

Gelatin Coatings and Tensile Strength of Gelatin Films

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Synopsis

Strips of gelatin film were prepared from three commercial gelatins and tested for tensile strength on an Instron universal tester. Some of the strips were made from plain gelatin and others from gelatin which had been deionized, treated with formaldehyde, chrome alum, or acetic acid. Strips were also prepared at 10 and 55°C. The results showed the greatest deviation for the acetic acid- and heat-treated gelatins. An attempt is made to account for the results.

I. Introduction

The behavior of gelatin coatings in the photographic industry is strongly influenced by physical and chemical properties of gelatin such as molecular weight, viscosity, sol-gel transformation, properties of dried films, swelling, adhesion between layers, etc. As reported by Ward¹ and Pouradier,² gelatin varies in its composition. This variation stems not only from differences in the original collagen but also from changes in composition resulting from conversion of the collagen to gelatin. In all photographic applications these variations may be of sufficient magnitude to cause changes in important photographic product properties related to the gelatin used.

One important property involved in the manufacture and use of photographic materials is the ease of achieving good anchorage between gelatin layers. An example of this is the application of gelatin in the form of a light-sensitive silver halide emulsion to a gelatin coating on a base support. During the first step of the manufacturing process, the initial gelatin layer normally designated subbing must be applied so that it is firmly anchored to the base support. This may be achieved by suitable gelatin-resin balance in the formulation which is applied by standard production coating methods. Following the coating operation in which the gelatin subbing is applied to the base, subsequent gelatin coatings such as the emulsion are applied. These gelatin coatings may be applied immediately or following long periods of storage of the gelatin-subbed roll.

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Natural variations in the gelatin batches available to photographic coaters requires the establishment of definitive parameters for use in selecting commercial gelatin suitable for subbing. Early efforts along these same lines aimed at the correlation of physical properties with gelatin and glue behavior was described by McBain and Hopkins.³ These authors showed the relationship between tensile strength and film performance in adhesive applications. Gelatin was found to be twice as strong as glue, and gelatin films were shown to embrittle when heated excessively. On the basis of their test results, differences in gelatin and gelatin treating materials, including crosslinking agents, as they influence gelatin film properties were detectable. Further studies aimed at the correlation of gelatin properties with film performance were reported by Hughes.⁴ He has also reported the influence of polar groups on orientation.

The film-forming ability of gelatin as a function of solution temperature, concentration, support temperature, and drying temperature has been reviewed by Kotina.⁵ Kotina's results show that the tensile strength of gelatin film is influenced by initial solution concentration owing to its influence on orientation, and drying temperature, owing to its influence on chain configuration, as well as the method of film casting. During the same year in which Kotina's work was reported, further investigations relating the mechanical properties of gelatin films to gelatin structure were reported by Bradbury and Martin.⁶ Their data show a strong correlation between final gel film strength and the temperature at which the gelatin solution is dried. The temperatures used in film preparation were room temperature and 60°C. Greater film strength was always obtained at the lower temperature, and the reason for this increased strength is discussed by the authors. A further review of these results was also given by these authors⁷ subsequent to their initial publication.

The influence of heat on gelatin films subsequent to film formation has been reported by Zaides.⁸ These results are in agreement with the findings of Bradbury and Martin^{6,7} that heating results in contraction of the gelatin molecules. This molecular contraction reduces interchain bonding and crystallinity and gives rise to a reduced tensile strength. Factors other

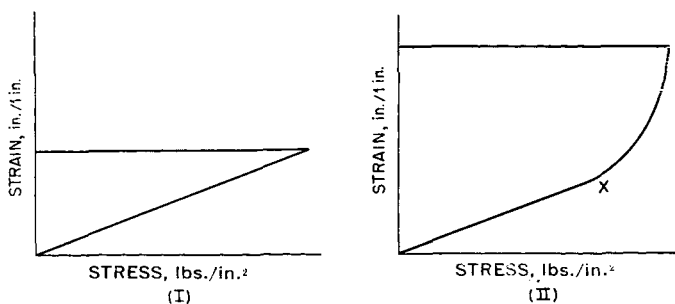


Fig. 1. (I); (II).

