of LIKI-1 on the rheological parameters of the interphase adsorption layers formed at the interphase boundary of a 0.1% aqueous solution of gelatin–metaxylene.

[*] Deceased.

[a]Moscow Cinema-Video Institute, Moscow, Russia; [b]M. V. Lomonosov Moscow State University, Moscow, Russia; email: Harlov@colloid.chem.msu.ru. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 76, No. 3, pp. 76–

1062-0125/03/7603-0562$25.00

TABLE 1. Molecular-Mass Distribution of Gelatin, %

Number of sample	Content of fractions with a definite molecular mass (kDa)				
	>285	285	190	95	<95
1	–	–	–	61.5	38.5
2	2.5	15.0	16.0	54.0	12.5

Objects and Methods of Investigation. In the work, we used two gelatin samples differing in their molecular-mass distribution, which were obtained by the alkaline method from the bone tissue of the cattle: sample 1 was produced at the Kazan' Gelatin Plant of the "Tasma" Production Enterprise and sample 2 was produced in France for color negative photographic materials.

The molecular-mass distribution of the gelatin samples was investigated by the method of high-efficiency liquid chromatography (Table 1).

The chemical modification of the gelatin was carried out with the use of the protected formaldehyde tanning agent LIKI-1 ($(HOCH_2)_2$ NCON $(HOCH_2)_2$ — tetraoxymethyl urea). "Ch"-grade (pure) metaxylene of the Angarsk Chemical-Agent Plant was used for the organic phase in the process of formation of interphase adsorption layers. Water was subjected to double distillation.

For experiments we prepared a 0.1% aqueous solution of gelatin by the standard method (swelling of gelatin for 0.5 h and dissolution at 40^{o}C). In the process of modification, the ratio of tanning agent–gelatin in solutions was $1\cdot10^{-2}$–$1\cdot10^{-4}$ mole of the tanning agent per 100 g of air-dried gelatin. The tanning was carried out at a temperature of 60^{o} for 1–3 h and the rheological tests were carried out at room temperature; pH of the modified solution of gelatin was ~5.69.

The rheological parameters of the interphase adsorption layers were determined using a Rebinder–Trapeznikov surface elastoviscometer [3].

The critical dead-load shear stress P_s (mN/m) was calculated from the formula

$$P_s = (C_0 S)\,(360^{o} R_1^2 n)^{-1}\,. \tag{1}$$

At constant diameters of the filament and the disk, the shear stress is equal to

$$P_s = KS\,, \tag{2}$$

where

$$K = C_0\,(360^{o} R_1^2 n)^{-1}\,. \tag{3}$$

The value of the deformation ε was calculated in fractions of the relative shear:

$$\varepsilon = 2R_2^2\,(\varepsilon'\tau - \varphi)\cdot 100\,(R_2^2 - R_1^2)^{-1}\,. \tag{4}$$

The modulus of elasticity was calculated from the formula

$$E = P_{r.s}\,(\varepsilon)^{-1}\,. \tag{5}$$

In the work, we used a tungsten filament with a cross section of diameter 0.05 mm. The measurement error was 6.5%. The rotational velocity of the table varied in the range $6\cdot10^{-4}$–$1.4\cdot10^{-1}$ rad/sec.

Results and Discussion. Gelatin is a typical representative of polyampholytes whose macromolecules contain both polar and nonpolar groups and are capable of producing surface-active anions or cations in the case of dissociation depending on the pH of the medium.

Gelatin macromolecules in solution can be in two different conformations: those of a coil and a collagen-like spiral. At a temperature of 308 K (35^{o}C) or higher, gelatin is in the first conformation, but when the solution is cooled to a temperature lower than 35^{o}C the processes of formation of a collagen-like spiral structure occur.

