

Dielectric and Thermal Analysis of the Film Formation of a Polymer Latex

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INTRODUCTION

Latex Emulsions and Floor Polish

Because of its ease of application and environmental friendliness, the polymer latex has become a popular alternative to the more traditional solvent-based coatings. The primary feature of a water-based latex is that the polymer is not dissolved in the water, but is instead a colloidal dispersion (or 'emulsion') of polymer particles in an aqueous medium. In this paper a latex formulation, which is representative of floor polish, was studied.

Floor polish is used as a protective coating over wood, tile, or concrete floors. It provides a barrier against water and soil, and extends the life of a floor. Early floor polishes were made of melted beeswax and later with harder waxes dissolved in solvents. Modern floor polishes still have a wax component in their formulation. However, there is now also a large polymer component (often the major component) that is in the form of a water-based emulsion or latex.¹ Because of the variety of applications, there are many different floor polish formulations with varying amounts of polymer and wax. The floor polish chosen for this study is a sealer, containing no wax component. Sealers are used primarily as an undercoat that seals the pores in the flooring surface. When the sealer dries, it forms a relatively hard amorphous film that is impervious to water and many other solvents.

For a latex emulsion to form a continuous film, the latex particles must be soft enough to deform and possibly interdiffuse. The glass transition temperature is a particularly useful parameter for assessing the hardness of the latex polymer. The paint and floor polish industry uses a more empirical parameter, analogous to the glass transition temperature, which is called the minimum film formation temperature (MFT).² A common way to manipulate this MFT (so that it is low enough to allow latex particle deformation without lowering the final film hardness) is to decrease the latex T_g with a coalescing solvent. The coalescent acts as a temporary plasticizer. After the film has dried (water evaporated), the coalescing solvent presumably evaporates over time and the film hardens. This is an important factor in the coa-

The real-time kinetics of film formation of a floor polish polymer latex coating has been investigated using dielectric measurements of the ionic conductance. Varying levels of ambient humidity were applied and had a dramatic effect on the drying rate, drying mechanism, and final film thermal and mechanical properties. At humidities below 30%, the drying curves followed a power law time decay with two distinguishable regions. The first region showed a drying rate dependence on the order of t^{-10} , while the second region showed a slower drying rate with a time dependence on the order of t^{-2} . At higher humidities, the curves become more complex. At the highest humidities, film cracking was observed. Besides dielectric analysis, thermal analysis experiments were conducted that indicated film formation continues over very long times (months). The data also indicate that considerable residual stress remains in the dried films even after these long times.

lescence of the film and should be considered when measuring the coalescence.

A second factor, common in floor polish formulations, is the use of zinc complexes that induce ionic crosslinks to form in the latex film as it dries.³ Though the exact chemical nature of the crosslink formed is still in question, the macroscopic effect is clearly a hardening of the final film. Another interesting aspect of these ionic crosslinks is that they can be selectively removed with alkaline strippers such as ammonia, which complex with the zinc. The crosslinking adds another variable to the understanding of film formation in a real-world latex

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Table 1—List of Components Used in Model Floor Polish Formulation, UDL01, Before and After Drying

Component	Amount in Latex Mixture	Amount of Non-Volatiles	Estimated Amount in Dried Film
Polymer (30 Styrene/17 MMA/40 IBMA/13 MMA)	54%	33%	84%
Resin (32 Styrene/38 α -Methyl Styrene/30 AA)	5%	20%	5%
Deionized water & NH ₄ OH (5%)	26%	5%	6%
Carbitol	7%		
Zonyl FSJ fluorocarbon	6%	1%	<1%
Zinc ammonium carbonate solution (15% ZnO)	1%	15%	<1%
Tributoxyethyl phosphate	1%	100%	5%

formulation such as floor polish. Also, when used in real applications, floor polish latexes have other additives that affect their coalescence and their final properties. These additional ingredients must be considered when measuring the coalescence of the film.

