A Study of Stress Development in Aqueous Gelatin Coatings

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ABSTRACT: A cantilever deflection technique was used to monitor stress during the drying of aqueous gelatin coatings. Photographic-grade gelatin was dissolved in deionized water and coated, chilled, and dried. The final average in-plane tensile stress ranged from 0 to 50 MPa. Measured stresses were independent of the coating thickness and initial solution concentration. At low relative humidity (0%) and low drying temperature ($\sim 20^{\circ}$ C), the stress grew with time, reaching a constant average magnitude of 46 MPa. Raising the relative humidity above 0% or raising the temperature above 50°C changed the manner in which stress evolved. Stress rose to a peak value and then relaxed to a lower final value. Humidity affected stress evolution more than did temperature, within the limits of this work. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 553–561, 1999

Key words: gelatin; stress; processing effects; stress relaxation

INTRODUCTION

Gelatin is found in many food, pharmacology, and cosmetic applications, but it is most widely used in photographic films as the dispersive media for optically sensitive silver halide particles.^{1,2} Chemically, gelatin is denatured collagen, the major protein component of connective tissues and bone in mammals. Below $\sim 35^{\circ}$ C, gelatin molecules in water partially renature into their original collagen triple helix structure to form physical crosslinks that lead to a gel. The properties of the gel depend on temperature, molecular weight, gelatin concentration, solution pH, and ionic forces between protein chains.^{1–5} Heated above 35°C, the gelatin undergoes a conformational change from the partially renatured state to a solution of randomly oriented protein chains.²⁻⁴ In photographic film, the emulsion layers also contain organic and inorganic hardeners that chemically crosslink the gelatin molecules, providing additional mechanical support.^{2,6}

The crosslinkable nature, the protective capability, and the swelling characteristics (for chemical processing) make gelatin an ideal media for dispersion of silver halide grains. However, the combination of crosslinking and solvent loss (drying) during film processing leads to significant stress development. Stress in the gelatin binder of photographic films can cause strain in silver halide grains, leading to optical density variations (known as fog) in the unexposed film.⁷ Stress minimization is, therefore, a major component of the film manufacturing process.

In coatings from polymer solutions, large volume changes result as solvent evaporates or as chemical reaction proceeds during processing. As solvent leaves and chemical reaction proceeds, the liquid transforms into an elastic, viscoelastic, or elasto-viscoplastic solid. Stresses develop because a coating is confined to nonequilibrium con-

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figurations due to adhesion to a rigid substrate. Since the coating adheres to the substrate, shrinkage is limited to the thickness direction. The constrained shrinkage in the plane of the substrate leads to an average in-plane tensile stress. In addition, particle additives or impurities, nonuniform drying conditions, and degradation can amplify shrinkage and stress. Thermal stresses can also develop (during heating and cooling) as a result of differences in the thermal expansion coefficients of the coating and substrate.

In addition to their effects on silver halide grains, stresses can cause unwanted curling, cracking, or reticulation.^{6,8–10} To counteract curling, gelatin layers are sometimes placed on both sides of the support material. Stress minimization techniques may also include annealing or plasticizer addition. Drying films more slowly (at a given temperature and relative humidity) also helps to minimize stress, but is not a desired option considering production rate.

The effects of processing variables on the solgel transition and optical properties of gelatin gels have been well documented.^{2-5,10-13} However, less is known about the mechanical properties and stress development in coatings. $^{\bar{8},9,1\bar{4}-18}$ Bradbury and Martin¹⁵ studied the elongation properties of gelatin films prepared under various conditions, showing that the structure of the gelatin (determined by X-ray analysis) changed with processing in direct correlation to differences in yield strength and maximum elongation. Umberger¹⁶ also characterized the curl of gelatin coatings on substrates. A thorough overview of gelatin film properties by Bourdygina and Kozlov¹⁸ gives examples of stress relaxation and some stress measurement, but the review concentrates mainly on temperature effects in previously dried films. In this article, we describe the *in situ* measurement of stress evolution and stress magnitude in aqueous gelatin coatings as they are prepared under various conditions (i.e., relative humidity, drying temperature, concentration, and thickness).