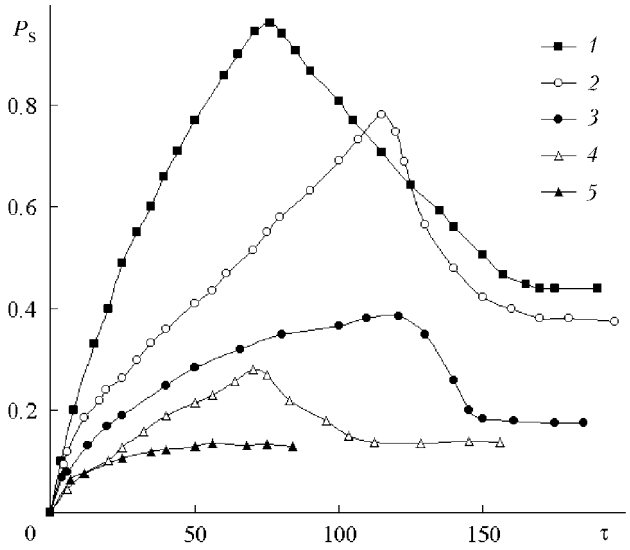

Fig. 1. Progress of the shear stress with time at the interface of a 0.1% aqueous solution of gelatin (sample 1)–metaxylene vs. depth of tanning at different amounts of the added tanning agent and different times of tanning; deformation rate is 0.461 sec^{-1}: 1) control sample of gelatin; 2) tanning for 1 h with a composition of the reaction mixture of $1 \cdot 10^{-4}$ mole of the tanning agent per 100 g of air-dried gelatin; 3) the same in the case where the content of the tanning agent is increased to $1 \cdot 10^{-3}$ mole; 4) the composition of the reaction mixture is as for curve 3; tanning time is 3 h; 5) tanning with a content of the tanning agent of $1 \cdot 10^{-2}$ mole, tanning time is 1 h.

Introduction of tanning agents into gelatin solutions makes it possible to fix the conformation of macromolecules existing at a given temperature. The tanning of gelatin at high temperatures (more than 35°C) in the volume of the aqueous phase leads to the fixation of the coil conformation, which remains unchanged when the temperature decreases further.

The results obtained are presented in Fig. 1 (for sample 1). It is shown that the concentration of the tanning agent LIKI-1 used in the process of tanning of the interphase adsorption layers influences the progress of the shear stress with time at the interface of an aqueous solution of modified gelatin–metaxylene. An increase in the concentration of LIKI-1 and in the tanning time leads to a decrease in the maximum rupture stress $P_{r.s}$ of the interphase adsorption layers and to its disappearance (curve 5). This points to the fact that the capacity for forming strong interphase adsorption layers is lost with the depth of tanning.

To obtain the quantitative rheological characteristics of interphase adsorption layers at the given interface and to determine the influence of the tanning agent LIKI-1 on them we conducted investigations at different deformation rates. It is seen in Fig. 2a that the curves of progress of the shear stress, obtained at different deformation rates (0.17–9.26 sec^{-1}) for the interphase adsorption layers in the system aqueous solution of gelatin–metaxylene, have pronounced maxima corresponding to $P_{r.s}$. After passage through the maximum, the shear stress decreases to the stationary stress of viscous flow of the ruptured layer, and $P_{r.s}$ increases with increase in the deformation rate. The chemical modification of gelatin with the tanning agent LIKI-1 leads to a decrease in the rupture shear stress of the interphase adsorption layers in proportion to the concentration of the tanning agent introduced into the reaction mixture; this effect was recorded at all deformation rates (Fig. 2b–d).

Based on the data obtained, we constructed the dependences of the deformation rate on the shear stress, i.e., curves of steady flow or total rheological curves (Fig. 3).

The curves of flow of the interphase adsorption layers of gelatin (Fig. 3a) after interaction with the tanning agent have a form characteristic of solid-like structures with yield points P_{c1} and P_{c2}. On this portion, one observes the rupture of individual bonds between macromolecules in the structure of the layer, but the number of restored and ruptured bonds is equal. In the region of shear stresses lower than the yield strength P_{c1} (lower than 0.05 mN/m), the