than molecular contraction have been shown to be involved through the work of Branswell⁹ and of Eliassof and Eirich.¹⁰

Gelatin investigations in this laboratory have been concerned with the use of gelatin on a variety of supports as a subbing layer or coating for photographic emulsions. We have compared the performance of gel subbing in this application as they relate to a number of variables. These variables include coating formulation, coating method, gel-subbed base storage conditions, gelatin history, and gelatin properties. This paper deals with the role of tensile strength of gelatin films in the performance of gelatin used for subbing photographic base materials.

II. Experimental

Test samples for use on the Instron tensile tester were prepared by the following procedure. A 5-g. portion of gelatin was soaked in 15 ml. of cold water for 30 min. Then 30 ml. of water heated to 75°C. was added to this and the gelatin brought into solution by stirring. While still warm, the solution was poured onto a sheet of Mylar polyester film (du Pont) held in a level position on a vacuum backed perforated metal plate. The gelatin sol was immediately drawn down with a round glass rod to a uniform wet film thickness of about $\frac{3}{16}$ in. After the sol had gelled, the Mylar was carefully removed from the plate, and the gel allowed to dry overnight at room temperature. Gelatin does not adhere to Mylar and can be easily lifted off. The next morning, while the film was still soft, it was removed from the Mylar and cut on a paper cutting board into $5 \times \frac{1}{2}$ in. strips. Even at this stage of the drying, it was sometimes impossible to avoid cracks at the edge of the film on cutting. No samples having edge cracks were used and any area containing air bubbles was avoided. After one or two more days of drying at controlled room temperature, the strips were tested on the Instron universal tester (table model). The test strip was placed vertically between the Instron tester jaws which were spaced 1 in. apart. The crosshead was lowered at 0.1 in./min. and the chart operated at 1 in./min. Full scale of 50 to 100 lb. was used as needed. Figure 1 shows two types of strain versus stress curves typical of those obtained.

The type II curve shows a yield point (labeled x) and is considered more reliable than the type I curve. Only data from type II curves have been used in compiling the results. Type I behavior was probably due to either a flaw in the strip such as an edge crack or brittleness such as found with acetic acid-treated gelatin. Before testing on the Instron, the width and thickness of the strips were measured, the thickness being measured with a micrometer graduated to 0.001 in. The relative humidity of the room was observed at the time of the Instron test. The Instron tester was housed in the area where the samples were dried so that equilibrium was considered to be established.

Three samples of gelatin were studied, the first a deionized gelatin; the second was ordinary photographic gelatin, designated gel A; and the third was a very pure, uniform grade, gel B.

TABLE I
 Tensile Strength of Gelatin Films

Test no.	Description of sample	Number of determinations	Relative humidity testing, %	Tensile strength, psi			Std. deviation
				Maximum	Minimum	Mean	
1	Deionized photo gel	4	25	21,800	19,000	20,125	—
2	“	6	22	22,100	19,700	21,100	1000
1	Std. photo gel A	5	25	19,300	16,300	18,100	1370
2	“	4	22	19,300	17,000	18,600	—
1	Std. photo gel B	1	25	18,900	—	—	—
2	“	5	22	19,100	15,500	17,800	1430
1	Deionized gel + formaldehyde	5	29	18,900	17,200	18,200	670
2	“	5	31	17,700	15,100	16,500	920
1	Std. photo gel A + formaldehyde	4	29	32,000	18,800	22,800	—
2	“	2	31	16,000	14,400	15,200	—
2	Std. photo gel B + formaldehyde	3	29	20,500	19,400	19,900	—
2	“	3	31	18,200	17,600	18,000	—
1	Deionized gel + chrom-alum	4	31	19,600	14,800	17,500	—
1	Std. photo gel A + chrom-alum	5	31	17,400	15,500	16,500	900
1	Std. photo gel B + chrom-alum	4	31	19,100	16,100	17,400	—
1	Deionized photo gel + acetic acid	2	29	5,460	5,100	5,280	—
2	“	3	38	5,720	4,570	5,060	—
1	Std. photo gel A + acetic acid	2	29	4,780	3,270	4,030	—
1	Std. photo gel B + acetic acid	2	29	6,000	4,900	5,450	—
2	“	1	38	3,110	—	—	—
1	Std. photo gel A, 55°C. film drying, no additives	4	30	3,620	940	2,040	—
1	Std. photo gel A, 10°C. film drying, no additives	4	22	23,000	13,400	18,200	—

