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The rigidity of gelatin-glycerin gels

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At 25° the presence of glycerin in gelatin gels increased the modulus of rigidity in all the samples used. An empirical relationship between rigidity and the concentrations of gelatin and glycerin was calculated which was valid within the range 4–15% gelatin and 0–40% glycerin. A critical concentration of gelatin was found at which neither Bloom number nor glycerin concentration affected the rigidity. No simple relationship was found between Bloom number and rigidity.

GELATIN is used in pharmaceutical preparations and gelatin-glycerin gels are still the basis for the preparation of many suppositories. The rigidity of gelatin gels has been extensively studied (Ferry, 1948a; Cumper & Alexander, 1952) but few equations have been derived relating rigidity to composition. Ferry (1948b) and Ferry & Eldridge (1949) have produced empirical equations relating gelatin concentration, weight molecular weight and temperature. The effect of certain nonelectrolytes on the modulus of elasticity has also been reported but not extensively studied (Sheppard & Sweet, 1921; Hatschek, 1932, 1933). Glycerin was found to increase the modulus of elasticity. No direct relationship has been reported between rigidity and molecular weight or any function of molecular weight such as Bloom number. In the present work the rigidity of gelatin-glycerin-water mixtures has been studied and an equation derived which relates the concentration of gelatin and glycerin to the rigidity of the gel.

Experimental

MATERIALS

Gelatins. Alkali processed hide gelatins with the characteristics given in Table 1 were used.

Glycerin. "Analar" grade material was used.

TABLE 1. CHARACTERISTICS OF GELATIN USED

Sample	Bloom No.	pH of solution	Isoelectric point	Viscosity of 6·67% solutions		Moisture content %
				40°	60°	
A	99	6·1	5·1	4·3 cps	2·9 mps	12·7
B	154	6·1	5·1	5·9 cps	3·9 mps	12·4
C	200	6·3	5·2	6·4 cps	4·3 mps	12·8
D	250	—	5·1	7·1 cps	4·9 mps	12·7

METHODS

Preparation of the gels. The gelatin and water mixture was allowed to swell at 5° for 1 hr before solution at 50°. The glycerin, also at 50°, was added and the mixture gently but thoroughly stirred. The gel was allowed to mature in a water-bath at 25 ± 0·1° for 16 hr before rigidity measurements were made.

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Measurement of rigidity. The rigidometer method used was originally devised by Kinkel & Sauer (1925) and was modified by Saunders & Ward (1954). The volume displacement of a gelatin column, maintained at 25° ± 0·1°, on the application of air pressure was measured by means of the movement of a mercury thread in a side arm (Fig. 1). This allowed

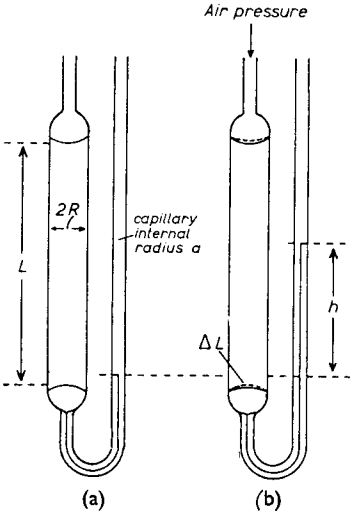

FIG. 1. Arrangement of apparatus (a) at rest; (b) under applied air pressure (after Saunders & Ward, 1954).

very small changes in volume to register as large movements of the mercury meniscus. Adhesion of the gel to the wall of the tube was sufficient to prevent slip. The rigidity is calculated using the formula

$$G = \frac{PR^4}{8La^2h} \quad .. \quad .. \quad .. \quad .. \quad (1)$$

where G = rigidity modulus in dynes/cm². P = net pressure corrected for the back pressure of displaced mercury. R = radius of tube, cm. L = length of gel column, cm. a = radius of mercury capillary, cm. h = displacement of mercury, cm. The formula was valid for the condition that $L \gg R$.