Latex Coalescence

When the latex emulsion is applied to a surface, the water evaporates and the latex particles pack together and coalesce. This coalescence may result in a continuous film. However, if the conditions are not favorable, the latex particles do not coalesce properly. Instead they form a powder or a very weak film that cracks. In order for a latex emulsion to be useful as a coating, it must coalesce into a continuous film. An understanding of the mechanism of the coalescence is of practical importance, since the final properties of a coalesced film will determine its performance as a useful polish.

Though there is still some discussion about the details of latex coalescence, the main features are generally agreed upon. There are three main stages in the drying of a latex.⁴⁻¹⁴ The first stage, known as the induction stage, occurs when the percentage of water is still high enough so the latex particles are, at best, in point contact with each other and are not yet deformed. Eventually the film formation moves into the second stage in which the latex spheres begin to deform into polygonal units rather than perfect spheres. In this stage, the latex spheres are driven together by the evaporation of interstitial water. The third and final stage occurs when the deformation of the latex particles reaches a plateau and the film undergoes coalescence, which is presumably caused by interdiffusion of polymer chains.⁵ However, depending on the type of surfactant molecule used, a membrane structure has been known to form that prevents interdiffusion of the interior latex polymer chains.^{6,7}

The second and final stages have the most direct effect on the final properties of the film, since they are where the particle fusion occurs. There have been many theories proposed to describe what is happening during this fusion, but there has not been general agreement. Dillon, Matheson, & Bradford⁸ first proposed a dry-sintering model where the particle deformation and fusion occurs after water evaporation. However, most of the theories are based on the wet-sintering concept first proposed by Brown,⁴ where capillary forces cause the particle deformation. As the interstitial water evapo-

rates, an increasing capillary pressure forces the particles closer together until the stabilizing layers (i.e., the charged layers surrounding the latex particles) rupture and there is polymer-polymer contact. At the same time a surface tension (actually a polymer/water interfacial tension) further increases the pressure on the particles and causes further flow and fusion of the polymer. An interesting twist to these ideas is given in a theory by Sheetz,⁹ who proposes that the capillary forces act on the surface particles first, thus forming an outer layer through which water must diffuse. Eckersley & Rudin¹⁴ more recently proposed a theory that describes some of the concepts of these previous theories in terms of a viscoelastic model where both capillary and interfacial tension forces are considered. With their model, they estimated the amount of deformation of the latex particles after drying and used scanning electron microscopy to verify their calculations. Though their model may be useful for understanding a simple latex formulation, unfortunately most practical applications of latexes include coalescents that complicate the drying mechanisms. For example, Hoy¹⁵ has shown that the coalescent may migrate from the water to the latex as water evaporates from the system.

Measurements Techniques

Of course, a theory is only as good as the experimental evidence that supports it. There are a number of different techniques that have been used to characterize latex film formation in real time. An early example is the mechanical impedance measurement of Myers & Knauss.¹³ In their experiments they measured a sample's response to a mechanical pulse as a function of drying time. In a series of papers, Anwari et al.¹⁶ used optical techniques to measure film formation. In particular, they measured the reflectance using a spectrophotometer and studied the effect of such things as particle size, coalescent solvent, and pigment. Sheetz,⁹ and more recently Dobler et al.,¹⁷ measured the solids content of a drying film by measuring the weight loss as water evaporated.

In addition, many techniques have been used to characterize the coalescence or third stage of film formation. As mentioned previously, scanning electron microscopy (SEM) has been used to measure the degree of coalescence by measuring the amount of contact between the fused particles.¹⁴ Transmission electron microscopy (TEM) and small angle neutron scattering have also been

used.^{6,7} Atomic force microscopy has been used to measure the surface relief of latex films.¹⁰ Fluorescence has been used to study interdiffusion.^{11,12}

