

## Stress Relaxation of Anhydrous Gelatin Rubbers

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### Synopsis

Anhydrous gelatin-glycerol compositions exhibit rubbery behavior in the temperature region  $-40$  to  $+40^{\circ}\text{C}$ . and in the gelatin weight fraction range 0.1-0.4. These rubbers are capable of sustaining considerable stress over several decades of time at room temperature or below but flow rapidly in the region  $45-60^{\circ}\text{C}$ . Stress relaxation moduli at  $25^{\circ}\text{C}$ . appear to be insensitive to the substitution of glycerol with water but shear viscosity data indicate that gelatin-glycerol rubbers flow at temperatures about  $15^{\circ}\text{C}$ . higher than their aqueous counterparts.

### INTRODUCTION

Gelatin films incorporating non-aqueous diluents such as dimethyl sulfoxide, glycerol, and ethylene glycol can be readily prepared.<sup>1</sup> At room temperature, depending on the concentration of diluent and the time scale of experimentation, these states of matter can behave as brittle glasses, semi-rigid plastics, rubbers, or viscous liquids. The ubiquity of moisture in the environment introduces a further factor which affects significantly the viscoelastic and thermal properties of these hydrophilic compositions in the transition region of viscoelastic behavior.

In particular, the anhydrous gelatin-glycerol system displays rubberlike behavior in the temperature range  $-40$  to  $+40^{\circ}\text{C}$ . when the weight fraction gelatin is in the range 0.10-0.40. By convention, polymer-diluent systems with a relatively high diluent-plasticizer content which develop substantial rigidity following prolonged annealing at room temperature have been referred to as gels and have been studied as somewhat exceptional states of matter. Inspection of a large body of data which has been accumulated recently<sup>1</sup> on the viscoelastic behavior of gelatin-glycerol "gels" leads, however, quite unequivocally to the conclusion that the response of these systems to an increase in temperature is qualitatively identical to that which is observed with undiluted synthetic amorphous polymers or with plasticized microcrystalline polymers. In fact, gelatin-glycerol gels can be vitrified if cooled below the glass transition temperature  $T_g$ ; following heating above  $T_g$ , these compositions display one by one the characteristic regions of viscoelastic behavior,<sup>2</sup> including an extended

rubbery plateau which is followed by flow. Such behavior has been also observed when gelatin has been diluted with either ethylene glycol or dimethyl sulfoxide.<sup>1</sup> In the interest of clarity, therefore, it is preferable to classify these gels as rubbers, thereby incorporating them within the spectrum of viscoelastic behavior which is typical of macromolecular amorphous or quasi-amorphous substances.

In the past, considerable study has been devoted to the aqueous gelatin gels.<sup>3-5</sup> These compositions can not be quenched readily to temperatures below  $-100^{\circ}\text{C}$ . without substantial crystallization of the aqueous component; the viscoelastic behavior of such multiphase materials over a wide temperature range is, therefore, not amenable to the simple characterization which is outlined above.

The results reported in this work provide the means of a direct comparison between the properties of aqueous and non-aqueous gelatin rubbers. This report also attempts to extend the viscoelastic characterization of gelatin-glycerol rubbers which, besides being of interest in themselves, have been recently used in a number of applications, such as materials for construction of models useful in photoelastic stress analysis.<sup>6</sup>

## EXPERIMENTAL METHODS AND ANALYSIS OF DATA

### Materials

The gelatin used in this work has been described previously in detail.<sup>1</sup> It derived from cattle bones (ossein) and had a weight-average molecular weight of approximately 300,000.

Glycerol (Spectroquality Reagent, Matheson, Coleman and Bell) was used without further purification. The freedom from potentially cross-linking aldehydic impurities<sup>7</sup> (such as glyceraldehyde and acrolein) in this reagent was inferred from the absence of any absorption peak at  $1725\text{ cm.}^{-1}$  and by the lack of reaction with dinitrophenylhydrazine.

### Casting and Dehydration of Films

Gelatin-glycerol films containing protein in weight fractions  $w_2$  of 0.101, 0.160, 0.204, 0.251, 0.291, 0.331, and 0.391 were prepared by an aquasol casting procedure which has been described previously.<sup>1,8</sup> These films were dehydrated (and simultaneously annealed) at  $25 \pm 0.2^{\circ}\text{C}$ . under a vacuum of  $10^{-3}$  mm. Hg over a period of 20 days or more. The treatment was interrupted when the moisture content was in the range 0.1-0.5 wt.-%. Below approximately 0.2 wt.-% moisture, gelatin becomes covalently crosslinked<sup>9</sup> and does not dissolve in excess de-ionized water at  $40 \pm 0.2^{\circ}\text{C}$ . over several days. In all cases, it was possible to terminate the dehydrative treatment without insolubilizing gelatin to an extent greater than 5 wt.-% (based on total weight of dry gelatin). The presence of this marginal amount of crosslinked gelatin in some of the specimens did not affect the results which are reported here. This conclusion arises from our

