

A Rheological Method for Measuring Skin Formation in a Latex and Application to a Coating Problem

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Abstract

A latex dispersion containing plasticizer and diluted with water and alcohol was applied by use of a direct flexographic process to a moving web. The application was accomplished by use of a rubber deposit roll and a chrome anilox cylinder with two stainless steel doctor blades, one trailing and the other reverse angle. At moderate coating speeds, aggregates of latex particles were observed coming off the reverse angle doctor blade, resulting in coating defects. Conventional rotational and oscillatory rheology, as well as surface tension, pH and other fluid characteristics, could not identify the source of the problem.

A rheological method was developed to measure the skin-forming tendency of a latex. The latex fills a large gap between parallel plates on a Rheometrics RFS2 rheometer, with the free surface exposed to the air. A small amplitude strain oscillation is applied to the fluid and the storage modulus (G') and $\tan \delta$ are measured as a function of time and temperature. An increase in G' is observed as a skin forms on the latex. This technique was used to determine the effect of temperature, latex concentration, alcohol content and plasticizer on skin formation. This enabled the optimization of both fluid and process parameters, resulting in extended defect free coating times. The technique is also used to monitor latex raw materials and can be applied to a variety of latex formulations and performance problems.

Introduction

As a latex loses water by evaporation, the colloidal polymer particles coalesce into a continuous polymeric film, beginning on the surface of the dispersion. The rate of formation of this "skin" and the subsequent drying of the film is of considerable importance in coating operations and other processes. There are three stages in the film formation and drying mechanism:¹⁻³ (1) an initial constant rate stage during which water evaporation increases the percent solids of the latex to the point where repulsive energy between the particles is overcome and flocculation occurs; (2) an intermediate stage in which the particles distort and compact, causing a decrease in the air-water interfacial area and a subsequent decrease in the water loss rate; (3) a final stage

where the remaining water slowly escapes by diffusion through capillary channels or through the polymer itself.

It is important to be able to measure the speed and progress of this process in order to optimize both latex formulations and drying conditions for specific applications. A number of methods have been reported in the literature.^{3,4} These include gravimetry,^{2,3} ultrasonic impedance,⁵ resistivity,⁶ light transmission,⁷ thermogravimetry and differential scanning calorimetry.^{8,9} The rheological method reported here is based on the fact that the stiffness and elasticity of the polymer film increases significantly throughout the drying process. Huang and Sen¹⁰ have published a similar rheological method based on a couette measurement geometry, where the skin forms in the horizontal meniscus of the partially filled gap between concentric cylinders.

The purpose of this work was to develop a measurement that would link a fluid property to an observed coating defect and solve a problem. The intent was not to rigorously study the phenomenon of film formation in latices, although the technique is well suited to that endeavor and may be continued by other investigators.

Experimental

The instrument used in this work is a Rheometrics RFS2 controlled strain rheometer equipped with a 50mm parallel plate measuring system. The upper plate is made of titanium and is attached to the torque transducer. A stainless steel lower plate is temperature controlled and is driven by an analog motor.

Operating parameters and conditions

The sample (4ml volume) is placed on the lower plate and the upper plate is lowered to a 2mm gap. Any excess material is carefully wiped from the edge of the plates such that the outside surface of the sample defines a flat cylinder with the edges of the plates. This must be done quickly and the test is started immediately, so as to minimize variability in the measurement. A small amplitude strain (0.5%) at a moderate frequency (10Hz or 62.8rad/sec) is applied to the sample by means of the bottom plate and the resultant stress and phase angle difference are measured on the top plate. This stress is separated into its viscous and elastic

components and is expressed as the storage and loss moduli. The storage or elastic modulus (G') describes the material's ability to store energy elastically and is the ratio of the elastic stress to strain. The loss or viscous modulus (G'') defines the material's ability to dissipate stress through resistance to flow and is the ratio of the viscous stress to strain. The complex modulus, G^* , is the vector sum of G' and G'' . Tan delta (the tangent of the phase angle, delta) is the ratio of the loss to storage moduli (G''/G') and describes the nature of the dissipation of energy for the system. Figure 1 shows a plot of these parameters as a function of time for a measurement that clearly shows all three stages of film formation. Since the three modulus curves have a similar shape and the elastic modulus, G' , shows the most change and reflects the elasticity of the film, only this parameter is plotted in subsequent graphs.