The primary technique used in the present study, dielectric analysis, has been used previously by Dissado et al.¹⁸ In their work, they used a simple two-electrode geometry that was in a coplanar arrangement on a glass substrate. Their data indicated a power law time decay in the conductance and hinted that there were multiple stages of drying. The present study strives to improve on their work by using a more sensitive electrode geometry and by using a more robust data analysis that eliminates the frequency dependence of the data and extends the range of the measurement. The purpose of this research is to provide insight into the physical mechanisms of latex film formation and the effect of ambient humidity. The model system studied in this work is not a simple latex emulsion but includes some ingredients that complicate the system. These ingredients not only affect the final characteristics of the film but also make the analysis of the film formation mechanisms more difficult. These ingredients were added, however, because they are representative of those used in commercial floor polish systems. It is hoped that the experiments described in this work will provide some foundation for further study of latex film formation with dielectric techniques.

EXPERIMENTAL

Material Formulation

The material used in this study, referred to as UDL01, is a typical formulation for a floor polish used as a sealer, and there was no low-molecular-weight wax component. Table 1 lists the ingredients used.

The main ingredient is the emulsion-based polymer. It contains 30% styrene, 17% methyl methacrylate (MMA), 40% isobutyl methacrylate (IBMA), and 13% methacrylic acid (MAA). There is also water, ammonium hydroxide, and an anionic surfactant necessary to stabilize the latex emulsion. In the dried film, the polymer is by far the dominant ingredient and is close to 85% of the content of the dried film. Differential scanning calorimetry (DSC) scans for the pure polymer component, as dried from the emulsion, are shown in Figure 1. This sample had none of the other additives. The first scan shows multiple glass transitions with inflection point temperatures at 29°, 101°, and 120°C. According to the DSC data, the beginning polymer was already multiphase. The sample in this scan was heated to 150°C then cooled back down and ramped again. The subsequent scan labeled as second shows the first T_g again, but the second and third T_g values have merged into one transition at 111°C. This is likely caused by the increased diffusional mobility and miscibility of these two phases above their glass transitions. Subsequent quenching then locks in the resulting phase behavior. These data were recorded at a heating rate of 20°C/min with a 16.8 mg sample.

Besides the main polymer, there is also an ingredient referred to as resin. The resin is actually a low molecular

weight polymer (<8000) that is used to improve leveling, gloss, and adhesion. The resin is soluble in an aqueous alkali medium and functions by increasing the viscosity of the emulsion. The resin used in the sample formulation contains 32% styrene, 38% α -methyl styrene, and 30% acrylic acid.

The Zonyl FSJ fluorocarbon is used as a surface-active agent. Anionic and non-ionic perfluorinated chemicals are often used to help leveling by lowering interfacial tension at the interface between the floor polish and substrate. The one used in this sample contains 40% mono- and bisfluoralkyl phosphates complexed with an aliphatic quaternary methosulfate. The fluorocarbon formulation also contains 15% isopropyl alcohol with the remainder being water.

The zinc ammonium carbonate (ZAC) is used to improve resistance of the final film to detergents and to enhance durability. Divalent metal ions such as zinc are used to form ionic crosslinks in the film as it dries (after evaporation of water and ammonia). In this formulation we used a ZAC solution containing 35% ZAC and 65% water. The existence of these ionic crosslinks has an impact on the final film properties. In addition, the formation of the crosslinks should affect ion mobility, and, therefore, the ionic conductivity measured during film drying. Thus it is an important consideration in understanding the sequence of events during coalescence of the floor polish film.

The final set of ingredients includes tributoxyethyl phosphate, a simple plasticizer, and Carbitol, a coalescent. Tributoxyethyl phosphate has a freezing point of -94°C and a boiling point of 222°C. It effectively lowers the T_g of the floor polish, moving it closer to room temperature so that films are less brittle. The Carbitol [or di(ethylene glycol) ethyl ether] acts much like the plasticizer by softening the latex particles. However, part or