observation that specimens which were fortuitously dehydrated to the point (approximately 0.3 wt.-% moisture) where they were completely soluble displayed viscoelastic behavior which was identical to that of marginally crosslinked specimens (moisture content approximately 0.2 wt.-% or lower), at least within the time scale over which measurements are reported here. Similarly, the viscoelastic behavior of soluble specimens which contained moisture to the extent of approximately 0.5 wt.-% was indistinguishable from that of soluble specimens, the moisture content of which was in the range of 0.3–0.4 wt.-%. It was concluded that the variation of moisture content in the narrow range 0.1–0.5 wt.-% from specimen to specimen did not affect the measurements. Significantly lower levels of moisture could be obtained by prolonged dehydration under vacuum. Specimens so treated often became insoluble<sup>9</sup> to the extent of 20 wt.-% (based on total weight of dry gelatin) or more and possessed significantly higher moduli than did specimens which were either completely soluble or were only marginally insoluble; measurements on such specimens are not reported here.

### Viscoelastic Measurements

The isothermal stress relaxation of specimens was observed in the time interval from approximately 0.01–30 hr., and in the temperature range 0–60°C. Following dehydration, rectangular specimens of known dimensions (typically 0.5 × 1 × 4 cm.) were mounted on the jaws of a stress relaxation balance which has been described previously.<sup>2</sup> The specimen-jaw assembly was immersed in silicone oil (Fluid 200, Dow Corning Corporation, Midland, Michigan) which was contained in a small cell equipped with glass windows; specimens were thereby protected from significant loss or gain of moisture while the measurement was in progress. Previous 50 hr. immersion of gelatin gels in this oil under identical conditions (but under zero strain) had shown that these specimens suffered no significant weight gain or loss nor any detectable change in modulus as a result of such exposure.

Following installation and attainment of thermal equilibrium within  $\pm 0.1^\circ\text{C}$ . inside the sample cell, the unstretched length  $L_0$  of the specimen was determined to within  $\pm 0.05\%$  by using a cathetometer. The sample was then stretched to a new length  $L$  within approximately 5 sec. and the load requisite to balance the stress  $\sigma(t)$  in the specimen was recorded over the desired period of time. The constant elongation ratio  $L/L_0$  chosen varied from 1.08 to 1.10.

### Analysis of Data

Under the conditions used in our measurements, the specimens behaved as if they were weak rubbers; a similar identification of aqueous gelatin gels with rubbers has been proposed by Ferry.<sup>10</sup> These compositions were soft bodies which recovered their original dimensions instantaneously following the release of uniaxial strain whenever the latter did not exceed

100%; higher strains caused these specimens to rupture. Accordingly, the isothermal, time-dependent Young's modulus,  $E_r(t)$ , was calculated from the well-known expression

$$E_r(t) = \sigma(t)/(1/3)[(L/L_0) - (L_0/L)^2] \quad (1)$$

which is a consequence of the theory of rubber elasticity.<sup>2</sup>

An estimate of the shear viscosity,  $\eta_s$ , was obtained (a) by considering the specimens as incompressible, thereby utilizing the relation<sup>2,10</sup>

$$\eta_t = 2(1 + \nu)\eta_s = 3\eta_s \quad (2)$$

where  $\eta_t$  is the tensile viscosity and  $\nu$  is Poisson's ratio (assumed to be time-invariant and equal to 0.5) and (b) by considering the behavior of the specimens as linearly viscoelastic, thereby making use of the expression<sup>2,10</sup>

$$\eta_t = \int_0^{\infty} E_r(t) dt \quad (3)$$

to compute the tensile viscosity directly from the stress relaxation data by graphical integration. The validity of the computation procedure shown by eq. (3) is limited insofar as within the temperature range 40–55°C. [where eq. (3) was generally used] the specimens did not behave as linear viscoelastic bodies; for this reason, the absolute values of  $\eta_s$  reported here must be considered exact only to a first approximation and are included to demonstrate the interesting trend of material properties with temperature in the flow region.

## RESULTS

Specimens of gelatin weight fraction 0.101, 0.160, and 0.204 ruptured almost immediately upon extension in the stress relaxation balance whenever the temperature exceeded approximately 25°C.; only measurements performed at 25°C. or below were therefore obtained on such compositions. Relatively complete sets of stress relaxation data in the range 0–60°C. were obtained for the remaining four compositions ( $w_2 = 0.251, 0.291, 0.331, \text{ and } 0.391$ ). It was observed that the viscoelastic behavior of all specimens was qualitatively identical, and for this reason the stress relaxation data presented in Figure 1 can be considered representative of the entire set.