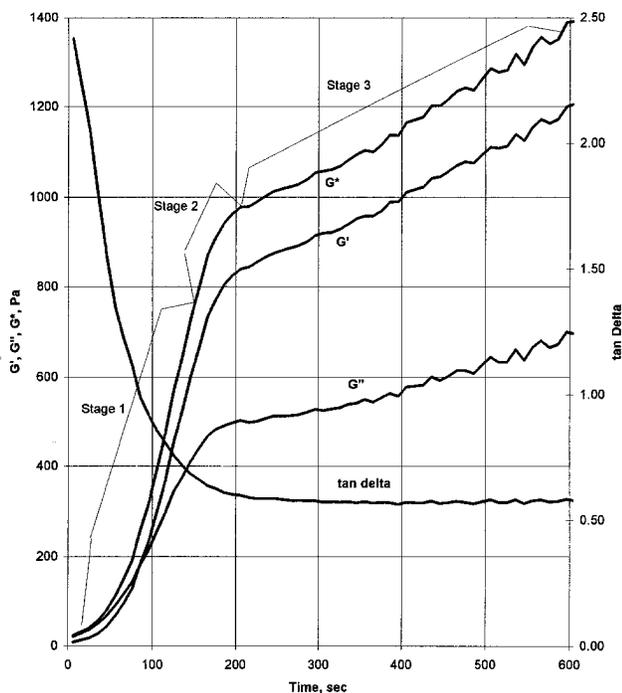


Figure 1. Rheometer response vs time during skin formation. Complex modulus, G^* ; elastic modulus, G' ; viscous modulus, G'' ; tan delta, G''/G' .

As water leaves the edge of the sample, the latex particles begin to coalesce and form a skin on the surface. Since this skin is forming at the edge of the plate where there is the most influence on the measured stress (longest lever arm), and because the skin is much stiffer and more elastic than the underlying liquid, the contribution of the bulk of the sample to the measured response is negligible. Thus the measured elasticity change is a direct measure of skin formation of the latex.

From the above argument, it is also evident that the sensitivity of the measurement can be enhanced by increasing the plate diameter and gap. Although the optimal

experimental conditions depend on the particular latex being studied, we have found that satisfactory results can be achieved over a range of applied strain amplitudes and frequencies, as long as the strain is kept low so as not to disturb the skin as it is forming. The response is influenced by factors that would change the rate of evaporation of water from the latex surface, such as humidity, air temperature and air currents, and appropriate controls must be implemented.

Results and Discussion

Use in solving a coating problem

The coating fluid consisted of a polyvinyl acetate latex dispersed in a water/isopropanol continuous phase. The solids content covered the range of 17.5 to 27 wt % and the water/alcohol weight ratio varied from 60/40 to 80/20. Initially, all of the fluids contained 1.4 wt% of a dibutyl phthalate plasticizer. This fluid was to be applied to a moving web by the two roll flexographic method. The coater consisted of a heated central impression cylinder and a two roll coating station, which employed a fluid chamber with both trailing and reverse angle doctor blades. The coating fluid was pumped through the closed chamber, metered onto an anilox cylinder by the doctor blades, transferred onto the rubber deposit roll and finally to the moving web. After several minutes at high coating speeds, lumps of white material identified as polyvinyl acetate polymer appeared under the stainless steel reverse angle doctor blade. These lumps would transfer to the web or cause streaks, resulting in a defective coating.

