

Thermal Degradation of Gelatin as Applied to Processing of Gel Mass

WILFRED C. LING

Received January 13, 1977, from *Pharmaceutical Research and Development, Pharmaceutical Products Division, Abbott Laboratories, North Chicago, IL 60064*. Accepted for publication May 13, 1977.

Abstract □ The rheological parameters of rigidity and viscosity were studied for gelatin, both as a 6% solution and a 38% gel mass containing glycerin, sorbitol, and water. A compressive test for rigidity and a rotational shear method for viscosity were used to characterize the thermal degradation of several lots of alkali-processed calf-skin gelatin. The objective of this study was to use kinetic data for process predictions in the manufacturing of the gel mass for soft gelatin capsules. Empirical equations relating degradation to time, temperature, and pH were derived for dilute gelatin solutions. Through parallel studies with a concentrated gel mass, other empirical equations were developed to predict degradation of the gel mass based on dilute solution data and processing conditions. Analysis of the kinetic data and empirical equations have generally confirmed earlier observations on degradation, except on quantitative aspects. While these equations are adequate for the intended use in process predictions, the study revealed substantial variability both within and among lots of commercial gelatin. These variabilities of uncertain causes contributed to inexact characterization of degradation, as demonstrated by the generally approximate results of process predictions.

Keyphrases □ Gelatin—thermal degradation, solution and gel mass, rigidity and viscosity, applied to processing predictions □ Degradation, thermal—gelatin solution and gel mass, rigidity and viscosity, applied to processing predictions □ Thermal degradation—gelatin solution and gel mass, rigidity and viscosity, applied to processing predictions □ Rigidity—gelatin solution and gel mass, thermal degradation, applied to processing predictions □ Viscosity—gelatin solution and gel mass, thermal degradation, applied to processing predictions

Rigidity in a gelatin gel is generally attributed to the helical structure of the macromolecules (1, 2). Whereas solution viscosity is a function of molecular weight, gel rigidity for dilute gelatin is independent of the molecular weight of the gelatin (3). Therefore, both rigidity and viscosity parameters are necessary to define the mechanical properties of the gelatin properly. The purpose of this study was to characterize gelatin degradation with respect to rigidity and viscosity to provide a degree of predictability to the manufacturing process for soft gelatin capsules.

Among reported studies on thermal degradation of gelatin, only a few (4, 5) have sufficiently detailed analysis for possible application. Most are limited to the study of dilute gelatin solutions, with little or no quantitative treatment of the degradation process. The approach taken for this study was to examine the thermal degradation of both the dilute gelatin and a concentrated gel mass containing glycerin and sorbitol, thus establishing a correla-

tion between the two processes with respect to rheological parameters.

The empirical kinetic approach taken was similar to that recommended for complex catalytic reactions (6) where a theoretical approach is either impossible or too complicated to be practical. The importance of the kinetic treatment is, therefore, not to elucidate the degradation mechanism but to provide a quantitative basis for predictive applications.

EXPERIMENTAL

Material—Gelatin—Pharmaceutical grade gelatin USP, <16–>60-mesh size, six lots, from alkali-processed calf skin was used (Table I). Preparation of the gel mass included the use of glycerin USP and 76% sorbitol¹.

Kinetic Procedures—Thermal Degradation of Dilute Gelatin Solution—The preparation of gelatin solution followed the standard procedures used in the testing of gel strength and viscosity (7). The gelatin was allowed to hydrate in distilled water at room temperature for 2 hr. The mixture was then heated to 61° in a 65° water bath for no more than 15 min until completely dissolved. The solution was pipetted immediately into several 50-ml glass ampuls and flame sealed. The sealed ampuls were then placed in a constant-temperature bath² controlled to ±0.2°. The time at which complete dissolution was achieved was taken as time zero. At different intervals, the ampuls were removed for later testing.

At each sampling, 28 ml of the ampul solution was poured into a glass ointment jar, measuring approximately 38 mm diameter × 28 mm deep, and covered tightly. The jar sample, as well as the remaining solution in an erlenmeyer flask, was stored at 5° for later testing.

All samples were tested for rigidity and viscosity by methods to be described. In addition, the pH³ of the 6% gelatin solutions was determined at 24°.

Thermal Degradation of Gel Mass—The gel mass was a specific formulation used in making a soft gelatin capsule product. The approximate composition, on a dry basis, is 38% (w/w) gelatin, 13% glycerin, 13% sorbitol, 1% dye and preservatives, and 35% water.

All ingredients were mixed in a beaker until uniform and then transferred to a filtering flask where the mixture was deaerated at an absolute pressure of 1000 torr. The gel mass, while still held in a closed vacuum, was heated in a 75° water bath for 30 min. Then the vacuum was released, and the melt was poured into several 125-ml erlenmeyer flasks. The flasks were stoppered and submerged completely in a constant-temperature bath controlled to within ±0.2°.

Zero time was taken as the time when the gel mass was removed from the melting bath but before placement into the constant-temperature bath. At predetermined intervals, the flasks were removed from the bath and the gel mass was poured into a 30-ml ointment jar for rigidity testing. A portion of the gel mass was molded into strips for moisture determination as described later. A cylindrical rod of gel mass, molded simultaneously with the strips, was kept in a closed bottle for use in the viscosity determination.

Rigidity Determination—The procedure involved subjecting a sample of gelatin or gel mass to penetrative compression by a flat-ended cylindrical plunger, 6.35 mm in diameter, at a constant speed, using a manual testing machine equipped with simultaneous recording of force and displacement⁴.