EXPERIMENTAL

Coating Preparation

The gelatin used for this study was a sensitizinggrade gelatin provided by Eastman Chemical Company (Rochester, NY) (lot no. 30-060). Coat-



Figure 1 Schematic of the stress measurement apparatus, ¹⁹ a controlled environment combination draw down coater, chill box, and cantilever stress measurement system.

ing solutions were prepared by dissolving the gelatin in deionized water and stirring at 45°C. Solution pH was ~ 5.4. All coating solutions were 8 wt % gelatin unless otherwise noted. Coatings were prepared in the stress measurement apparatus described below. The solutions were delivered by syringe (at 45°C) onto cantilever substrates (steel feeler-gauge stock with thicknesses between 0.40 and 0.50 mm cut to clamped dimensions of 45 × 6 mm). An automated drawdown coater was used to meter initial thickness at a constant coating speed (~ 0.70 cm/s). Cantilever length-to-width ratios were chosen (on the basis of finite element analysis) so as to avoid significant effects caused by cupping.

To mimic industrial practice, all coatings (unless noted otherwise) were chilled at 5°C prior to drying. Chilling took place in a cooled sleeve incorporated into the stress measurement apparatus (discussed in the next paragraph). Chill time was varied depending on coating thickness. The effectiveness of chilling treatments was tested by physical probing.

Stress Measurement

A controlled environment coating and stress measurement apparatus, based on a cantilever deflection measurement principle, was used to study stress development during drying. A schematic of the device is shown in Figure 1. Deflection was measured with an optical lever and all data were acquired via computer. The specifics of the system can be found elsewhere.¹⁹

The instrument in Figure 1 allows us to calculate an average in-plane stress from the end deflection of the cantilever by:

$$\sigma = \frac{dEt^3}{3cL^2(t+c)(1-\nu)} \tag{1}$$

where *E* and ν are the elastic modulus and Poisson's ratio of the substrate, respectively; *t* and *L* are the thickness and the clamped length of the substrate, respectively; *c* is the coating thickness; and *d* is the end deflection of the cantilever.²⁰ A discussion of the assumptions behind this analysis is found in earlier works.^{19,21,22} It is important to note here that conditions were chosen such that only the elastic properties of the steel substrate (and not the coating properties) are needed to calculate the stress in the coating from the beam deflection.

Humidity was controlled by bubbling nitrogen through water and mixing (in varying amounts) with dry nitrogen in a gas proportioner (Air Products, Allentown, PA #E22-150MM41). Drying temperature was controlled by heating the drying gas with a resistive heating coil before entering the drying chamber and by heating the drying chamber itself with cartridge heaters (Omega Engineering, Inc., Stamford, CT #CIR-1042/120V). All coatings reached thermal equilibrium quickly (before any stress was detected) and were dried isothermally.

RESULTS AND DISCUSSION

We will present the evolution of stress with drying time. The coating stress depends on drying temperature, relative humidity (RH) during drying, and coating history. Figure 2 shows a typical stress evolution curve and drying curve for a gelatin coating dried at 20°C and 0% RH. Initially, very little stress develops because the elastic modulus of the moisture-laden coating is not large enough to support a measurable stress (stress is the product of a modulus and a strain using a simple elastic treatment) and the molecular relaxation rate is high. Likewise, any thermal stress that arises should be small and relaxed quickly. As water leaves (see the drying curve in Fig. 2), the elastic modulus of the coating grows, the molecular relaxation rate slows, and therefore, the coating develops an in-plane tensile stress from its constrained shrinkage. With continued drying, the water loss further increases the shrinkage and the modulus, both of which cause the stress to rise. Eventually, a nearly constant stress is reached when most of the water is removed. No relaxation (i.e., decrease) of the developed stress is observed under these conditions.