The initial suspicion was that the fluids were rheologically unstable and were undergoing shear induced coagulation, since the reverse angle blade configuration results in greater flow disturbance and possibly higher shear rates in the fluid. Rotational flow curves to 20,000/sec shear rates showed no evidence of instability in the fluids. Conventional oscillatory rheometry did not show viscoelastic differences significant enough to cause the problem and surface tension measurements were, likewise, non-predictive. We then began to develop a way to measure film formation or "skinning", the results of which are reported here. The following factors were investigated with this technique: solids content, liquid phase composition, plasticizer concentration, and temperature.

The rate of skin formation was found to correlate well with the observed defect. Those coating fluids which showed a rapid increase in G' per unit time at 35 degrees C also produced the polymer clumps that resulted in the coating defect. Fluids which did not readily form a skin could be coated at higher speeds for longer periods of time. By removing the plasticizer and adjusting the fluid composition to minimize skin formation, it was possible to coat at 500ft/min for five hours without any incidence of streaking or material build-up under the doctor blade.

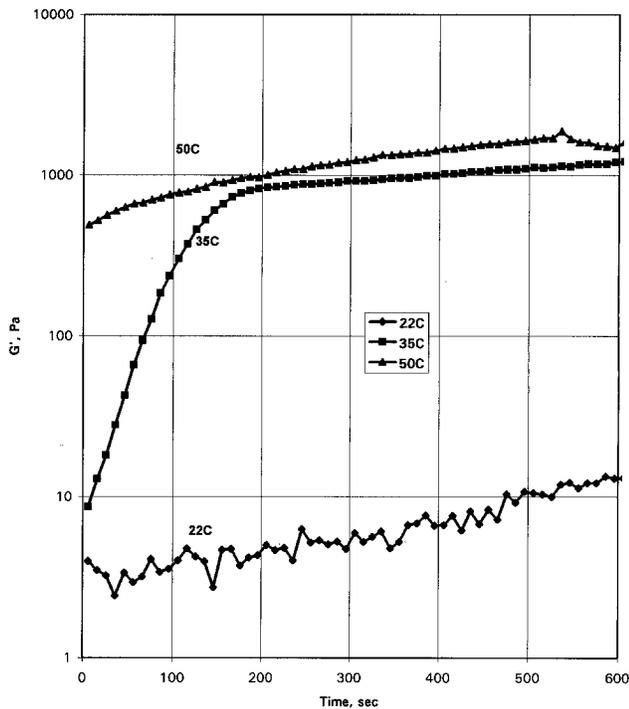


Figure 2. Effect of temperature on skinning rate of a polyvinyl acetate latex.

Effect of temperature

Reducing the web speed from 500 to 350 ft/min reduced the intensity and frequency of the defect. When the stainless steel blade was replaced with a low friction carbon fiber composite material or an HDPE blade, the frequency of the defect was also reduced. At 350 ft/min the coating was free of the defect with these blades. This led to the hypothesis that increased temperature played a role in causing the defect. This was speculation since a reliable method of measuring the temperature at the source point was not available.

Figure 2 shows a plot of $\log G'$ vs time at 22, 35 and 50 degrees C for a 28.6% solids polyvinyl acetate latex. At 22°C, the response remains flat for several minutes then begins to increase slowly. The signal is noisy because the fluid is thin and the measured stress is low. At 35°C, a skin begins to form almost immediately and the elastic modulus increases at a constant rate of about 6Pa/s up to 170 seconds. At this point, the rate of film formation slows substantially and transitions to another linear region where the rate of increase is about 0.85Pa/s. This corresponds to the three stage drying process proposed by Vanderhoff, et.al.³ and described briefly in the introduction. The curve at 50°C begins much higher than the other two and increases slowly. This indicates that a skin had formed on the exposed surface of the fluid while the gap was being set and before the measurement was started. This is an operational difficulty at elevated temperatures. It is interesting to note that, once the film is formed, the rate of increase in stiffness at 50°C is only slightly higher than at 35°C. Most of the