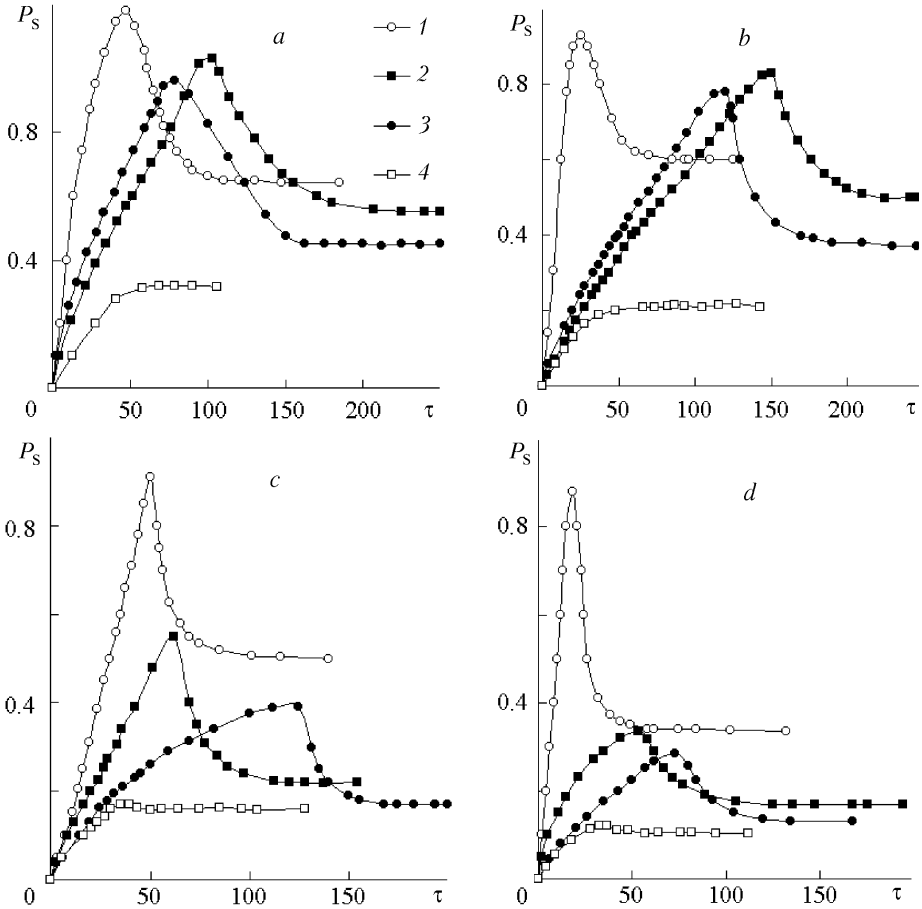

Fig. 2. Influence of tanning on the rheological properties of the interphase adsorption layers (progress of the shear stress with time at the interface of a 0.1% aqueous solution of gelatin (sample 1)–metaxylene: a) control sample of gelatin; b–d) tanning for 1 h with different contents of the tanning agent in the reaction mixture ($1\cdot10^{-4}$, $1\cdot10^{-3}$, and $1\cdot10^{-2}$) mole respectively and at different deformation rates (sec^{-1}) [1–4) 9.2610, 0.9247, 0.4601, and 0.1769].

structure of the interphase adsorption layers is characterized by the modulus of elasticity and the infinite viscosity (Fig. 3b). Then there is the region of the first plastic viscosity — Shvedov viscosity (η_0^*):

$$\eta_0^* = (P - P_{c1})\,[(d\varepsilon/d\tau)]^{-1}\,. \tag{6}$$

Then, at shear stresses higher than the second yield point P_{c2}, we have the region of the second plastic viscosity — Bingham viscosity (η^*):

$$\eta^* = (P - P_{c2})\,[(d\varepsilon/d\tau)]^{-1}\,. \tag{7}$$

The rheological parameters of the interphase adsorption layers of gelatin modified with the tanning agent LIKI-1 are presented in Table 2.

It is seen in Fig. 3 and Table 2 that after the interaction with the tanning agent, the interphase adsorption layers of gelatin are characterized by a decrease in the modulus of elastic deformation and in the Shvedov and Bingham viscosities.