Results and discussion

Early reports asserted that the elasticity of gelatin gels was increased by a number of substances, one of which was glycerin. Hatschek (1932, 1933), who measured Young's modulus for 10% gels of "hard" gelatin with different percentages of glycerin at 10·8° and 21°, found that the modulus of elasticity increased continuously with time. These early results were incidental to the main purpose of our work and were not followed up. In the early reports, the gelatin was often not characterised and the different methods employed gave results which could not readily be correlated one with another. The method of measuring the rigidity we used gave an absolute value.

The effect of glycerin concentration on the rigidity of gelatin-glycerin-water gels is shown in Fig. 2. At all the gelatin concentrations studied, the curve was essentially linear up to 40% w/w glycerin concentration.

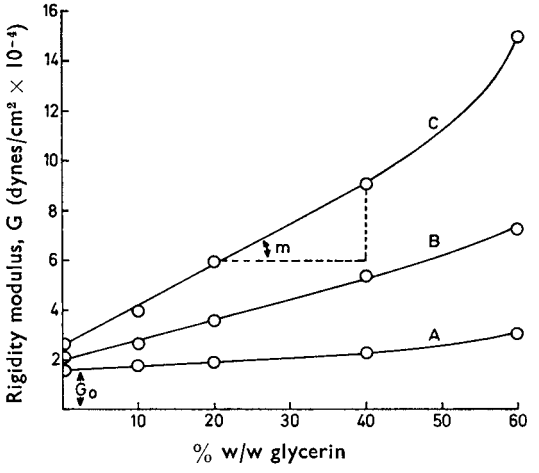

FIG. 2. The effect of glycerin concentration on the rigidity of gelatin/glycerin/water gels. Gelatin % w/w (99 Bloom): A, 5; B, 10; C, 15. Temperature, 25° ± 0·1°.

The non-linear increase in rigidity at higher glycerin concentrations could be correlated with the similar non-linear increase in the viscosity of the liquid phase (glycerin-water) at high glycerin concentrations.

For gels which contained up to 40% w/w glycerin it was possible to write the following equation

$$G = G_0 + mC \qquad (2)$$

where G = rigidity ($G \times 10^{-4}$ dynes/cm²), G_0 = rigidity at zero glycerin content, m = slope, C = concentration of glycerin (% w/w). If the value of G_0 is plotted against the square of the gelatin concentration (Fig. 3) then a second linear relationship is found

$$G_0 = \alpha + \phi Z^2 \qquad (3)$$

where α = intercept on rigidity axis at zero gelatin concentration, ϕ = slope, Z = gelatin concentration (% w/w).

Substituting for G_0 in equation (2)

$$G = \alpha + \phi Z^2 + mC \qquad (4)$$

The slope m depends on the concentration of gelatin, as is seen in Fig. 2, and is a linear function of the gelatin concentration (Fig. 4). The slope m could therefore be written as

$$m = \beta + \psi Z \qquad (5)$$

where β = the intercept with the m axis, ψ = slope.

Substituting for m in equation (4)

$$G = \alpha + \phi Z^2 + (\beta + \psi Z)C \qquad (6)$$

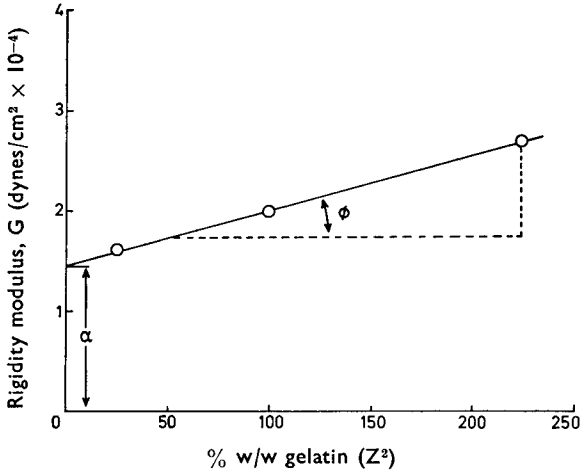

FIG. 3. The relationship between rigidity and gelatin concentration in the absence of glycerin. Gelatin (99 Bloom). Temperature, 25° ± 0·1°.