Table I—Characteristics of Gelatin Used

Lot	Nominal Bloom, g	Rigidity Index, g	Viscosity, mps	pH	Moisture, %
A	150	63.5	34.0	5.50	10.5
B	150	62.4	38.3	6.10	10.0
C	130	59.4	35.4	5.80	9.7
D	170	71.0	40.1	5.30	9.4
E	150	63.5	34.6	5.45	8.9
F	150	62.9	37.7	6.20	9.7

¹ I.C.I. United States, Wilmington, Del.

² Model 6566, Precision Scientific Co., Chicago, Ill.

³ Zeromatic pH meter, Beckman Instruments Corp., Fullerton, Calif.

⁴ Instron floor model TT Universal testing instrument, model 1115, Instron Corp., Canton, Mass.

Table II—Parameters of Rigidity Index Testing

Sample	Rigidity Index Symbol	Plunger Compression		Pretest Aging	
		Rate, mm/min	Depth, mm	Hours	Temperature
Dilute gelatin	<i>f</i>	50.8	2.00	70	0°
Gel mass	<i>F</i>	5.08	1.27	96	23°

Each test sample was poured into a 38-mm diameter ointment jar to a depth of 22 ± 2 mm and allowed to cool on a level surface until gelation and then was kept for a designated aging period prior to testing. Samples in the gel state were heated to $45\text{--}50^\circ$ prior to pouring into the jars. The specific aging period and depth of compression are defined in Table II for both dilute gelatin and the concentrated gel mass.

Viscosity Determination—The viscosities of the gelatin solution and the gel mass were determined with a rotational viscometer equipped with programmable shear rate control and simultaneous recording of shear rate and shear stress⁵. For standardization, all determinations were made at $60 \pm 0.2^\circ$ with viscosity computed at shear rates of 3234 and 36 sec^{-1} for the 6% gelatin solution and 38% gel mass, respectively. Each sample was allowed to equilibrate in the temperature-controlled sensing cup for 15 min prior to the run. The repeatability of viscosity determinations was within $\pm 5\%$ (95% of all cases, 95% confidence level).

Moisture Determination for Gel Mass and Gelatin—The moisture of the gel mass was determined by drying strips extruded from the molten gel mass. The strips, measuring $1 \times 2 \times 33$ mm long, were weighed⁶ and dried for 20 hr in a vacuum oven⁷ maintained at $60 \pm 0.5^\circ/10\text{--}20$ torr. The weight loss divided by the initial weight was taken as the moisture content.

RESULTS AND DISCUSSION

Many methods of gel strength have been reported (8–11). None, however, was suitable for this study from the standpoint of accuracy and convenience.

The linear force–displacement curve (Fig. 1) characterizes the gelatin rigidity in a form analogous to the stress–strain diagram of an elastic body, confirming earlier observations (12). However, the lack of a well-defined dimensional relation with respect to the force, area, and deformation in the penetrative type of compression precluded the calculation of rigidity or shear modulus. The term “rigidity index” expresses relative rigidity and is defined as the force required to depress the gelatin surface

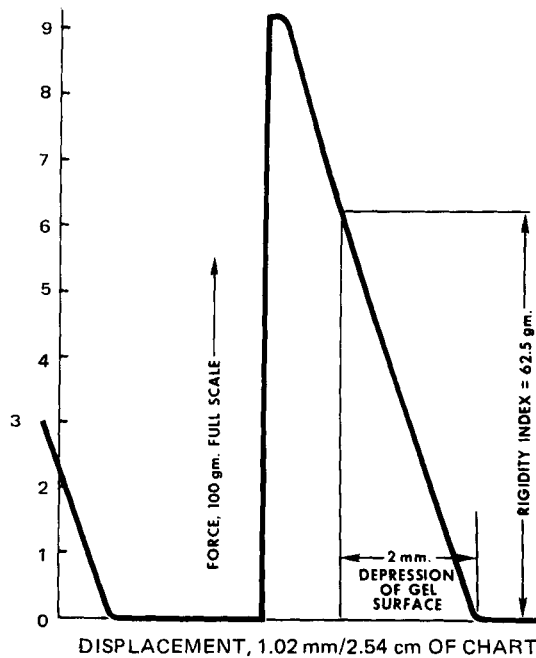


Figure 1—Typical force–displacement curve of rigidity testing for 6% gelatin at 0°.

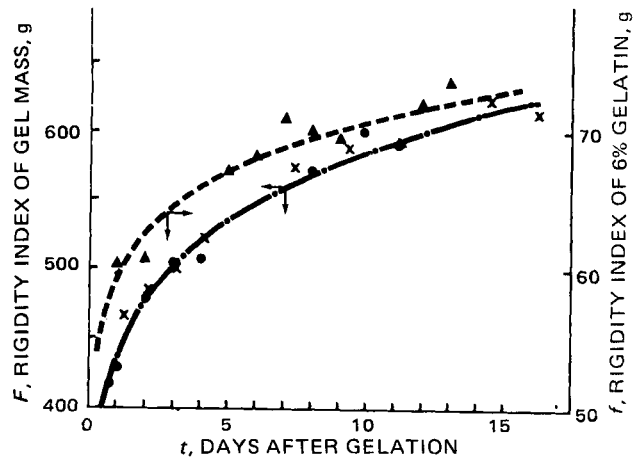


Figure 2—Effect of aging on rigidity of 6% gelatin and gel mass containing 38% gelatin. Key: \blacktriangle , 6% gelatin (Lot 01); \bullet , 38% gel mass containing Lot 01 gelatin; and \times , 38% gel mass containing Lot 02 gelatin. Dotted curves are transposed from linear regression curves of $\log F$ versus $\log t$ and $\log f$ versus $\log t$.

a fixed distance when tested within a specific set of parameters. It is similar to the Bloom gelometer test commonly used in the gelatin industry. One difference is the strain rate. In this method, the strain rate is constant and independent of stress. In the Bloom test, the stress rate is constant but only to the extent that the flow rate of the lead shots is regulated.