The final stress in Figure 2 is approximately 50 MPa, significantly higher than most solvent-cast



Figure 2 Typical stress evolution for a gelatin coating dried at 20°C and 0% RH.

polymer coatings [final stresses in polystyrene coatings (cast in toluene) can typically reach magnitudes of ~ 15 MPa].^{23,24} Similar stress magnitudes were observed by Berry et al.8 and Umberger¹⁶ for gelatin coatings. The high stress can be partially attributed to the high ultimate glass transition temperature (T_g) of pure gelatin (~ 200°C as measured by dynamic mechanical analysis). Croll²⁴ and others²³ have shown that higher T_g polymers develop greater stresses because of larger amounts of post-solidification shrinkage. For example, Croll²⁴ reports the final stresses in polystyrene ($T_g = 100^{\circ}$ C) and poly-isobutylmethacrylate ($T_g = 58^{\circ}$ C) coatings dried at room temperatures are 14.3 and 4.5 MPa, respectively. The continued increase in stress even after 2 h of drying is likely caused by small amounts of moisture leaving the coating.

Though industrial practice dictates chilling gelatin coatings prior to drying, this did not significantly change the final stress magnitude relative to coatings that were simply coated and dried (see Fig. 3). This lack of dependence on chilling indicates that stress is mainly determined by drying. All subsequent data is presented for chilled coatings. Figure 3 also shows that maximum stresses are independent of dried coating thickness within the range of thicknesses studied (9–30 μ m). Finally, stress was independent of initial solution concentration (see Table I).



Figure 3 Final maximum stress observed in gelatin coatings that were chilled prior to drying (open symbols) or simply dried without chilling (closed symbols). Final maximum stresses were independent of dried coating thickness and the chilling step.

These findings agree with what is typically observed in an industrial setting.²⁵

Drying Temperature

To study the effects of drying temperature on stress, coatings were dried in 0% RH at increasing drying temperatures (Fig. 4). Despite faster initial stress development, due to increased drying rate, the final stress was lower in coatings dried at higher temperatures. At high drying temperatures, the stress reaches a peak value and then relaxes. This effect was most pronounced at 0% RH. The rate of stress change with increasing

Table IConcentration Effects on MaximumStress^a

Gelatin (wt %)	Maximum Stress (MPa)
8.0	45.8 + 2.5
10.1	42.5 + 5.2
15.0	48.2 + 4.0
25.0	46.6 + 6.8

 $^{\rm a}$ Higher variances at 10, 15, and 25 wt % due to measurements being made on older instrument with lower resolution.



Figure 4 Stress evolution for gelatin coatings dried at 0% RH and different temperatures.

temperature was not as large for coatings dried at 10% RH (Fig. 5).

Relative Humidity

To study the effect of RH, coatings were dried at room temperature under constant nitrogen flow



Figure 5 Maximum stress versus drying temperature for coatings dried at 0 and 10% RH.



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Figure 6 Stress evolution for gelatin coatings dried at 20°C and different RHs.

 $(\sim 50 \text{ ml/min})$ at increasing RHs (Fig. 6). The rate of stress development slowed and the final stress (after ~ 2 h) decreased as the RH rose. However, in coatings dried in humid gas, the stress evolved differently than in dry gas. These coatings reached a stress maximum and then gradually relaxed over time. Coatings dried at 0% RH showed no signs of relaxing. In fact, stress gradually increased over time. In coatings dried at higher RHs, the decrease in stress indicates the higher rate of stress relaxation for these conditions.

Figure 7 shows the average maximum stress versus RH, where each data point represents the average of at least four separate experiments at that condition. The contour plot in Figure 8 represents how maximum stress varied with both drying temperature and RH.

Processing history can also play a large role in determining the stress behavior of a coating. To study this, coatings were dried at room temperature under various RHs. Once the stress equilibrated, the RH changed. Figure 9 gives an example of the stress behavior for a coating initially dried at 5% RH and then cycled between 0 and 5% RH conditions. The cycling of RH results in a change in the coating stress. This result is different from moisture absorption/desorption isotherms observed for gelatin and other biological materials^{1,2} because the stress never recovers to

Figure 7 Maximum stress versus %RH during drying at 20°C.

the original magnitude measured during initial drying. Vrtis and Farris²⁶ observed similar behavior during swelling experiments with gelatin films.

For a given drying temperature and RH, the final stress in gelatin coatings was found to be



Figure 8 Summary plot of maximum stress dependence on drying temperature and RH for gelatin coatings made with 8 wt % solutions.