Of great practical interest is investigation of the influence of the molecular-mass composition of gelatin on the rheological parameters of the interphase adsorption layers formed at the interface of an aqueous solution of a modified

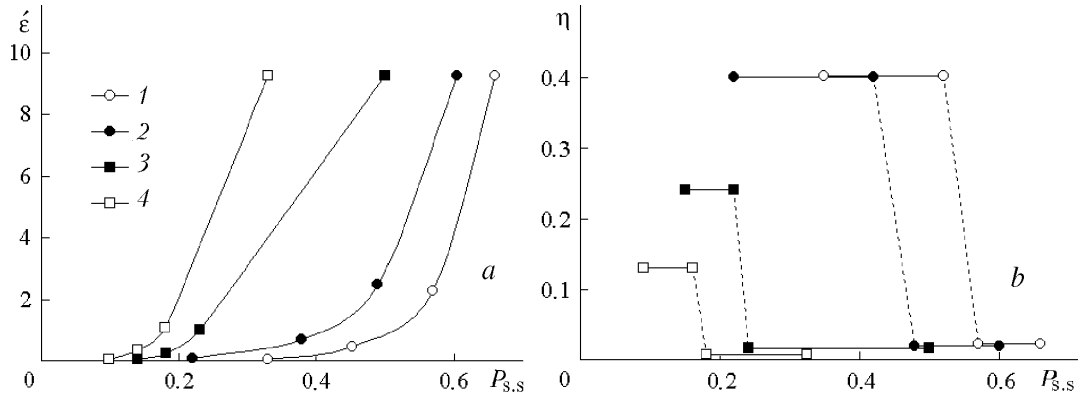

Fig. 3. Dependence of the deformation rate (a) and the viscosity (b) on the shear stress for interphase adsorption layers modified in the process of tanning of gelatins (sample 1): 1) control gelatin sample; 2–4) for gelatins tanned in the case of tanning-agent concentrations of $1\cdot10^{-4}$, $1\cdot10^{-3}$, and $1\cdot10^{-2}$ mole respectively.

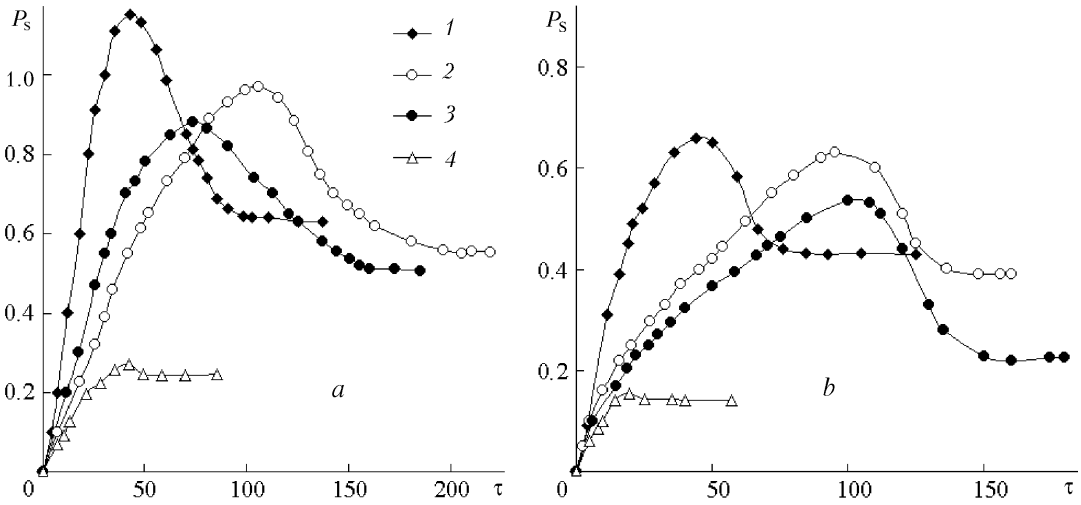

Fig. 4. Progress of the shear stress with time for interphase adsorption layers of gelatin (sample 2) at different deformation rates [1–4) notation is the same as in Fig. 3]: a) control gelatin sample; b) gelatin tanned for 3 h in the case of concentration of the LIKI-1 tanning-agent of $1\cdot10^{-4}$ mole.

gelatin–metaxylene. Figure 4a shows the progress of the shear stress with time for the interphase adsorption layers of gelatin sample 2, which is characterized by a high content of α-chains and high-molecular-weight fractions.

The chemical modification of gelatin (sample 2) with the tanning agent LIKI-1 in an amount of $1\cdot10^{-4}$ mole per 100 g of air-dried gelatin also leads to a decrease in the rupture shear stress of the interphase adsorption layers, and this decrease is larger than that detected for sample 1 under analogous conditions. This effect was also recorded at all the deformation rates (Fig. 4b). At the same time, the character of the curves of flow of interphase adsorption layers, corresponding to solid-like structures with yield points P_{c1} and P_{c2}, was retained.