The advantages of a constant strain rate and relative freedom from human error were the reasons for using the standard material testing machine instead of the gelometer. In view of the wide difference in rigidity between dilute gelatin and gel mass, two sets of standard test parameters were used as defined in Table II. The repeatability of the rigidity index determination was within $\pm 3\%$ (95% of all cases, 95% confidence level) for the 6% gelatin and $\pm 6\%$ for the 38% gel mass. The decrease of reproducibility in the case of the gel mass is believed to be due more to compositional variations than instrument error.

Effect of Aging—The phenomenon of progressive rigidity increase after gelation is well known. Figure 2 shows the effect of aging on the rigidity of both dilute gelatin and the gel mass. The selection of 70 and 96 hr for aging of the dilute gelatin and gel mass, respectively, in the standard test procedure (Table II) was dictated primarily by convenience of test scheduling and the reduced sensitivity of rigidity change with time. A 10 times faster compression rate for the dilute gelatin was selected to

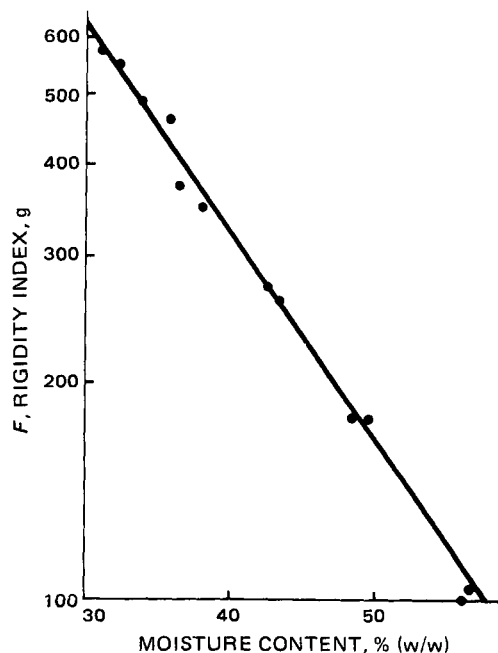


Figure 3—Effect of moisture content on rigidity of gel mass.

⁵ Rotovisco model RV-3, Haake Instruments, Rochelle Park, N.J.
⁶ Sartorius model 2462, Brinkmann Instruments, Westbury, N.Y.
⁷ Model 634 vacuum oven, Hotpack Corp., Philadelphia, Pa.

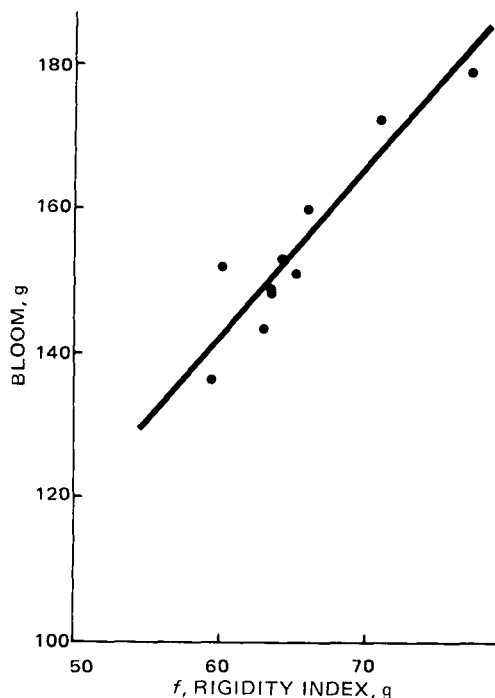


Figure 4—Relation between bloom and rigidity index of 6% gelatin.

shorten the test duration and thereby minimize the effect of ambient temperature.

Effect of Gelatin Concentration—The gelatin solution was prepared as a 6.67% solution based on the weight of the commercial gelatin. For an average moisture content of 10% in the commercial gelatin, the gelatin concentration in the solution was about 6% on the dry basis. No attempt was made to make all gelatin solutions at precisely 6%. Ferry (13) found that rigidity was proportional to the square of the gelatin concentration for dilute gelatin. By using this relationship, it can be calculated that a maximum error of 4.6% in rigidity may be encountered due to the normal variation of gelatin moisture between 10 and 12%.

The effect of moisture on rigidity variation, however, is much greater for the gel mass. Figure 3 shows the effect of moisture on the rigidity index of a gel mass sample. Based on this relationship, each percent moisture change represents a rigidity change of 6.8%. It follows, therefore, that any

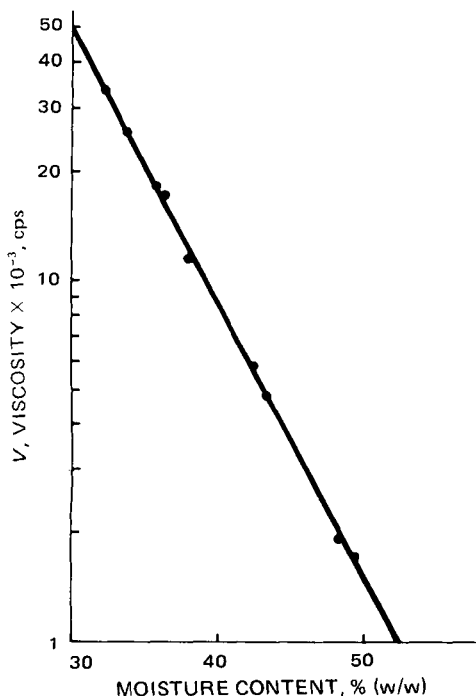


Figure 5—Effect of moisture content on viscosity of gel mass.