Figure 1 displays the behavior of a typical gelatin rubber in stress relaxation at several isothermal steps. Within the time scale 0.01–10 hr. and at temperatures below 25°C. this material exhibits a well-developed rubbery plateau with a quasi-static modulus in the range  $10^6$ – $10^7$  dyne/cm.<sup>2</sup>. At higher temperatures,  $E_r(t)$  is seen to relax rapidly with time; for example, at 46.6°C. the specimen relaxed completely in 26,000 sec., and at 49.75°C. complete relaxation occurred within 9000 sec. Above 50°C., the relaxation occurred within the 5 sec. interval requisite for

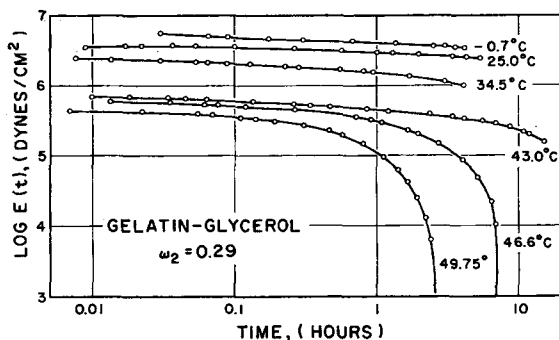


Fig. 1. Isothermal stress relaxation of an anhydrous gelatin-glycerol rubber containing 29.1 wt.-% protein.

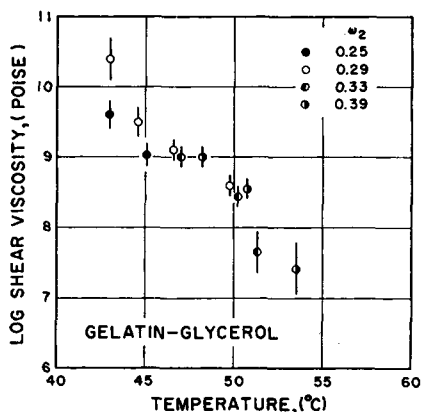


Fig. 2. Rapid decay of the computed shear viscosity with temperature in the flow region for several anhydrous gelatin-glycerol rubbers. The weight fraction of protein  $w_2$  is indicated.

imposition of the constant strain and gross flow occurred in the region 50–55°C.

It is also quite evident from Figure 1 that stress relaxation data obtained at different isotherms do not superpose by simple horizontal shift along the  $\log(t)$  axis. In fact, these isotherms are quite reminiscent of equivalent data obtained on semicrystalline polymers such as polyethylene and polytrifluorochloroethylene.<sup>2</sup> This superficial resemblance will be discussed further below.

Figure 2 presents the variation of the computed shear viscosity  $\eta_s$  with temperature for several specimens. The viscosity of these materials decreases monotonously with temperature; this decrease is quite sharp, amounting to approximately three orders of magnitude (poise) per 10°C. rise in temperature. For all of these specimens, the shear viscosity dropped to below approximately  $10^7$  poise, and gross flow occurred in the temperature range 52–58°C.

By contrast with the thermal variable, the concentration of gelatin affected the viscoelastic properties to a rather minor extent. Figure 2 shows that the flow behavior of these compositions in the temperature interval 40–60°C. is insensitive to gelatin concentration in the relatively narrow weight fraction range 0.30–0.40. Similarly, in the same temperature interval, the directly determined, 0.1 hr. relaxation modulus,  $E_r$  (0.1 hr.), was also found to be quite insensitive to gelatin concentration.

TABLE I  
 $E_r$  (at 0.1 hr.) of Gelatin–Glycerol Rubbers

Gelatin weight fraction $w_2$	$T$ , °C.	$E_r$ (0.1 hr.), dyne/cm. <sup>2</sup>
0.101	25.0	$3.4 \times 10^5$
0.160	24.8	$6.3 \times 10^5$
0.204	24.9	$9.1 \times 10^5$
0.251	25.2	$2.1 \times 10^6$
0.291	25.0	$3.5 \times 10^6$
0.331	25.1	$3.5 \times 10^6$
0.391	24.7	$4.4 \times 10^6$

At temperatures considerably below the flow region and in the region of the rubbery plateau, however,  $E_r$  (0.1 hr.) showed a distinct dependence on gelatin weight fraction. Pertinent numerical data appear in Table I, where it is apparent that the modulus (determined at fixed time and temperature) increases with gelatin weight fraction, although not in a simple manner.

