

Creep Studies on Gelatin at 100% Relative Humidity

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INTRODUCTION

The study reported in this paper is part of a research effort on the action of gelatin as an adhesive. Our main object was to gain understanding of the alleged poor performance at high temperatures and high humidities. It has been pointed out that the examination of film strength is probably the most significant and unambiguous single test for glue performance.¹ Consequently, we have carried out creep tests of gelatin films in an atmosphere saturated with humidity at various temperatures. To explain our results we have also determined the water uptake of the gelatin under these conditions.

EXPERIMENTAL

The gelatin studied was a commercial grade pigskin gelatin designated P1, supplied by Peter Cooper Corporation, which had an intrinsic viscosity of 60 cc./g. in 0.04*M* NaCl solution at 44°C. Studies of other gelatine samples are closely similar to the results obtained with P1.

We prepared our films by making up 10% gelatin solutions by weight, keeping the temperature always below 50°C. The solutions were poured on trays and dried at ambient temperature. Dumb-bell-shaped samples were cut from the films with a die whose parallel center section was 0.4 cm. by ca. 0.05 cm. Only such samples whose thickness deviated not more than 10% from the mean value were used for our tests.

Preliminary tests indicated that for obtaining reproducible results not only good temperature control is essential but also prevention of moisture condensation on the gelatin. Therefore, the following method was developed. Each sample is contained in a separate glass cylinder provided with a tightly fitting metal cover and carrying a hook from which the gelatin film is suspended. Weights are attached to the clamp at the lower end of the film. These are held by movable hooks so

that the samples can be kept in an unstressed state till the start of the experiment. Some distilled water is placed in each tube. The tubes are almost completely submerged in a thermostatted water bath whose temperature fluctuations are less than $\pm 0.1^\circ\text{C}$. Condensation of water on the sides of the tubes and on the underside of the cover are thus avoided, and equilibrium humidity at the thermostat's temperature will prevail soon after submerging of the tubes. The elongation of the film is observed by means of a cathetometer trained onto the sample.

When a sample is subjected to stress immediately after being placed into the high humidity atmosphere, deformation takes place first slowly and then with increasing speed. After a short time the rate of elongation decreases again; at this point either final equilibrium elongation is attained or the film breaks. The unconditioned samples are more rigid at first and yield more slowly under load, but progressively so as the moisture penetrates from the outside. When the diffusion of moisture has wetted the last layer of the interior of the film, creep proceeds at full speed. If, on the other hand, the sample is kept in the tube for conditioning without load for about 1 hr. and is then stressed, it initially elongates very fast; the elongation then slows down, and, again, either the sample reaching equilibrium or extends to break. The equilibrium is reached within a few hours, after which no further creep is observed. We have studied these equilibrium elongations as function of equilibrium stress at 26.5, 31.5, 36.5, and 46.5°C. The results for all temperatures except 31.5°C. are summarized in Figure 1.

RESULTS AND DISCUSSION

Although there is considerable scattering in the results, we notice certain characteristics of the curves. At 26.5°C., the gelatin films are easily extended up to 80%, the modulus of rigidity being rather low (5×10^6 dynes/cm.²). Elongations

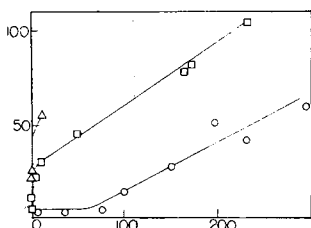


Fig. 1. Equilibrium stress vs. equilibrium strain from creep experiments at (O) 26.5, (\square) 36.5, and (Δ) 46.5°C. Some points have been omitted for the sake of clarity. The curve at 31.5° has been omitted completely. Abscissa: elongation, %; ordinate: stress, kg./cm.².

larger than 80% are governed by a modulus of about 3×10^7 dynes/cm.². At 36.5°C., on the other hand, there is a critical threshold stress below which the material is very stiff (the modulus being well over 10^9 dynes/cm.²), so that in this range of loads no elongation could be detected by our method. If higher elongations are enforced, the modulus drops to about 3×10^7 dynes/cm.².