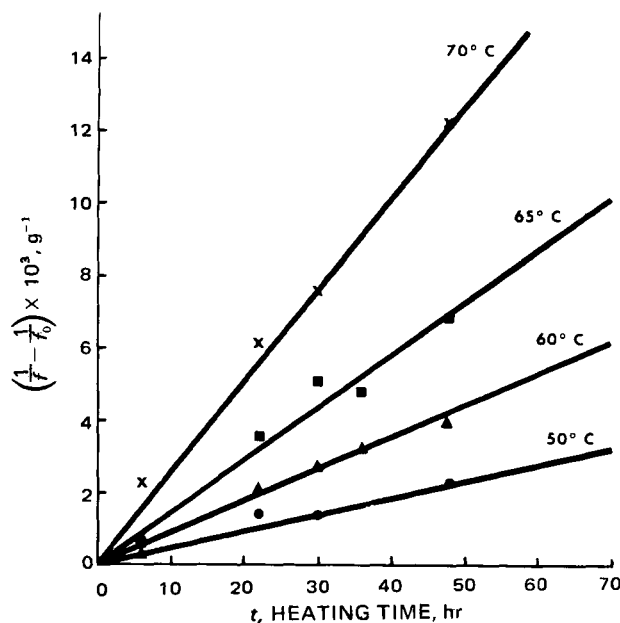


Figure 6—Rigidity degradation of 6% gelatin at different temperatures (gelatin Lot A).

rigidity measurement of gelatin degradation must be based on a standard moisture content. All results of rigidity determination were corrected to a standard moisture content of 35% by means of:

$$\log F_2 = \log F_1 + 0.0287M_1 - 1.0045 \quad (\text{Eq. 1})$$

where F_1 is the rigidity index of the gel mass at moisture M_1 , F_2 is the rigidity index at 35% standard moisture, and M_1 is the percent moisture of the gel mass sample. Equation 1 is derived by incorporating the 35% standard moisture into the regression equation of Fig. 3, which is significant at $p < 0.001$.

Although based on experimental data of only one lot of material, Eq. 1 should be applicable for all gelatin lots for moisture correction within the 30–40% range. By differentiating the regression equation, it can be seen that the slope of 0.0287 relates to fractional rather than absolute change of rigidity with respect to moisture change.

Correlation of Rigidity Index to Bloom Reading—Although the rigidity index method was used in the testing of the 6% gelatin, each gelatin also was tested for rigidity by the Bloom gelometer method (7). Figure 4 shows the correlation of the two methods by testing 10 different gelatin lots. The linear correlation is significant at $p < 0.001$.

Viscosity Determination—Figure 5 shows the effect of moisture on the viscosity of a gel mass identical in formulation to the gel mass used for the degradation studies. Based on this correlation, the results of every viscosity determination were adjusted to a standard moisture of 35% for analysis of viscosity degradation. The following equation was used:

$$\log V_2 = \log V_1 + 0.0757M_1 - 2.6495 \quad (\text{Eq. 2})$$

where V_1 is the viscosity of the gel mass at moisture M_1 in centipoises, V_2 is the viscosity at 35% moisture in centipoises, and M_1 is the percent moisture of the gel mass sample. Equation 2 shows that moisture in the 30–40% range has a much more pronounced effect on viscosity than on rigidity. A 1% change in moisture creates a viscosity change of 19% for the particular gel mass under study.

Treatment of Kinetic Data—A total of 20 runs was made in the study of rigidity and viscosity degradation of 6% gelatin solutions (12 runs) and the 38% gel mass (eight runs). The experimental data were treated empirically to fit simple kinetic models. The apparent order of reaction was arrived at by trying integral increments of the exponent, n , in the following equation:

$$\frac{-dx}{dt} = kx^n \quad (\text{Eq. 3})$$

where $-dx/dt$ is the rate of loss of the rheological parameter of either rigidity or viscosity, k is the rate constant, x is the value of the rheological parameter at time t after heating begins, and n is the apparent reaction order. The experimental data were used to fit the integrated forms of Eq. 3.

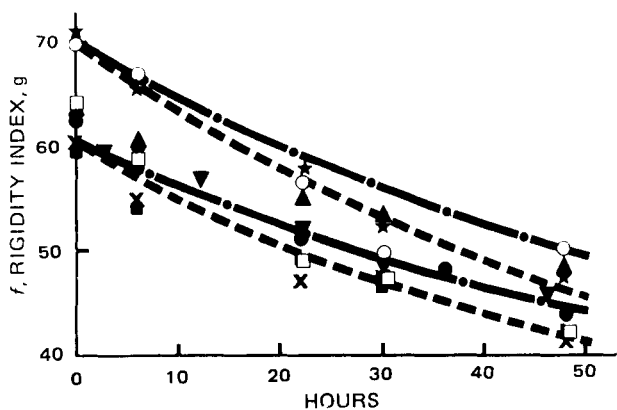


Figure 7—Rigidity-time profile of 6% gelatin heated at 65°. Key: ●, gelatin Lot A; ▲, Lot B; ■, ×, Lot C; ○, ★, Lot D; □, Lot E; ▼, Lot F; ···, pH 6.20; and ---, pH 5.35. Curves were calculated from Eqs. 5 and 14 using f_0 of 60 and 70.