## DISCUSSION

The stress relaxation data reported in this work are in good accord with data obtained on identical specimens using a torsional-creep apparatus.<sup>1</sup> In the latter case, observations could be extended to specimens containing a gelatin weight fraction as low as 0.1. In both cases, the moduli became immeasurably small and the specimens flowed when the temperature exceeded a rather narrow range. Such viscoelastic behavior is also characteristic of semicrystalline polymers such as polytrifluoroethylene,<sup>2</sup> polyethylene,<sup>2</sup> and plasticized poly(vinyl chloride),<sup>11–13</sup> all of which exhibit well-characterized melting or flow above a certain narrow temperature range. Furthermore, anhydrous gelatin–glycerol solutions in the  $w_2$  range 0.1–0.4 have been observed to develop (rubbery) moduli of  $10^5$ – $10^7$  dyne/cm.<sup>2</sup> only following annealing over several days at temperatures below the flow point; the same solutions have exhibited no rubbery plateau whenever quenched to below the glass transition temperature, and subsequently heated above it. These observations are consistent with the conclusion that anhydrous gelatin–glycerol compositions are three-dimensional networks held together by ordered regions which act as noncovalent crosslinks; such ordered regions can sustain relatively high stresses over several decades

of time at low temperatures ( $-40$  to  $+40^{\circ}\text{C}.$ ) but suffer reversible damage at high temperatures ( $40$ – $60^{\circ}\text{C}.$ ).

In a previous dilatometric study of gelatin incorporating ethylene glycol<sup>14</sup> ( $w_2 = 0.10$ ), it was observed that reversible melting occurred at  $46^{\circ}\text{C}.$  Our observations are in accord with this early finding and indicate that (a) ordering of gelatin macromolecules can occur in the absence of water and (b) the stability of the ordered regions is, to a first approximation, not affected when ethylene glycol is replaced with glycerol. However, x-ray diffraction patterns of gelatin films incorporating glycerol, ethylene glycol or dimethyl sulfoxide are very diffuse<sup>1</sup> and do not provide any opportunity for further analysis of the chain structure.

It is remarkable that values of moduli reported here for gelatin–glycerol systems, as well as values for gelatin–ethylene glycol and gelatin–dimethyl sulfoxide systems which have been reported previously,<sup>1,8</sup> agree closely with equivalent parameters which have been independently determined<sup>15,16</sup> on gelatin–water systems in the  $w_2$  range 0.1–0.4. Such agreement leads to the conclusion that, to a first approximation, the mechanical behavior of gelatin–diluent systems in the rubbery region is independent of the nature of the diluent. This approximation becomes invalid in the region of flow. Several determinations of the melting points of gelatin–water gels<sup>14,17</sup> in the  $w_2$  range 0.3–0.4 have shown these to lie in the temperature range  $35$ – $40^{\circ}\text{C}.$ ; by contrast, gelatin–glycerol specimens in the same gelatin concentration range were, in this work, observed to flow within the significantly higher interval  $50$ – $60^{\circ}\text{C}.$  However, it is possible to conclude that the viscoelastic parameters (though not the macroscopic dimensions) of these hydrophilic gelatin rubbers in the temperature region  $0$ – $40^{\circ}\text{C}.$  are insensitive to the absorption or loss of moisture from the atmosphere. This conclusion may simplify greatly the experimental study as well as the possible uses of these proteinaceous rubbers.

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### Résumé

Des compositions à base de gélatine anhydre et de glycérine montrent un comportement caoutchouteux dans la région de température de  $-40^{\circ}$  à  $+40^{\circ}\text{C}$  et pour une fraction en poids de gélatine variant de 0.1 à 0.4. Ces caoutchoucs sont capables de supporter une tension considérable sur plusieurs décades de temps à température de chambre et en-dessous, mais coulent rapidement dans un domaine de  $45$  à  $60^{\circ}\text{C}$ . Les modules de relaxation du tension à  $25^{\circ}\text{C}$  ne sont pas sensibles à la substitution de la glycérine par l'eau et les données de viscosité de cisaillement indiquent que les caoutchoucs gélatine-glycérine s'écoulent à des températures d'environ  $15^{\circ}\text{C}$  plus élevées que leur correspondants aqueux.

### Zusammenfassung

Wasserfreie Gelatin-Glycerin-Gemische zeigen in einem Temperaturbereich von  $-40^{\circ}$  bis  $+40^{\circ}\text{C}$  und bei einem Gelatingewichtsbruch von 0,1 bis 0,4 kautschukartiges Verhalten. Diese Kautschuke können bei Raumtemperatur oder darunter während mehrerer Zeitdekaden eine beachtliche Dehnung aushalten, fließen aber schnell in Bereich von  $45$  bis  $60^{\circ}\text{C}$ . Spannungsrelaxationsmoduli bei  $25^{\circ}\text{C}$  scheinen gegenüber einem Ersatz des Glycerins durch Wasser unempfindlich zu sein, aber die Scherviskositätsdaten zeigen an, dass Gelatin-glycerin-Kautschuke bei um etwa  $15^{\circ}\text{C}$  höheren Temperaturen fließen als die entsprechenden wässrigen Gemische.

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