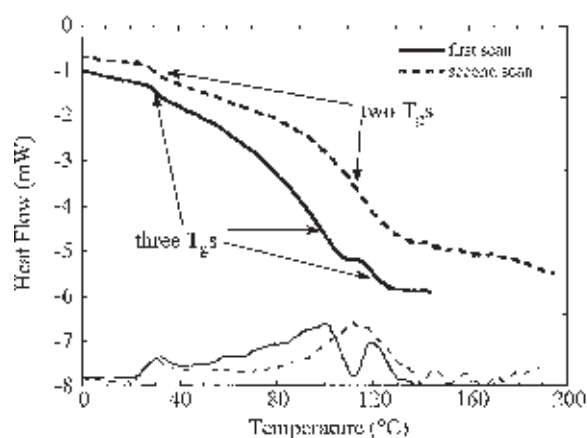
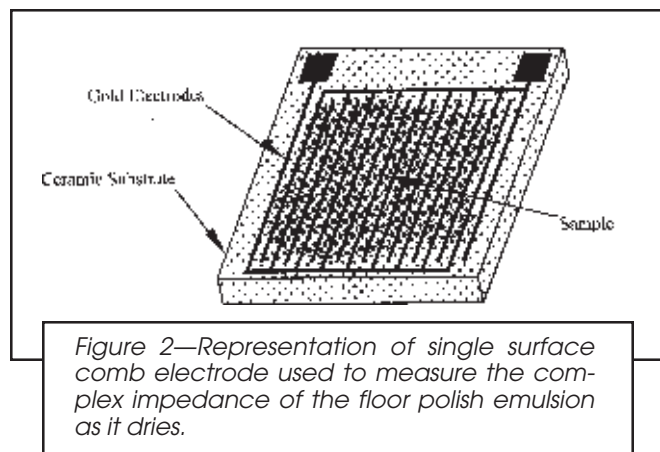


Figure 1—Pure polymer (dried from the emulsion) DSC scans showing multiple glass transitions. The first scan is the polymer as dried, and the second scan is after a quench from 150°C. The bottom two curves show the derivatives of the heat flow so the T_g s can be more easily located.



all of the Carbitol, with a boiling point of 202°C, presumably evaporates over time making it only a temporary plasticizer.¹ Carbitol is also hygroscopic so it may attract water molecules to the polymer causing further plasticization.

Dielectric Apparatus

Dielectric measurements were used to characterize the drying of the latex floor polish film in real-time. These measurements were conducted with a Hewlett-Packard 4192A impedance analyzer. The basic method consisted of measuring a sample response over a range of frequencies as a function of drying time.

The sample conductivity was measured with a single surface interdigitated comb electrode. It consists of interlaced gold fingers on a ceramic substrate and has a surface area of approximately 2 cm². A schematic representation of the electrodes is shown in Figure 2. The sample was cast on top of the electrodes, and then the response at different frequencies was measured. The HP 4192A impedance analyzer is capable of frequencies up to 13 MHz, and a one volt excitation signal was used for this experiment. The typical frequency range used in the scans for this study ranged from 10 Hz to 10 Mhz, and the data were sampled at four to eight different frequencies per decade. Because of the high frequencies used in this experiment, care was taken with the design of the connection to the sample electrode so that phase errors would be minimized. In addition, the impedance analyzer was zeroed with an offset that accounted for any residual impedance caused by the electrode connection geometry.

In the analysis of the dielectric data, quantitative values of the conductivity and permittivity were not calculated. This is because the comb type electrode geometry is not as easily modeled as a parallel plate arrangement. In the parallel plate case, there is usually some fringe electric field at the edges of the electrodes (because they are not infinite). However, this fringe field is a very small contribution to the overall capacitance and is typically neglected. In the comb electrode used in this study, the fringe fields are no longer negligible; in fact they are likely the major contributor to the measured response.