Degradation of 6% Gelatin Solution—Kinetic Models—An apparent second-order model represented by:

$$\frac{-df}{dt} = k_f f^2 \quad (\text{Eq. 4})$$

and the integral form:

$$\frac{1}{f} - \frac{1}{f_0} = k_f t \quad (\text{Eq. 5})$$

gave the best fit of the rigidity degradation data, where f is the rigidity index of 6% gelatin at time t in grams, f_0 is the rigidity index at $t = 0$ in grams, k_f is the rate constant (reciprocal of gram hours), and t is the heating time in hours.

Figure 6 shows the degradation function, $(1/f - 1/f_0)$, plotted against heating time at four different temperatures. The solid lines are based on linear regression forced through zero. The rate constant for each temperature was obtained from the slope of the lines. Figure 7 shows the rigidity profile for eight runs at 65° using six lots of gelatin. Dotted curves are based on calculations using equations developed later.

The viscosity loss proceeded much more rapidly than rigidity loss during the initial period of heating, confirming several earlier observations (5, 14). The best fitting model for the viscosity degradation, fol-

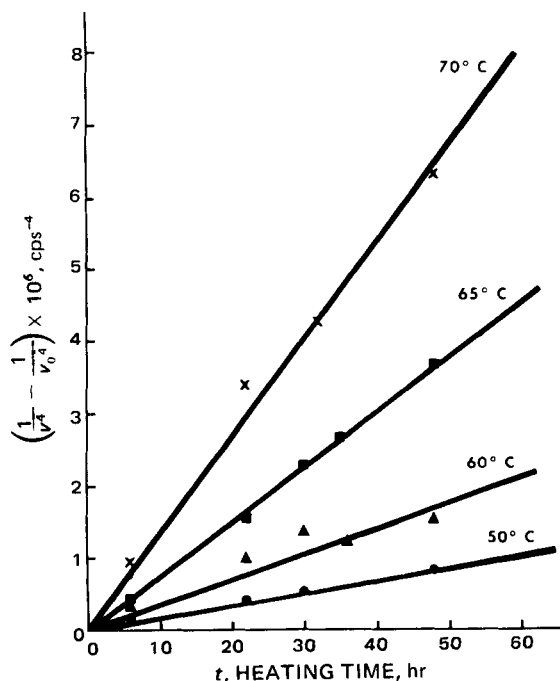


Figure 8—Viscosity degradation of 6% gelatin at different temperatures (gelatin Lot A).

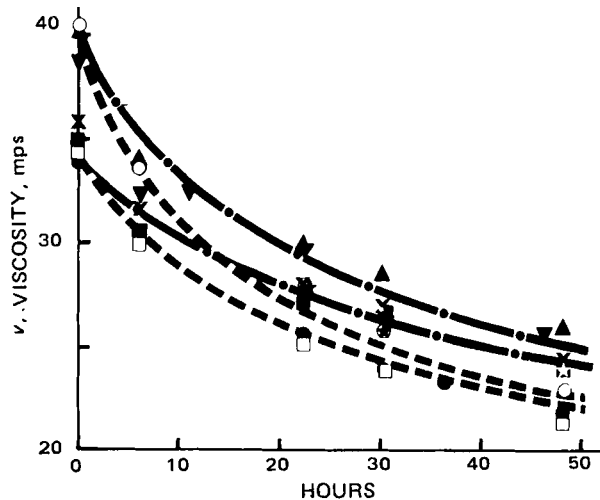


Figure 9—Viscosity-time profile of 6% gelatin heated at 65°. Key: ●, gelatin Lot A; ▲, Lot B; ■, ×, Lot C; ○, ★, Lot D; □, Lot E; ▼, Lot F; ···, pH 6.20; and ---, pH 5.35. Curves were calculated from Eqs. 7 and 15 using v_0 of 34 and 40.

lowing the approach of Eq. 3, was:

$$\frac{-dv}{dt} = k_v v^5 \quad (\text{Eq. 6})$$

which, upon integration within limits, gives:

$$\frac{1}{v^4} - \frac{1}{v_0^4} = 4k_v t \quad (\text{Eq. 7})$$

where v is the viscosity of the 6% gelatin solution (60°) at time t in millipoises, v_0 is the viscosity of the 6% gelatin solution at $t = 0$ in millipoises (mps), k_v is the rate constant ($\text{mps}^{-4} \text{hr}^{-1}$), and t is the heating time in hours.

Figure 8 shows the plot of $(1/v^4 - 1/v_0^4)$ versus t for the degradation of a 6% gelatin at four temperatures. The viscosity profile of eight gelatin solutions, sampled during thermal degradation at 65°, was plotted in Fig. 9, corresponding in time scale to the rigidity degradation of the same eight gelatin solutions as shown in Fig. 7.

It is apparent from Figs. 6 and 8 that the actual degradation reactions were more complex than represented by Eqs. 5 and 7. The presence of complex curves, showing periods of increasing and decreasing rates, seems to be characteristic of most runs. The irregularities cannot all be explained as experimental errors.