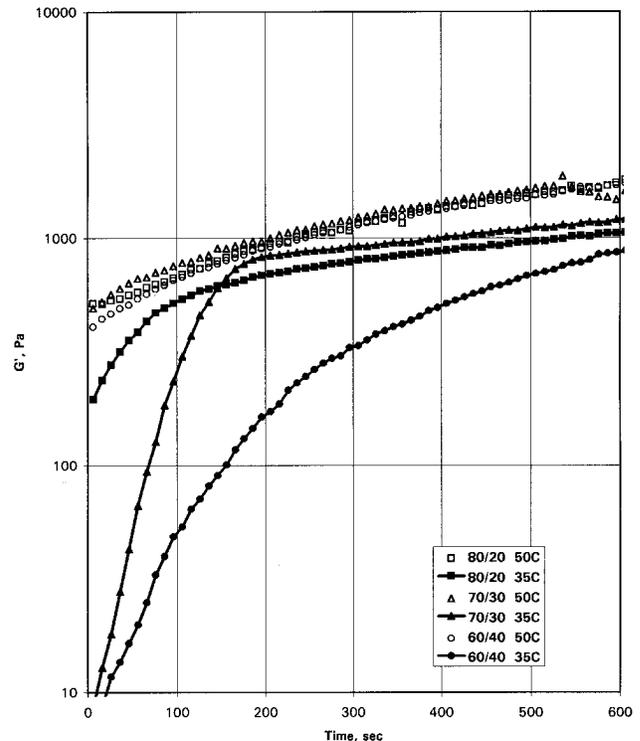


Figure 3. Effect of water/isopropanol ratio on skinning rate of a 28.8% solids latex at 35 and 50 degrees C.

subsequent measurements were made at 35°C because this temperature correlated best with the observed coating defect, gave a wide ranging response with fluid changes, and was the easiest operationally.

Effect of solvent composition and solids content

The weight ratio of water/isopropanol in the continuous phase was varied between 60/40 and 80/20. The effect of solvent composition on skinning rate of a 28.8% solids latex is shown in Figure 3 at both 35 and 50 degrees C. Lower isopropanol content results in a more rapid film formation at 35°C, while at 50°C, there is little effect. The alcohol in this case may be retarding film formation by stabilizing the emulsion or by inhibiting the coalescence of the latex particles. The final film stiffnesses are similar with all three solvent ratios.

Another example of the effect of water/alcohol ratio is shown in Figure 4. The latices in this case are at 22.8% solids content. A similar trend of less isopropanol resulting in more rapid skin formation is seen. This figure also demonstrates the strong relationship between solids content and skinning rate. By comparing the 70/30 solvent curves at 22.8 and 28.8% solids, it is evident that a skin forms much faster at higher solids levels. This is as expected, since at higher solids levels, the latex particles are closer together and less liquid must be lost before the particles make contact and coagulate."