For most conductive materials, such as the floor polish emulsion, an appropriate model for the material is a

resistor and capacitor in parallel. For this circuit, the admittances (1/impedance) are additive,

$$Y^* = \frac{1}{Z^*} = \frac{1}{R} + i\omega C \quad (1)$$

where R is the resistance, C is the capacitance, and ω is the angular frequency. Since $Z^* \equiv Z' - iZ''$, solving for real and imaginary impedance then gives the following equations,

$$Z' = \frac{R}{1 + \omega^2 R^2 C^2} \quad \text{and} \quad Z'' = \frac{\omega R^2 C}{1 + \omega^2 R^2 C^2} \quad (2)$$

It can be shown that these equations are the parametric equations for a circle of radius R/2, centered at $Z' = R/2$ and $Z'' = 0$ (when plotting Z'' versus Z').

When making dielectric measurements on conductive materials, blocking electrode effects can obscure the bulk properties of the sample.^{19,20} In brief, this blocking effect is caused by the pile-up of the sample's mobile ions at the electrode/sample interfaces. As the ions accumulate at the electrodes, the sample becomes polarized, so a large false contribution to the dielectric constant is measured.²¹ Besides the sample itself, two major experimental factors may be varied to control the electrode polarization. The first factor is the time scale. As the length of time for the experimental measurement is increased, the ions have more time to accumulate at the electrodes. Thus the blocking effect is minimized by taking data at higher frequencies (shorter time scales). The frequency at which blocking becomes important depends on the concentration of ions and the sample viscosity. The second factor that influences electrode polarization is the

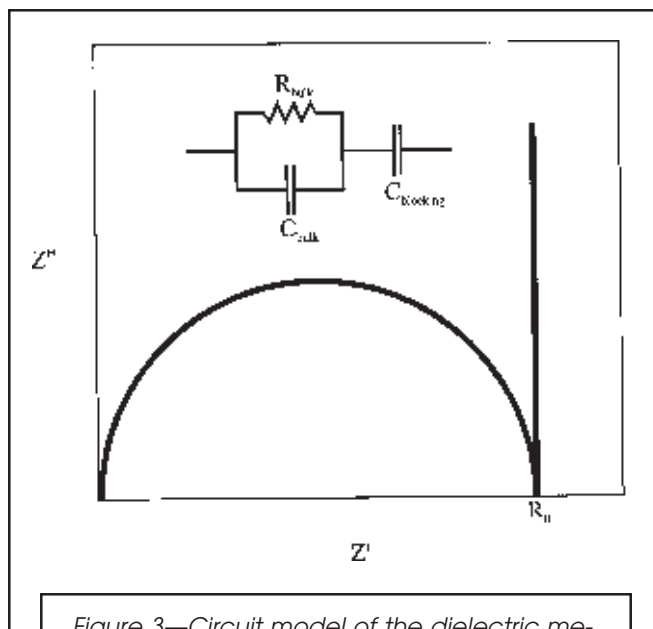


Figure 3—Circuit model of the dielectric medium that includes the electrode blocking effects as well as the bulk material impedance. The theoretical complex impedance plot for this material includes a semicircle characteristic of the bulk and a tail indicative of electrode blocking.

sample geometry. As the distance between the electrodes decreases, the amount of ions that pile up in a given amount of time increases. Thus increasing the spacing between electrodes can be used to minimize blocking effects.

Because of the high conductivity of a water-based emulsion, there is definitely a problem with electrode blocking effects. However, because the raw data (e.g., impedance) are available with the measuring system used in this study, it is relatively easy to diagnose when ions are piling up at the electrodes. For the latex floor polish, electrode blocking occurs only at the earliest stage of drying, when the water content is high and the ions have an easy path to the electrode. After enough water evaporates and the latex particles begin to pack into a regular array, ion mobility is restricted, so electrode blocking disappears. If not detected, electrode blocking can lead to erroneous results. However, diagnosis of these effects is easily accomplished by looking at a complex impedance plot of the data.²⁰

To account for the pile-up of ions at the electrodes, the parallel resistor and capacitor model must be modified. Though there exist more complicated models of blocking effects,²² the simplest model is made by adding a second capacitance in series with the original circuit. This is pictured in *Figure 3*.