Effect of Temperature—The rate constant, k_f , for rigidity degradation was plotted against the reciprocal of absolute temperature in Fig. 10. The equation of the k_f regression line, expressed in exponential form, becomes:

$$k_f = 5.9031 \times 10^7 e^{-9025.56/T} \quad (\text{Eq. 8})$$

Equation 8, which is significant at $p < 0.05$, is in the familiar form of the Arrhenius equation as:

$$k = A e^{-\Delta H_a/RT} \quad (\text{Eq. 9})$$

where ΔH_a is the activation energy for the degradation reaction, T is the absolute temperature, A is a constant, and R is the gas constant. The term ΔH_a may be taken as the activation energy for rigidity degradation. When equating the exponential terms of Eqs. 8 and 9, ΔH_a was determined to be about 17,900 cal/g mole.

The rate constants k_v for viscosity degradation at the four temperatures were obtained as 0.25 of the slopes of the regression lines of Fig. 8. The plots of k_v versus $1/T$ and k_f versus $1/T$ are both shown in Fig. 10. The equation of the k_v regression line, after transformation to the exponential form, becomes:

$$k_v = 1.3471 \times 10^7 e^{-11573/T} \quad (\text{Eq. 10})$$

The experimental fit of Eq. 10 is significant at $p < 0.05$. When equating the exponential term of Eq. 10 to $\Delta H_a/RT$ of Eq. 9, the activation energy, ΔH_a , for viscosity degradation was calculated to be about 23,000 cal/g mole, which, when compared at the probability level of 0.1, is not significantly different from the ΔH_a of 17,900 for rigidity degradation.

Effect of pH—An appropriate mathematical relationship can be de-

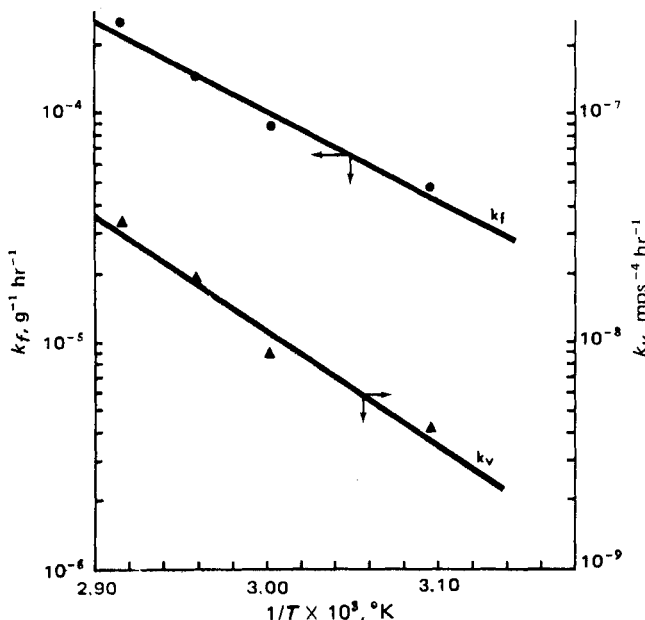


Figure 10—Semilogarithmic plot of degradation rate constants, k_f and k_v , versus reciprocal absolute temperature (pH 5.5).

rived, showing the rate constants k_f and k_v for the degradation of six different gelatin solutions at 65°, as a function of the initial pH of the solutions. The following equations represent the least-squares lines for k_f and k_v versus pH:

$$k_f = (36.1851 - 3.9596 \text{ pH}) \times 10^{-5} \quad (\text{Eq. 11})$$

$$k_v = (55.243 - 7.2414 \text{ pH}) \times 10^{-9} \quad (\text{Eq. 12})$$

Both linear correlations are significant at $p < 0.1$. The weak correlations suggest that other undefined factors might contribute to variations in the degradation rates.

The final equation to predict the average rate constant, k_f , was obtained by combining the separate equations relating to temperature (Eq. 8) and pH (Eq. 11). The combined equation is:

$$k_f = c(590.31)(36.1851 - 3.9596 \text{ pH})e^{-9025.56/T} \quad (\text{Eq. 13})$$

The value of c was calculated as 6787.3 by substituting experimental values of pH, T , and k_f in Eq. 13 and calculating the average. In this treatment, any interaction of pH on the activation energy within the pH 5–7 range was assumed to be negligible. Equation 13 is thus reduced to:

$$k_f = (1.4498 \times 10^8 - 1.5865 \times 10^7 \text{ pH})e^{-9025.56/T} \quad (\text{Eq. 14})$$

Similar consolidation of temperature (Eq. 10) and pH (Eq. 12) effects yields the following equation for viscosity degradation:

$$k_v = (4.3172 \times 10^7 - 5.6591 \times 10^6 \text{ pH})e^{-11573/T} \quad (\text{Eq. 15})$$

Degradation of Gel Mass—Kinetic Models—The degradation of the rigidity index for the 38% gel mass fits the second-order model as follows:

$$\frac{1}{F} - \frac{1}{F_0} = K_F t \quad (\text{Eq. 16})$$

where F is the rigidity index of the gel mass at time t in grams, F_0 is the rigidity index of the gel mass at time 0, K_F is the rate constant (reciprocal of gram hours), and t is the heating time in hours.

The viscosity degradation of the gel mass differs substantially from that of the dilute gelatin; instead of a fifth-order decay, the kinetic data follow more closely a second-order model as defined by:

$$\frac{1}{V} - \frac{1}{V_0} = K_V t \quad (\text{Eq. 17})$$

where V is the viscosity of the gel mass at time t in centipoises, V_0 is the viscosity of the gel mass at $t = 0$ in centipoises, K_V is the rate constant (reciprocal of centipoise hours), and t is the heating time in hours.