We have omitted the points for 31.5°C. from the diagram in order to avoid overcrowding. The behavior at this temperature is intermediate between behavior at 26.5 and 36.5°C. There is an initial modulus of 8×10^7 dynes/cm.² and a final modulus of 4×10^7 dynes/cm.².

At 46.5°C., gelatin is a stiff material with a limiting extension of about 10%. If larger elongations are enforced, the films break. Moreover, we have observed spontaneous two-dimensional contractions of the unstressed films up to 10% of their original length and width when they were brought up to 46.5°C. This "hydrothermal shrinkage" is a well known property of collagen and has been observed also in gelatin by Pankhurst.²

The water uptake was determined by conditioning films in the same way as for the creep tests, weighing them, and then drying them over phosphorus pentoxide to constant weight. In Table I we report the water content as obtained from

$$\% \text{ water} = \frac{100(\text{Wet Weight} - \text{Dry Weight})}{\text{Dry Weight}}$$

Several samples were run at each temperature.

We see that the moisture uptake of gelatin films

TABLE I
Moisture Content at Various Temperatures

Temperature, °C.	26.5	36.5	46.5
Water content, %	27.0 \pm 0.9	22.0 \pm 0.1	15.1 \pm 0.4

exposed to an atmosphere saturated with water vapor decreases with increasing temperature. That there is a true thermodynamic equilibrium between gelatin and water vapor can be seen from the fact that gelatin equilibrated with water at a lower temperature will lose water at a higher temperature.

It is well known that the rigidity of aqueous gelatin gels decreases with increasing temperature, vanishing around 30–40°C.³ This was shown to be true for gelatin gels containing as little as 180% moisture.⁴ Our results seemed to be at variance with this, but actually we are comparing systems containing very much smaller amounts of water. We consider this to be the decisive factor in determining the behavior of gelatin films. Dry gelatin is a glassy material, and water acts as a plasticizer. Whereas the small amount of water taken up by gelatin at 46.5° does not modify appreciably this glasslike behavior, the larger amounts taken up at 26.5°C. plasticize gelatin sufficiently to make it display rubberlike behavior. This assumption is supported by the results reported by Bradbury and Martin,⁵ who showed that the tensile strength of gelatin drops with increase of humidity of the atmosphere (at constant temperature) to which the films are exposed.

We do not know at this juncture what the effect of temperature change alone would be on samples of constant water content. As soon, however, as there is any water in excess of the adsorption equilibrium, i.e., free water sufficient to form a phase of aqueous gelatin gel, this gel will melt with increasing temperature and thus lose all its mechanical strength. We have, then, the contrasting behavior of essentially dry gelatin, which absorbs water at low temperatures and loses it at higher temperatures, and that of aqueous gelatin, which melts in the range of 30–40°C.

Our determinations of moisture uptake from water vapor agree qualitatively with those of Ghost and Gyany.⁶ (These authors do not state whether their results refer to air-dried or to desiccator-dried material, so that no quantitative comparison can be made.) Their absorption isotherms for gelatin are very much like those found for other water-soluble proteins⁷ and like those reported for water-insoluble polymers such as viscose rayon, cotton, and acetate cotton.⁸ The fact that gelatin absorbs less water at 40° than at 25° was found by Bull.⁹ He has shown that this holds also for collagen and various albumins and globulins as well as for nylon, silk, and wool. The

amount of moisture absorbed is of the same order of magnitude for all these substances. Finally, water-insoluble silica and alumina absorb less water at increased temperatures, just as water-soluble gelatin.⁶ This behavior is in accord with general thermodynamic reasoning (principle of Le Chatelier) and applies to all absorptions from the vapor phase, irrespective of the corresponding solubilities in the condensed vapor. Exceptions are deliquescent materials, which provide nuclei with respect to which the water vapor becomes supersaturated. In other words, gelatin is seen not to be deliquescent, even at 100% R.H. This is true, the great affinity which gelatin has for water in the liquid form notwithstanding. The explanation to this apparent contradiction must be sought in the study of the mechanism of swelling and dissolution of gelatin.