For this model, the complex impedance is then given by,

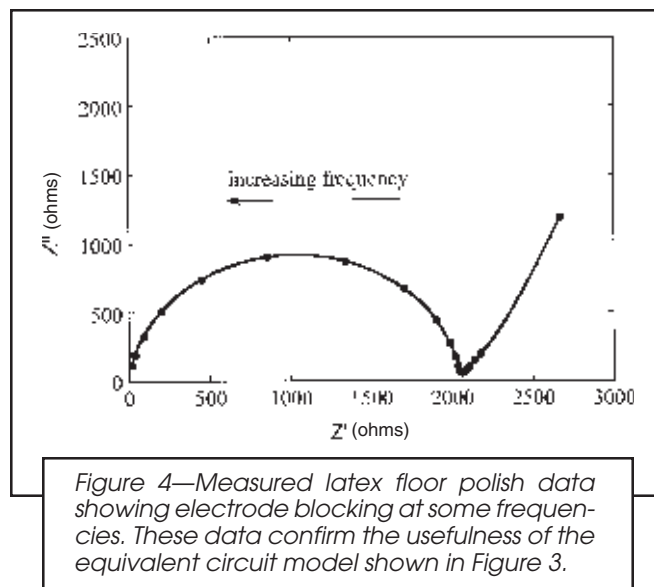
$$Z' = \frac{R_{\text{bulk}}}{1 + \omega^2 R_{\text{bulk}}^2 C_{\text{bulk}}^2} \quad \text{and} \quad Z'' = \frac{\omega R_{\text{bulk}}^2 C_{\text{bulk}}}{1 + \omega^2 R_{\text{bulk}}^2 C_{\text{bulk}}^2} + \frac{1}{\omega C_{\text{blocking}}} \quad (3-4)$$

These equations can be plotted on a complex impedance plot; this is also shown in *Figure 3*. Again there is a semicircle that represents the impedance of the material being tested, but there is also a vertical line that is caused by the ions blocking the electrode. R_0 is the resistance of the sample in the limit of zero frequency. Pictured in *Figure 4* for comparison are some actual data from the latex floor polish sample under study. These data show the usefulness of the model in diagnosing the existence of electrode blocking in latex samples.

The blocking effect is geometry dependent, so interpreting electrode blocked data is difficult if not useless. Because it depends on the speed with which the ions can accumulate at the electrode, it is also time (or frequency) dependent. In *Figure 4*, each data point corresponds to a different measurement frequency. There are electrode effects at lower frequencies where the ions have more time to accumulate. At higher frequencies, electrode blocking is no longer a problem, and the data are a valid measure of the material characteristics.

Thermal Analysis Measurements

In addition to the dielectric measurements, dried latex floor polish films were subjected to other thermal analysis measurements. The data taken include differential scanning calorimetry (DSC) and thermomechanical analysis (TMA). These data were all taken with TA Instruments modules. For the DSC measurements, a TA Instruments DSC 2910 was used. A relatively fast tem-



perature ramp of 20°C/min was used to sharpen the transitions, N_2 was used as a purge gas, and the reference pan was balanced with additional aluminum to minimize the startup hook. DSC sample sizes varied from 10 to 20 mg. For the TMA measurements, a TA Instruments TMA 2940 with a thin film fixture was used. Measurements were performed in a tensile mode with the sample clamped at both ends. A small amount of force held the sample in place (0.01 newtons), and the temperature was ramped at 1°C/min. TMA sample dimensions were 25 mm by 4 mm.

RESULTS AND DISCUSSION

Dielectric Measurements

As previously mentioned, the main emphasis of this work has been to follow the drying of a latex film by measuring the conductance of the sample on a single-surface comb electrode. While the conductivity depends only on the sample, the conductance is not solely a material property but depends also on the electrode geometry. Thus the conductance does not provide quantitative data on latex film drying, but it is still an effective parameter for observing qualitatively, the mechanisms of latex film formation.