Estimating Initial Values, F_0 and V_0 , of Gel Mass—Rigidity and viscosity measurements of most gel mass samples at time zero showed

lower than expected values based on extrapolation. Due to uncertainties of complete dissolution of the gelatin particles in the concentrated gel mass, the actual rigidity and viscosity at time zero were not used in the data treatment. Instead, F_0 was obtained by extrapolating the $1/F$ versus t regression line to $t = 0$. The value V_0 was obtained by extrapolating the $1/V$ regression line to $t = 0$.

Earlier work had shown that the rigidity of the gel mass was higher than that of the dilute gelatin not only because of the increased gelatin concentration but also because of the additional rigidity contributed by molecular interactions with plasticizers such as glycerin (12, 15). For a specific composition of the gel mass, however, the rigidity is expected to be proportional to the rigidity of the dilute gelatin in the standard 6% concentration. The rigidity indexes of six lots of gelatin were correlated to those of the gel mass made from the respective lots as follows:

$$F_0 = 147.9 + 7.93f_0 \quad (\text{Eq. 18})$$

where f_0 and F_0 are, respectively, the rigidity index of the 6% gelatin and that of the gel mass made from the same lot of gelatin prior to heating. The correlation of Eq. 18 is significant at $p < 0.01$.

In a like manner, the initial viscosities, V_0 , for six runs were correlated to the respective initial viscosities, v_0 , of the dilute gelatin. The resulting regression equation is:

$$V_0 = -42019 + 1915.05v_0 \quad (\text{Eq. 19})$$

Equation 19 gave a significant fit to the data at $p < 0.001$.

Relating Gel Mass Degradation to Dilute Gelatin Degradation—The rate constants K_F and K_V for gel mass degradation were determined for eight runs at 60 and 65° utilizing gelatin lots previously evaluated for thermal degradation at identical conditions as 6% gelatin solutions. The objective of these parallel runs was to relate the rate constants K_F to k_f and K_V to k_v so that Eqs. 16 and 17 may be used to predict gel mass degradation based on the kinetics of the 6% gelatin solution.

Another commonly used approach for predicting gel mass degradation is to assume that fractional degradation of the dilute gelatin is the same as that of the gel mass at any given time. This assumption may be represented by Eqs. 20 and 21 for rigidity and viscosity, respectively:

$$F = f\left(\frac{F_0}{f_0}\right) \quad (\text{Eq. 20})$$

$$V = v\left(\frac{V_0}{v_0}\right) \quad (\text{Eq. 21})$$

Experimental data, however, have not supported these assumptions fully. Thus, even though the initial rheological parameters of the gel mass and that of the 6% gelatin were related according to Eqs. 18 and 19, the relation changed as heating progressed, depending upon the initial pH of the solution.

The following empirical equation shows how the ratio of the two rate constants, K_F/k_f , is dependent on the pH of the 6% gelatin solution:

$$\phi_F = \frac{K_F}{k_f} = -0.2757 + 0.06166 \text{ pH} \quad (\text{Eq. 22})$$

The experimental fit of Eq. 22 is significant at $p < 0.001$.

The rate constant ratio for viscosity, K_V/k_v , is related to the pH of the 6% gelatin solution as follows:

$$\phi_V = \frac{K_V}{k_v} = -165.02 + 39.12 \text{ pH} \quad (\text{Eq. 23})$$

Although the correlation of ϕ_V and pH is weaker than that developed for ϕ_F , it is significant, nonetheless, at $p < 0.1$.

By combining Eqs. 14, 16, 18, and 22, an overall expression is obtained for estimating the rigidity index of the specific gel mass from data of rigidity and pH of the 6% gelatin:

$$\frac{1}{F} = \frac{1}{147.9 + 7.93f_0} - (3.996 - 1.3313 \text{ pH} + 0.09782 \text{ pH}^2) \times 10^7 t e^{-9025.56/T} \quad (\text{Eq. 24})$$

Similarly, by combining Eqs. 15, 17, 19, and 23, the following overall equation is obtained for calculating gel mass viscosity:

$$\frac{1}{V} = \frac{1}{-42019 + 1915.05v_0} - (7.1241 - 2.6229 \text{ pH} + 0.2214 \text{ pH}^2) \times 10^9 t e^{-11573/T} \quad (\text{Eq. 25})$$

Equation 25 allows the estimation of gel mass viscosity on the basis of the initial viscosity and pH of the 6% gelatin, heating time, and temperature.

Table III—Comparison of Calculated and Actual Data

Calculated Parameter	Input Parameter	Equations Used	Estimated Limits ^a of Error ^b , %
Rigidity index for 6% gelatin, f	f_0	5, 14	-7.2 to +9.7
Rigidity index for gel mass, F	f_0	24	-12.9 to +8.7
Rigidity index for gel mass, F	f_0	5, 14, 18, 20	-19.8 to +9.6
Rigidity index for gel mass, F	f_0, V	18, 19, 27	-15.4 to +15.8
Viscosity for 6% gelatin, v	v_0	7, 15	-7.5 to +8.9
Viscosity for gel mass, V	v_0	25	-28.8 to +18.9
Viscosity for gel mass, V	v_0	7, 15, 19, 21	-26.6 to +51.3

^a Estimated to include at least 95% of all cases at 95% confidence level. ^b Error = (calculated - actual)/actual, compared with 33 actual data points, except the first and fifth items where there were 47 points.