Figure 9 Stress relaxation after initial stress development for a coating dried at 20°C and 5% RH, cycled between 5 and 0%.

independent of final dried coating thickness and initial solution concentration. These findings are similar to results obtained for some solvent-cast $polymers^{22,24,27}$ and support the idea that stress in the gelatin coatings mainly depends on the difference between the volume fraction of moisture present at the point of solidification and that present in the final dried coating. For the purposes of this discussion, solidification is defined as the point at which the modulus of the coating is large enough to support a measurable stress. The shrinkage due to drying after solidification (postsolidification shrinkage) depends on this volume fraction difference. The fact that chilling had no affect on stress values also supports the idea that stress is mainly dependent on the difference in water loss after solidification. The same amount of moisture must leave the coatings, under particular drying conditions, whether the coating is chilled or not.

The stress magnitude and evolution rate at any stage in the solidification process are the result of a competition between shrinkage (due to solvent loss and, to a lesser extent, physical crosslinking) and stress relaxation. Both the shrinkage rate and the relaxation rate vary during the drying process. The shrinkage rate will be constant initially and then fall as water is depleted, whereas the stress relaxation rate will decrease continuously as drying removes water from the coating.

At 20°C and 0% RH, the initial shrinkage rate is much larger than the relaxation rate as evidenced by the development of large stresses. The lack of any relaxation over time indicates that relaxation rate is slowed considerably as water is removed. As the drying temperature is raised (keeping the RH constant), the drying rate increases, leading to faster shrinkage and faster stress development. This does not affect the overall amount of shrinkage though, since at 0% RH, most water will leave the coating. However, drying at higher temperatures means that less solvent is present at the point of solidification²⁴ (i.e., less post-solidification shrinkage occurs). The higher temperature also allows the gelatin molecules to relax more quickly in response to a developing stress. In addition, it is likely that coatings dried at temperatures of 40 and 50°C return to a liquid state (from the gelled state established by chilling) and develop stress in a manner similar to an unchilled coating. This change in structure does not impact the trend in the stress data with temperature (Fig. 4), further supporting the importance of water loss to stress.

If the temperature remains constant and the RH is raised, the scenario changes. The driving force for solvent removal (i.e., the concentration gradient between the coating and the surrounding atmosphere) is reduced, leading to a slower rate of stress development and a longer time period over which the gelatin network can relax stresses. The amount of moisture in the coating is also larger, hence less shrinkage and stress. Moisture in the coating will also act as a plasticizer, decreasing the modulus (see Fig. 10) and allowing faster molecular relaxation in response to a developing stress.

Simple, elastic interpretations treat stress as a product of the modulus and strain. As discussed above, the strain results mainly from shrinkage after solidification. The amount of post-solidification shrinkage decreases as the drying temperature and/or RH increase. Modulus decreases with RH (Fig. 10) due to the plasticizing effect of water and should be lower at higher temperatures. An additional factor expected to impact modulus and perhaps stress development is crystallinity. In general, crystallinity enhances a polymer's modulus²⁸; however, the results are less clear for gelatin. Bradbury and Martin¹⁵ show that more crystalline gelatin has a lower modulus than a less crystalline gelatin sample when measurements are taken at 45% RH, but the effect of crystallinity is negligible when measurements



Figure 10 Load versus percent strain for gelatin films tested at various RHs. Data was taken on a Perkin-Elmer DMA 7e using the fiber tensile fixture at 20°C and a loading rate of 100 mN/min.

were taken at 65% RH. Kozlov and Burdygina¹⁴ report a lower modulus (measured at 65% RH) for a more crystalline gelatin. One factor which may account for this deviation from expected behavior is that the equilibrium water content of crystalline gelatin can be higher than the equilibrium content of amorphous gelatin.^{1,2} In an attempt to understand the effect of film structure on stress, X-ray diffraction was performed to determine the crystalline nature of the coatings used here for stress measurements. A Siemann's D500 wideangle diffractometer was used in glancing angle mode to examine the coatings while still adhered to the steel cantilevers. The spacings of interest are 2.85, 4.5, and 11 Å.^{2,3,15,29} No peaks were observed for a spacing of 2.85 Å, but peaks were seen that coincided with the larger spacings (Figs. 11 and 12).