There are two types of conductances that can be measured. One is the apparent conductance, G_{apparent} , which can be derived from the parallel resistor and capacitor model discussed previously.

$$G_{\text{apparent}} = \frac{1}{R} = \frac{1}{Z'(1 + \tan^2 \delta)} \quad \text{where} \quad \tan \delta = \frac{Z''}{Z'} = \omega RC \quad (5-6)$$

In an ideal material, this apparent conductance is independent of frequency. However, in most real systems the apparent conductance does indeed depend on the measurement frequency. In data taken for the latex floor polish formulation, the apparent conductance was found to vary by a factor of 10 or more over the range of measurement frequencies used (10 Hz to 10 MHz).

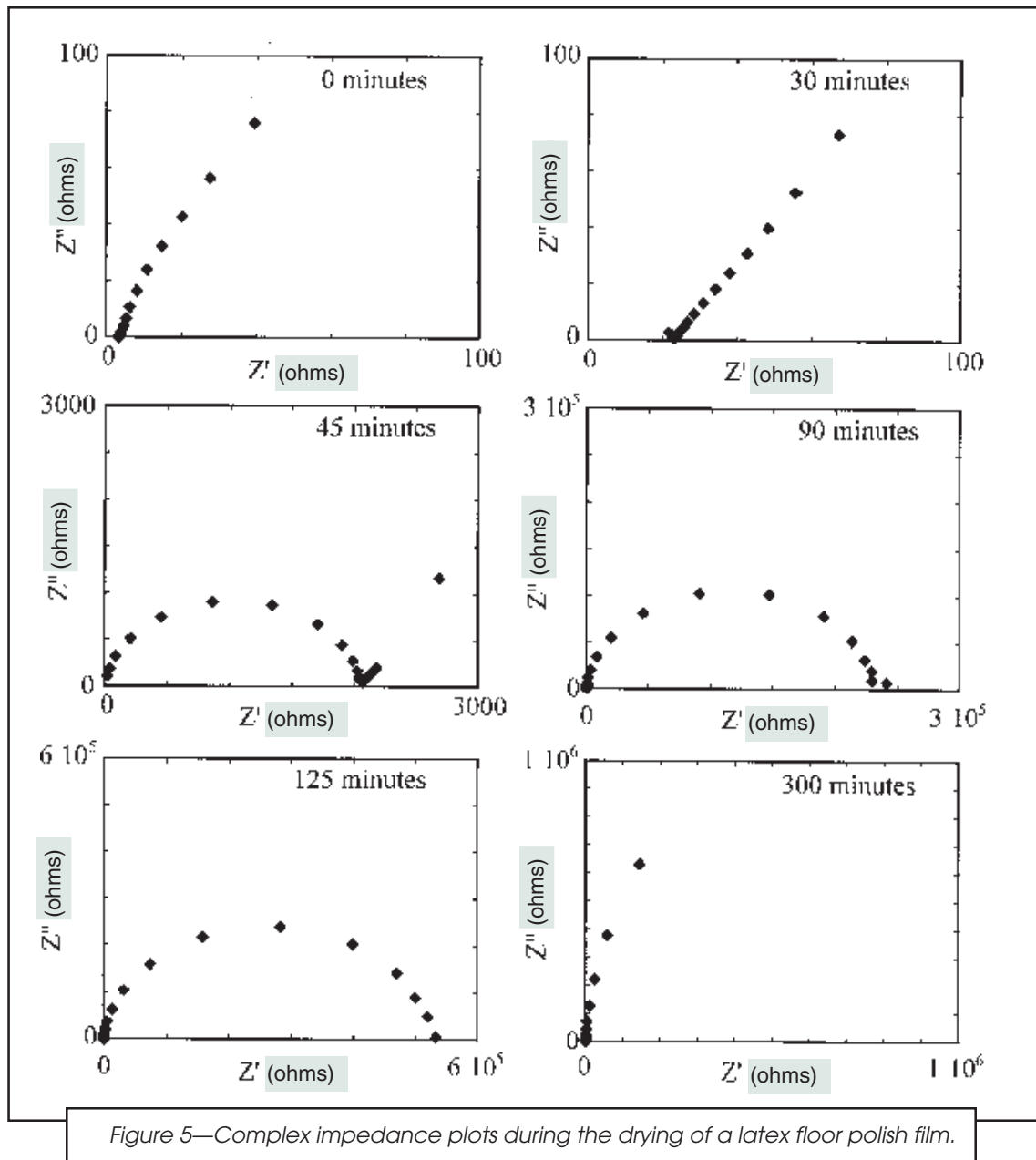


Figure 5—Complex impedance plots during the drying of a latex floor polish film.

An alternative conductance that is perhaps more useful (since it cannot vary with frequency) is the conductance in the limit of zero frequency. This zero frequency conductance, or bulk conductance, is denoted as G_0 . Bulk conductance is calculated with a Cole-Cole analysis²³ on complex impedance data measured over a range of frequencies. The empirical expression developed by Cole and Cole when applied to impedance is,

$$Z^* [= Z' - iZ''] = \frac{Z_0}{1 + (i\omega\tau_0)^{1-\alpha}} \quad (7)$$