Estimating Rigidity Degradation Based on Viscosity Degradation—Dividing Eq. 16 by Eq. 17 and rearranging result in:

$$\frac{1}{F} - \frac{1}{F_0} = \frac{K_F}{K_V} \left(\frac{1}{V} - \frac{1}{V_0} \right) \quad (\text{Eq. 26})$$

When substituting the equivalents of K_F and K_V in Eqs. 22 and 23, the following results:

$$\frac{1}{F} = \frac{1}{F_0} + \left(\frac{1}{V} - \frac{1}{V_0} \right) \times \left(\frac{3.9966 - 1.3313 \text{ pH} + 0.09782 \text{ pH}^2}{712.41 - 262.29 \text{ pH} + 22.14 \text{ pH}^2} \right) e^{2547.44/T} \quad (\text{Eq. 27})$$

By using Eq. 27, the rigidity index of a gel mass may be computed based on the experimental values of gel mass viscosity, provided that the initial values of the 6% gelatin rigidity, viscosity, and pH and the heating temperatures are known. Such an equation is useful if the rigidity of the gel mass cannot be determined either due to the nonavailability of the test facilities or the lack of time necessary for proper aging of the test sample.

Equation 27 may be rearranged into the following form:

$$\frac{[(F_0 - F)/F_0]}{[(V_0 - V)/V_0]} = \frac{F}{V} \psi e^{2547.44/T} \quad (\text{Eq. 28})$$

where ψ is a function of pH as indicated by the term in parentheses in Eq. 27.

The left-hand side of Eq. 28 represents the ratio of fractional degradation of rigidity to viscosity. It can be shown that, for the gelatin lots studied, within the normal pH range of 5-6.5 and temperature range 50-70°, the percentage degradation of viscosity is always greater than that of rigidity. Furthermore, as pH increases, the rigidity loss tends to increase more than the increase of the viscosity loss. As temperature increases, however, viscosity loss tends to increase more than rigidity loss. Both the pH and temperature effects confirm observations made by Ames (5).

Test of Empirical Equations against Actual Data—The usefulness of the empirical equations was tested by computing the rheological parameters and comparing them with the experimental values. Estimated

limits of errors were then computed based on the application of tolerance limits (16).

Table III summarizes the limits of error in using the various equations. In general, the thermal degradation of the 6% gelatins is predicted with better accuracy than that of the 38% gel mass. This statement is true for both the rigidity index and viscosity. The largest error is in the estimation of gel mass viscosity (Eq. 25). The larger prediction error with gel mass is probably due, in part, to increased nonhomogeneity with concentrated gel mass. Such things as presence of air bubbles and undetected moisture differences possibly contribute to errors in the rigidity and viscosity determinations. Other errors might appear through interactions between viscosity and rigidity of the concentrated gel mass, even though rigidity was reported to be independent of viscosity in dilute solutions (e.g., 6%) (13).

The premise of Eqs. 20 and 21 was that the conditions producing a given percentage degradation of the dilute gelatin will cause the same percentage degradation of the concentrated gel mass. Comparison of errors associated to the use of Eqs. 24 and 25 versus Eqs. 20 and 21 in Table III shows that Eqs. 20 and 21 are oversimplified and that more accurate predictions are possible using Eqs. 24, 25, and 27.

REFERENCES

- (1) J. W. Janus, "Recent Advances in Gelatin and Glue Research," G. Stainby, Ed., Pergamon, New York, N.Y., 1956.
- (2) A. Todd, *Nature*, **191**, 567 (1961).
- (3) G. Stainby, P. R. Saunders, and A. G. Ward, *J. Polym. Sci.*, **12**, 325 (1954).
- (4) P. J. Tiemstra, *Food Technol.*, **22**, 1151 (1968).
- (5) W. M. Ames, *J. Soc. Chem. Ind. (London)*, **66**, 279 (1947).
- (6) S. Weller, *A.I.Ch.E. J.*, **2**, 59 (1956).
- (7) "Standard Methods for Sampling and Testing of Gelatins," Gelatin Manufacturers Institute of America, New York, N.Y., 1964.
- (8) C. E. Sheppard, S. S. Sweet, and J. W. Scott, Jr., *J. Ind. Eng. Chem.*, **12**, 1007 (1920).
- (9) M. Briefer and J. H. Cohen, *Ind. Eng. Chem.*, **19**, 252 (1927).
- (10) J. D. Ferry, *Rev. Sci. Instrum.*, **12**, 79 (1941).
- (11) P. R. Saunders and A. G. Ward, in *Proc. 2nd Int. Congr. Rheol., Oxford*, 1954, p. 284.
- (12) S. E. Sheppard and S. S. Sweet, *J. Am. Chem. Soc.*, **43**, 539 (1921).
- (13) J. D. Ferry, *ibid.*, **70**, 2244 (1948).
- (14) P. R. Saunders and A. G. Ward, *Nature*, **176**, 26 (1955).
- (15) J. E. Carless and J. R. Nixon, *J. Soc. Cosmet. Chem.*, **21**, 427 (1970).
- (16) A. Hald, "Statistical Theory with Engineering Applications," Wiley, New York, N.Y., 1952.

ACKNOWLEDGMENTS

The author expresses appreciation to Dr. J. A. Seitz for comments and suggestions, to Dr. Saul Borodkin for assistance and suggestions in data treatment, and to Mr. Roy Hill for experimental assistance.