Coatings dried at low temperature and any humidity showed distinct crystalline peaks on top of a wide amorphous hump. Raising the drying temperature above the gel temperature ($\sim 35^{\circ}$ C) and drying at any humidity decreased the crystallinity. The loss of crystallinity for coatings dried at high temperature is consistent with the results of Kozlov and Burdygina¹⁴ and Bradbury and Martin.¹⁵ The final stress in the more crystalline coatings (prepared at lower drying temper-



Figure 11 Glancing angle X-ray data for gelatin dried at 20°C and different RHs.



Figure 12 Glancing angle X-ray data comparing the signals from coatings dried at 0% RH and different temperatures.

atures) is higher than the less crystalline coatings (prepared at higher drying temperatures); this contrast is likely due to the differences in postsolidification shrinkage and stress relaxation rate, but perhaps also compounded by a higher modulus in the less crystalline coatings. Crystallinity changes with changing RH are more difficult to quantify (see Fig. 11); therefore, no attempt is made here to correlate stress and crystallinity in this case.

The coating stress evolution can be further changed by cycling between different relative humidity conditions. In Figure 8, a coating was dried at 5% RH and the stress equilibrated to a value of 37 MPa. Upon decreasing the RH to 0%, stress rapidly increased and reached a value of 46 MPa. After increasing the RH back to the original level (5%), the stress equilibrated at a value about smaller than that observed after initial drying. This result suggests that the initial RH decrease (and subsequent stress increase) led to an irreversible change in coating structure so that reintroducing moisture resulted in a lower stress than expected on the basis of the initial drying. Comparing these results with theoretical modeling of stress development in elasto-viscoplastic coatings,³⁰ the change in structure may be explained in terms of yielding and a change in the stressfree state of the coating.^{30,31} When the coating on a substrate yields as it develops stress, it does not undergo a permanent shape change, but rather, its equilibrium stress-free state changes. Reintroducing moisture into the coating after yielding will result in a different state of stress. These ideas and the modeling results are the subject of another article.³⁰

Figure 13 demonstrates this phenomena for a coating cycled between 40 and 0% RH. Note the slight stress recovery at high humidities in Figure 13. The behavior is similar to that observed during stress relaxation experiments using magnesium,³² copper, and aluminum³³ at high temperatures. In these metals, stress recovery is linked to back stresses resulting from dislocation motion. The thixotropic nature of some biological materials³⁴ may also explain the stress recovery. During yielding, the structure of the coating is partially broken down. Upon release of stress (by increasing RH), the coating can partially restructure. The fact that this behavior is not seen at lower RHs (as in Fig. 8) suggests that a critical moisture content exists, below which gelatin molecules are not able to move and restructure.



Figure 13 Stress relaxation after initial stress development for a coating dried at 20°C and 40% RH, cycled between 40 and 0%.

CONCLUSIONS

An apparatus, based on the cantilever deflection technique, was used to monitor average in-plane tensile stress in aqueous gelatin coatings as they dried under varying conditions. The final stresses were independent of chilling, final coating thickness, and initial solution concentration. Drving temperature and RH had a large effect on stress evolution and final observed magnitudes. Despite faster stress development, coatings dried at higher temperatures reached smaller final stress magnitudes relative to coatings dried at room temperature because of their lower post-solidification shrinkage and faster stress relaxation rates. Less shrinkage and the plasticizing effect of moisture caused smaller stresses in coatings dried at high RHs.

The present results can be useful in the design of improved processing schedules for gelatinbased coatings. Drying quickly at increased temperatures can alleviate some stress in the final product. Likewise drying slower at low temperature and high RH will also lead to lower stresses. In most systems, plasticizers (e.g., ethylene glycol) and other agents (e.g., mucochloric acid, formaldehyde) are added to relieve stresses and create a more chemically bonded system. The effect such additives have on stress in gelatin and other coatings is the topic of our current work. We acknowledge support from the Center for Interfacial Engineering, an NSF-sponsored Engineering Research Center at the University of Minnesota, through its Coating Process Fundamentals Program, and from DuPont through a Young Professor's Grant. We also acknowledge B. Bell, E. Cohen, E. Garcia, and L. E. Scriven for many helpful discussions. Finally, we acknowledge P. Petersen, J. Kern, and W. Gruhlke for their technical assistance and advice.

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