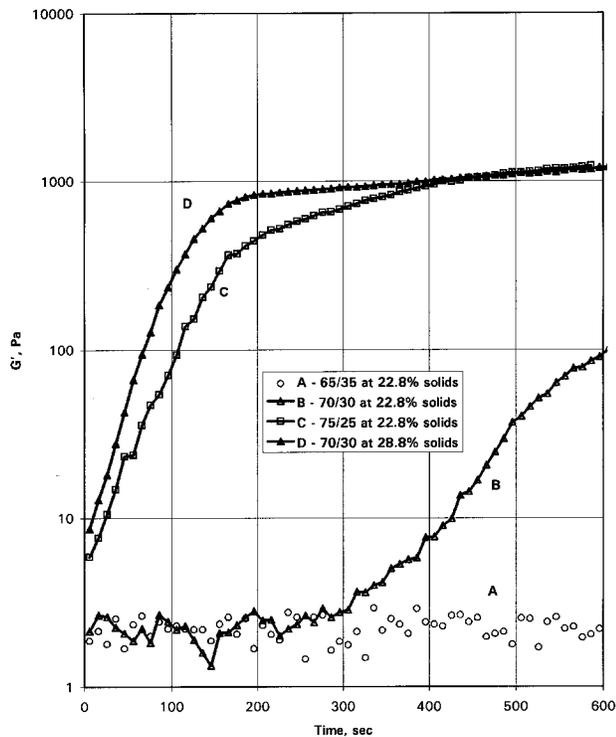


Figure 4. Effect of water/isopropanol ratio on skinning rate of a 22.8% solids latex at 35 degrees C. Curve B (70/30 at 22.8%) and curve D (70/30 at 28.8%) show the effect of solids content on skinning rate.

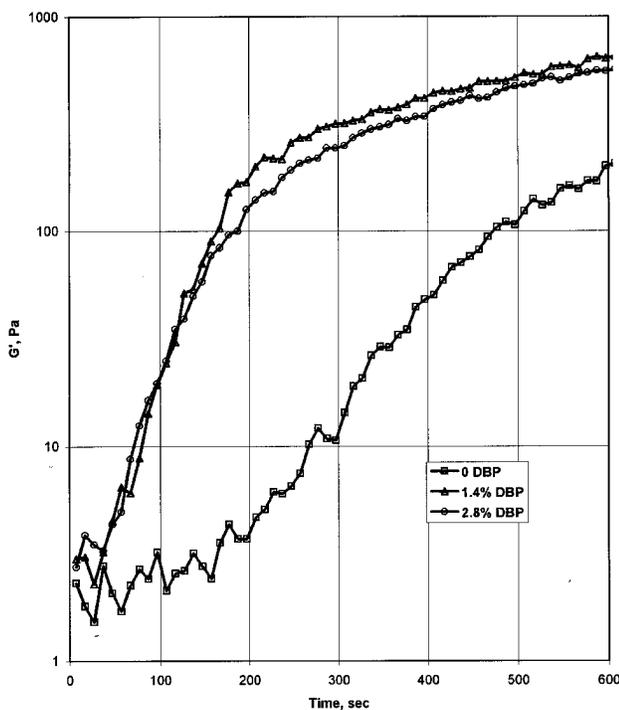


Figure 5: Effect of plasticizer concentration on skinning rate.

Effect of plasticizer

Dibutyl phthalate (DBP) was originally present in the coating fluids at 1.4wt % as a plasticizer for the dry polyvinyl acetate film. Figure 5 shows the effect of varying the plasticizer level on the skinning rate. The beginning of skin formation is delayed by about 200 seconds when the plasticizer is removed and the rate of formation is slower. There is no difference in the rate of film formation when the DBP concentration is doubled. Plasticizers can increase the setting speed of PVAc latices by softening the polymer particles and hastening their coalescence.¹¹ Elimination of the plasticizer also reduced the incidence of the coating defect.

Commercial latex glues

The skin-forming properties of a series of commercial polyvinyl acetate white glues and aliphatic wood glues were tested as a further evaluation of the applicability of this technique. The rate of skin formation at 22 degrees C varied widely, as shown in Figure 6. This properly would influence the open working time and the setting time of these materials in normal use. In general, the aliphatic wood glues formed films faster than the white glues, and the rate of skin formation for the white glues followed their solids content.