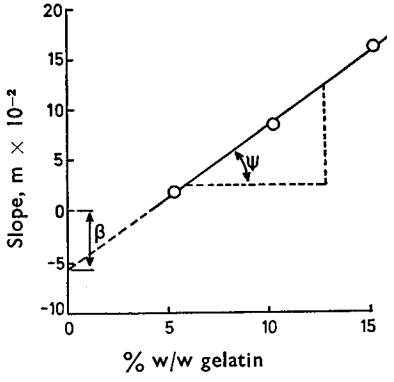

FIG. 4. The effect of gelatin concentration on the slope of the rigidity curve of gelatin/glycerin/water gels. Gelatin (99 Bloom). Temperature, 25° ± 0·1°.

Substituting the values for the constants calculated from Figs 2, 3 and 4

$$G \times 10^{-4} = 1{\cdot}48 + 5{\cdot}5 \times 10^{-3}Z^2 + (1{\cdot}45 \times 10^{-2}Z - 5{\cdot}45 \times 10^{-2})C \quad .. \quad (7)$$

This mathematical treatment was derived using a gelatin of 99 Bloom strength, but equivalent relationships were found with other gelatins. The constants for the other gelatins examined are given in Table 2 and a comparison of experimental and calculated rigidities is shown in Table 3. The general equation appeared to be valid for alkali treated hide gelatins at gelatin concentrations between 4 and 15% w/w and containing up to 40% w/w glycerin.

The equation was empirical and the criterion for distinguishing between the gelatins was Bloom number, which gives no indication of the molecular

TABLE 2. CONSTANTS FOR SAMPLES OF DIFFERENT GELATIN

Sample	Bloom No.	Constant			
		α	β	ϕ	ψ
A	99	1·48	$-5{\cdot}45 \times 10^{-2}$	$0{\cdot}55 \times 10^{-2}$	$1{\cdot}45 \times 10^{-2}$
B	154	1·46	$-4{\cdot}69 \times 10^{-2}$	$2{\cdot}2 \times 10^{-2}$	$1{\cdot}30 \times 10^{-2}$
C	200	1·52	$-11{\cdot}9 \times 10^{-2}$	$2{\cdot}68 \times 10^{-2}$	$2{\cdot}71 \times 10^{-2}$
D	250	1·57	$-7{\cdot}55 \times 10^{-2}$	$4{\cdot}38 \times 10^{-2}$	$2{\cdot}09 \times 10^{-2}$

TABLE 3. EXPERIMENTAL AND CALCULATED RIGIDITIES FOR GELATIN-GLYCERIN-WATER GELS

Bloom No.	% Gelatin-% Glycerin	Rigidity (dynes/cm²) × 10^{-4}								
		5/10	5/20	5/40	10/10	10/20	10/40	15/10	15/20	15/40
99	Experimental	1·76	1·94	2·34	2·66	3·6	5·47	3·97	5·97	9·1
	Calculated	1·79	1·98	2·34	2·93	3·8	5·65	4·3	5·97	9·23
	Difference %	+1·7	+2	0	+7·4	+5·5	+1·8	+7·7	0	+1·1
154	Experimental	2·15	2·41	2·76	4·3	5·0	6·91	7·6	9·5	13·1
	Calculated	2·18	2·37	2·73	4·49	5·32	6·98	7·89	9·37	12·37
	Difference %	+1·4	−1·7	−1·1	+4·4	+6	+1	+3·8	−1·4	−5·6
200	Experimental	2·3	2·7	3·3	5·29	6·88	9·9	9·96	12·2	16·8
	Calculated	2·35	2·52	2·85	5·7	7·24	10·28	10·42	13·29	18·6
	Difference %	+2·2	−6·6	−13·6	+7·5	+4·9	+3·8	+4·6	+8·9	+10·7
250	Experimental	3·02	3·3	4·0	7·5	9·5	12·2	12·51	16·49	24
	Calculated	2·98	3·27	3·85	7·32	8·65	11·32	13·83	16·21	20·97
	Difference %	−1·3	−0·9	−3·7	−2·41	−8·9	−7·2	+10·5	−1·6	−12·6