In addition to preparing strips from plain gelatin, strips were also made from gelatin treated with formaldehyde, chrome alum, and acetic acid. In preparing the formaldehyde strips, the same procedure as above was followed except that 40 ml. rather than 45 ml. of water was used to dissolve the gelatin. Then, 5 ml. of formaldehyde solution (1 ml. 37% HCHO/9 ml. H₂O) was added to the warm sol and the film immediately prepared on Mylar. To prepare the chrome alum strips the original procedure was used, except that the water was again reduced to 40 ml. While the sol was still

warm, 5 ml. of water containing 0.025 g. of chrome alum $[\text{CrK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}]$ in solution was added.

To prepare the acetic acid strips, 5 g. gelatin was soaked in 10 ml. water for $\frac{1}{2}$ hr. Then 30 ml. of glacial acetic acid was added and the mixture was allowed to stand for $1\frac{1}{2}$ hr. The mixture was then heated to 45°C . with stirring to obtain a homogeneous sol. The gelled film was dried at room temperature to minimize brittleness.

Tests were also run on "hot" and "cold" gelatin. To prepare the "hot" gelatin, the usual 10 wt.-% solution was prepared and rolled into film on a sheet of Mylar supported on a glass plate which had been previously warmed. The film was dried in an oven for 3 hr. at 55°C . and immediately tested on the Instron. The strips were very brittle.

To prepare the "cold" gelatin, 5 g. gelatin was soaked in 15 ml. of water at 17°C . for $\frac{1}{2}$ hr. Then 30 ml. of water heated to 40°C . was added. The film was prepared on a sheet of Mylar supported on a glass plate. After gelling at room temperature, it was dried in a refrigerator for a week and tested on the Instron.

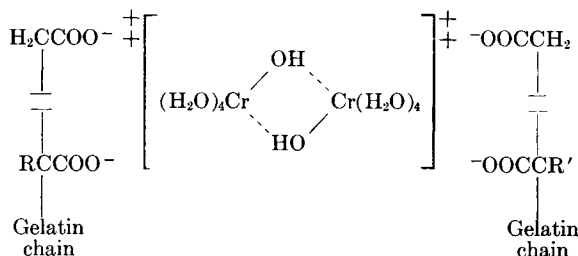
The results of the tests are tabulated in Table I. The largest error resulted from the thickness measurement: possibly a maximum of 8%. However, most of the strips were quite uniform in thickness.

III. Discussion

Of the first three gelatin samples, in Table I, which were water-treated, the deionized gelatin shows the largest and most uniform tensile strength values. This might be attributed to the lower salt concentration in the deionized sample which would possibly allow greater hydrogen bond formation of the $>\text{CO}-\text{HN}<$ type, since it is believed that salts such as CaCl_2 complex with the chains to tie up electron-rich positions on the gelatin chains. Also, it may be said that lower salt concentration enhances molecular symmetry which would impart greater uniformity to any physical properties. Conductivity measurements made by the authors on these samples substantiate a lesser concentration of salts in the deionized sample.