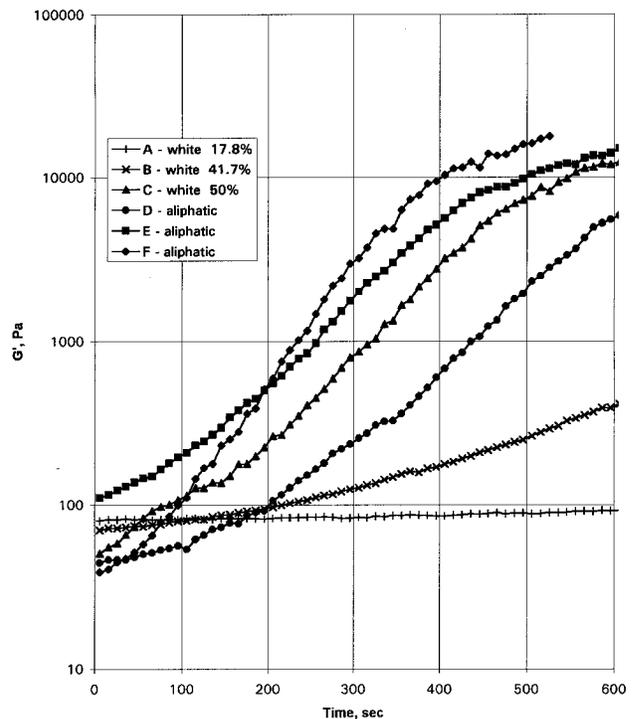


Figure 6. Skinning rate of commercial latex glues. Curves A-C are white PVAc glues and curves D-F are aliphatic wood glues.

Styrene-Butadiene latex

The skin measurement technique was also tested on a commercial styrene-butadiene type latex. Latex "A" has a nominal particle size of 153nm and is 50.4 wt% solids,

while latex "B" has a particle size of 210nm and is 52.0% solids. The two samples were tested at 22 degrees C, using the same conditions as for the polyvinyl acetate latices described above. The results, as shown in Figure 7, indicate that the smaller particle size material forms a skin at nearly twice the rate as the larger latex. This may be related to the fact that smaller particles are more resistant to dense packing¹² and begin to coalesce at a lower volume concentration. This example shows that the technique can be used to measure the film formation of different types of latices.

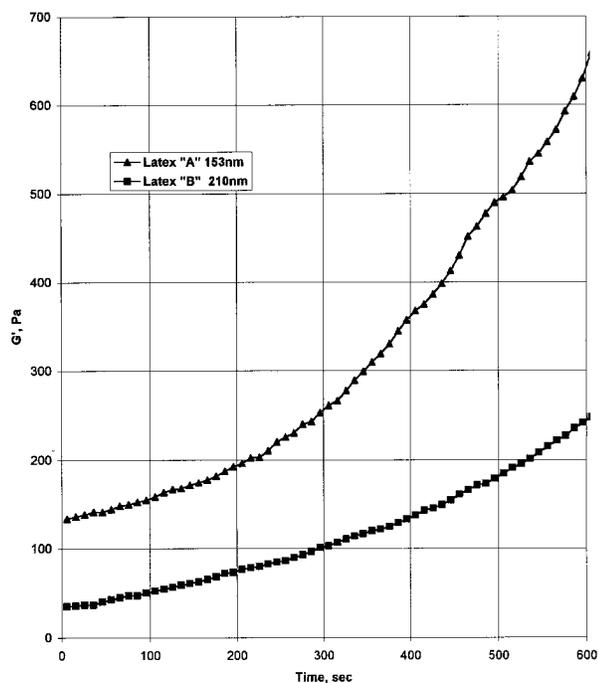


Figure 7. Skinning of styrene - butadiene latex. Sample A is 153nm particle size and sample B is 210nm.

Conclusions

A rheological method was developed to measure the formation of a film or skin on latex dispersions. This method was used to study the effect of temperature, latex concentration, alcohol content and plasticizer on skin formation in a polyvinyl acetate latex. This information was used to optimize both fluid and process parameters in a coating operation, resulting in the elimination of a coating defect and extended high speed coating times. The technique can also be used to study the mechanism of film formation, to characterize latex raw materials, and to optimize latex performance in a variety of applications.

Acknowledgments

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