weight of the sample. In general a high Bloom number indicates a gelatin molecule of long chain length, but there is no simple relationship. None of the constants β, ϕ, ψ, showed any direct relationship to Bloom number. β and ψ depended on both the gelatin and glycerin concentration whilst ϕ depended on the gelatin concentration only. However, for each percentage w/w gelatin : glycerin ratio, it was possible to calculate a linear relationship between rigidity and Bloom number. As an example, when 5% w/w gelatin and 20% w/w glycerin were used,

$$\sqrt{G} = F + kN \qquad (8)$$

where F is the intercept on the rigidity axis, N is the Bloom number and k the slope.

The numerical values of the constants were $1{\cdot}11 \times 10^{-2}$ and $2{\cdot}84 \times 10^{-5}$ respectively and using the equation, a gelatin with a stated Bloom strength of 180 was found from rigidity measurements to be 179·5 Bloom.

Fig. 5 shows the effect of glycerin concentration on the rigidity modulus of gelatin gels. The rapid increase in rigidity at higher glycerin concentration is paralleled by the increased viscosity of the glycerin : water phase which occurred when the glycerin concentration exceeded 20%. The glycerin may therefore increase the rigidity either by providing weak extra linkages for the gel network or simply by increasing the resistance

to movement of the gelatin molecules. At low liquid phase viscosities the gelatin molecules may be easily moved on the application of a force, but if the viscosity of the interphase is very high then the ability of the gel network to distort under a given force will be severely restricted and be manifest as a high rigidity.

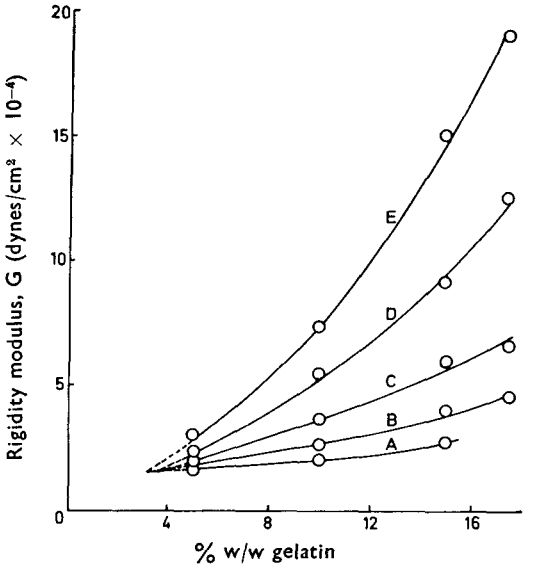

FIG. 5. The effect of gelatin and glycerin concentration on the rigidity of gelatin/glycerin/water gels. Gelatin (99 Bloom). Glycerin % w/w: A, 0; B, 10; C, 20; D, 40; E, 60. Temperature, 25° ± 0·1°.

If the curves in Fig. 5 were extrapolated, they intersected at a gelatin concentration of 3·2% w/w; below this the 'rigidity' was found to be constant and independent of glycerin concentration and Bloom number. The value of this critical rigidity was $1{\cdot}5 \times 10^{-4}$ dynes/cm² and corresponded to the apparent rigidity when the rigidometer was filled with water. Therefore no gel was detected under our experimental conditions at concentrations below 3 to 3·5% gelatin.

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