Summing up, we have made this study in order to understand the alleged poor performance of glue joints under heat and high humidity. Contrary to common expectation, we infer from our results that a glue joint does not melt at elevated temperatures (as long as kept out of contact with liquid water), but may become harder due to further drying. Eventual failure may be due to the hydrothermal shrinkage which causes strong stresses in the joints. Another cause of "failure" under conditions of high humidity may be ascribed to a drop in temperature below the dew point which causes water to condense. The failure then is caused by the liquid water and not by atmospheric humidity.

We wish to thank Dr. R. Sabia for experimental assistance at the early stages of this investigation and the National Association of Glue Manufacturers for financial assistance which made this work possible.

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Synopsis

The creep behavior of gelatin films was studied at 100% R. H. Under a given load the films either extend to an equilibrium length or break. Equilibrium stress-strain curves were obtained at 26.5, 31.5, 36.5, and 46.5°C. At 26.5°C., gelatin films exhibit essentially rubberlike behavior; at the higher temperatures they become stiffer. The films are brittle at 46.5°C. This course of behavior is explained by a decrease in uptake of moisture from the surrounding atmosphere with increasing temperature. At 26.5°C., enough water is absorbed (27%) to plasticize the gelatin, whereas the reduced amount absorbed at 46.5°C. (15%) is insufficient to modify the glass-like behavior of dry gelatin. These results indicate that poor performance of gelatin used as glue under hot and humid conditions is not due to a deliquescent behavior; the latter occurs only on direct contact of gelatin with liquid water.

Résumé

Le rétrécissement de films de gélatine a été étudié à une humidité relative de 100%. Sous une charge donnée, les films ou bien s'étendent jusqu'à une longueur d'équilibre ou bien ils se brisent. Les courbes d'équilibre poids-tension ont été obtenues à 26,5°, 31,5°, 36,5°, et 46,5°C. À 26,5° les films de gélatine se comportent principalement comme du caoutchouc. Aux températures plus élevées, ils deviennent plus raides et ils sont cassants à 46,5°. Ce comportement s'explique par une décroissance de l'humidité de l'air environnant à mesure que la température s'élève. À 26,5°, il y a absorption d'eau en quantité suffisante (27%) pour plastifier la gélatine tandis que la quantité moindre (15%) absorbée à 46,5 est insuffisante pour modifier le comportement vitreux de la gélatine sèche. Ces résultats indiquent que les faibles performances de la gélatine en tant que colle sous des conditions chaudes et humides ne sont pas dues à un comportement déliquescent, celui-ci ne se produisant que par contact direct de la gélatine avec l'eau liquide.

Zusammenfassung

Das Kriechverhalten von Gelatinefilmen wurde bei 100% relativer Feuchtigkeit untersucht. Unter einer gegebenen Last werden die Filme entweder zu einer Gleichgewichtslänge gedehnt oder reißen. Gleichgewichts-Spannungs-Dehnungskurven wurden bei 26,5°, 31,5°, 36,5° und 46,5°C erhalten. Bei 26,5° zeigen Gelatinefilme ein im wesentlichen kautschukartiges Verhalten. Bei höheren Temperaturen werden sie steifer und sind bei 46,5° spröde. Dieses Verhalten wird durch eine Abnahme der Feuchtigkeitsaufnahme aus der umgebenden Atmosphäre bei steigender Temperatur erklärt. Bei 26,5° wird eine zur Weichmachung der Gelatine genügende Wassermenge aufgenommen (27%), während die verringerte absorbierte Menge bei 46,5° (15%) zur Modifizierung des glasartigen Verhaltens der trockenen Gelatine nicht genügt. Die Ergebnisse zeigen, dass das mangelhafte Verhalten von Gelatine als Leim unter heißen und feuchten Bedingungen nicht auf ein Zerfließen zurückzuführen ist, welches nur bei direktem Kontakt von Gelatine mit flüssigem Wasser eintritt.

Received May 2, 1960