It will be noted that the results for the formaldehyde-treated gelatin do not vary, on the average, from the values for the water-treated standard samples. While this is in agreement with the observations of McBain and Hopkins,³ in the opinion of the authors, this result would not be anticipated. The following may be a possible hypothetical interpretation. The formation of a $>\text{N}-\text{CH}_2-\text{N}<$ bond from reaction of CH_2O with the polypeptide chains destroys at least two hydrogen bonds and perhaps more by spatial blocking; that is, by a restriction on chain configuration or flexibility conducive to hydrogen bond formation. The $\text{C}-\text{N}$ bond strength is approximately 60 kcal./mole and that of a hydrogen bond about 6 kcal./mole. It would then follow that if ten hydrogen bonds were destroyed in the formation of one $-\text{CH}_2-$ crosslink, the tensile strength should remain the same.

It was observed that the water-treated samples of deionized gelatin and the formaldehyde- and chrome alum-treated samples all exhibited rubber-like or plastic flow properties beyond the yield point. This can be attributed to the flexibility of the crosslinks: hydrogen bonds in the deionized sample, and formaldehyde and chromium crosslinks in the others. The chromium-treated samples showed the greatest degree of plastic flow. This would indicate the greater flexibility of the chromium crosslink. The tensile strength, however, was not different from that of the untreated gelatin, indicating that the chromium crosslink, which might be as shown in I, is no stronger than the interchain bonds in plain gelatin.



Extensive plant-scale studies on the behavior of gelatin in photographic applications must be made to determine whether there is a correlation between this behavior and tensile strength. However, the authors are inclined to believe that the deionized gelatin will yield the best and most uniform results in photographic practice.

Only a few tests were made on acetic acid-treated gelatin, since the strips were brittle and cracked easily on cutting. However, the results obtained were uniform, but only about one-third as large as the tensile strengths of untreated gelatin. These lesser values may be attributed to some acetic acid remaining in the film competing with hydrogen bonds for active centers along the chains.¹¹

As for the gelatin films prepared at 55°C., the tensile strengths were considerably reduced. It may be postulated that α -gelatin in which intra-chain bonds predominate was present. It is reasonable to believe that interchain bonds are mainly responsible for tensile strength. These predominate in β -gelatin, which is believed to be the type present in the film prepared in the cold at 10°C. The values found for the "cold" film are in agreement with those of plain gelatin film prepared at room temperature which is below the α - β transition temperature, believed to be about 35°C.

The results obtained for the acetic acid- and heat-treated gelatin would indicate that acetic acid and improper temperature control are both detrimental to gelatin behavior, especially adhesion, in subbing. One reason acetic acid works at all is possibly due to some solvent action on the base coating.

It is the present intention of the authors to extend these investigations by use of precise relative humidity control.

The authors wish to acknowledge the technical assistance rendered in the Keuffel & Esser Laboratories by Mrs. Ursula Mainz and Mr. Daniel Spechler in this work.

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Résumé

Des bandes de film de gélatine ont été préparées à partir de trois gélatines commerciales et ont été essayées du point de vue de leur élasticité sur un appareil "Instron Universal." Certaines de ces bandes ont été réalisées avec de la gélatine ordinaire et d'autres à partir de gélatine préalablement déionisée et traitée avec le formaldéhyde, l'alun de chrome, ou l'acide acétique. Des bandes ont aussi été préparées à 10 et 55°C. Les résultats montrent la plus grande déviation pour l'acide acétique et les gélatines traitées à chaud. Une hypothèse a été émise pour justifier les résultats.

Zusammenfassung

Gelatinefolienstreifen wurden aus drei handelsüblichen Gelatineproben hergestellt und mit einem Instronuniversaltester auf ihre Zugfestigkeit geprüft. Einige Streifen wurden aus gewöhnlicher Gelatine und andere aus deionisierter, formaldehyd-, chromalaun- oder essigsäurebehandelter Gelatine hergestellt. Weiters wurden Streifen bei 10 und 55°C. erzeugt. Die grössten Abweichungen traten bei den essigsäure- und hitzebehandelten Filmen auf. Ein Erklärungsversuch für die Ergebnisse wird gegeben.

Received October 15, 1963