Table 3 allows one to track the influence of the molecular-mass distribution of gelatin and of the tanning on the rheological parameters of the interphase adsorption layers formed at the interface of a 0.1% aqueous solution of gelatin–metaxylene.

Conclusions. In all probability, the experimental data obtained point to the fact that the chemical modification of gelatin with a tanning agent at 60°C, which leads to a compaction of polypeptide chains of gelatin, causes in turn a decrease in the surface activation of gelatin or a decrease in the interaction between individual macromolecules in the interphase adsorption layer. The rheological parameters of the interphase adsorption layers strongly depend on the

TABLE 2. Influence of the Tanning Agent LIKI-1 on the Rheological Parameters of the Interphase Adsorption Layers Formed at the Interface of 0.1% Aqueous Solution of Gelatin–Metaxylene

C	E	η_0^*	η^*
Without a tanning agent	0.25	0.4	0.02
10^{-4}	0.16	0.4	0.02
10^{-3}	0.1	0.24	0.016
10^{-2}	0.03	0.13	0.007

TABLE 3. Influence of the Molecular-Mass Distribution and the Tanning Agent LIKI-1 on the Rheological Parameters of the Interphase Adsorption Layers Formed at the Interface of 0.1% Aqueous Solution of Gelatin–Metaxylene

Number of a sample	C	E	η_0^*	η^*
1	Without a tanning agent	0.25	0.4	0.02
	10^{-4}	0.16	0.4	0.02
2	Without a tanning agent	0.23	0.5	0.02
	10^{-4}	0.11	0.3	0.01

molecular-mass distribution of the gelatin and the concentration of the tanning agent in the process of tanning. The presence of a large amount of α-chains and high-molecular-weight fractions in the sample leads to a structural modification of the gelatin and to a decrease in the rheological parameters even at low concentrations of the tanning agent. This circumstance must be taken into account in production of cinema-photographic materials.

This work was carried out with financial support from the Russian Foundation for Basic Research, project 01-03-32129a.

NOTATION

P, shear-stress components; $P_{s.s}$, equilibrium critical shear stress of the two-dimensional structure; P_s, critical dead-load shear stress, mN/m; C_0, twisting constant of a filament, mNm/rad; S, deviation of the light spot, m; R_1, radius of the glass disk, m; n, coefficient of conversion of degrees into scale meters; K, constant for the tungsten filament, mN/m; ε, deformation, %; τ, time of rotation of the table with a disk, sec; φ, angle traversed by a suspended system (inner vessel); R_2, radius of the vessel, m; $\dot{\varepsilon}$, rotational velocity of the table, rad/sec; E, modulus of elasticity, mN/m; $P_{r.s}$, critical rupture stress, mN/m; P_{c1} and P_{c2}, first and second yield points, mN/m; η_0^* and η^*, Shvedov and Bingham viscosities, mN·sec/m; C, content of the tanning agent LIKI-1 per 100 g of air-dried gelatin. Subscripts: r.s, rupture of the surface; s.s, static surface; c, critical.

REFERENCES

1. P. M. Zavlin, V. N. Izmailova, M. A. Sakvarelidze, and G. P. Yampol'skaya, *Zh. Prikl. Khim.*, **66**, Issue 3, 320–325 (1993).
2. P. M. Zavlin and A. N. D'yakonov, *Organic Compounds in the Production and Treatment of Light-Sensitive Materials. Tanning Agents* [in Russian], Leningrad (1984).
3. V. N. Izmailova and P. A. Rebinder, *Structure Formation in Protein Systems* [in Russian], Moscow (1976).
4. V. N. Izmailova, S. R. Derkach, S. M. Levachev, et al., *Zh. Nauch. Prikl. Fotogr.*, **45**, No. 6, 18–46 (2000).
5. P. M. Zavlin, P. V. Nuss, A. N. Ovchinnikov, et al., *Zh. Nauch. Prikl. Fotogr.*, **38**, No. 5, 151–160 (1993).
6. V. N. Izmailova, S. M. Levachev, M. A. Sakvarelidze, et al., *Zh. Nauch. Prikl. Fotogr.*, **47**, No. 1, 29–35 (2002).