where Z_0 , τ_0 , and α are empirical constants, and $1/Z_0$ corresponds to the bulk conductance, G_0 . With the expression $i^{1-\alpha} = e^{i(1-\alpha)\pi/2}$, the following relationship can be obtained,

$$Z'' = \sqrt{\left(\frac{Z_0}{2} \sec \frac{\alpha\pi}{2}\right)^2 - \left(Z' - \frac{Z_0}{2}\right)^2} - \frac{Z_0}{2} \tan \frac{\alpha\pi}{2} \quad (8)$$

The measured data from each frequency scan were fit to the above non-linear equation using a multi-dimensional minimization algorithm.²⁴ A table of Z_0 values versus time were generated and then converted into conductance and plotted as a drying curve.

Figure 5 shows a set of complex impedance graphs that are typical raw data taken during the drying of the latex floor polish film. The individual data points in each plot correspond to complex impedance values at different measurement frequencies. Hence, this sequence of plots shows the progression of the measured impedance values as time increases and the film dries.

The first graph in this set taken at zero minutes. At this time, the impedance is very low and the electrode blocking effect is dominant at all measurement frequencies. The next plot, at 30 min, shows that enough water has evaporated so that at the highest frequencies, the electrodes are no longer blocked and the semi-circle

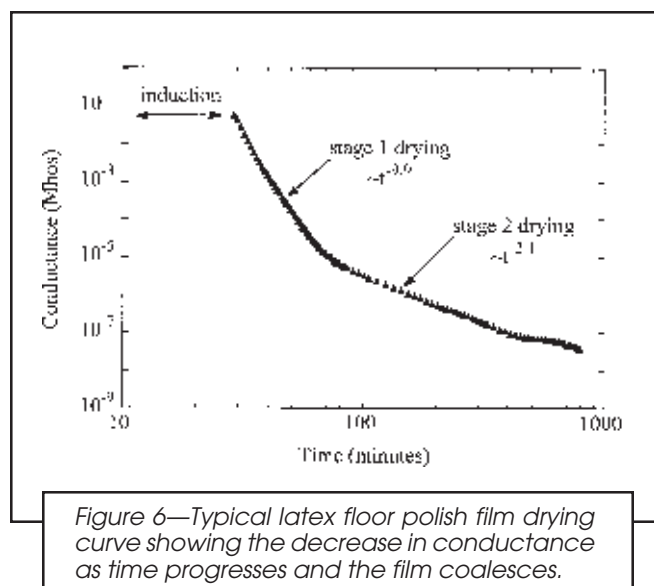
predicted by the parallel resistor and capacitor model is just beginning to form. The minimum in the curve corresponds to the zero frequency impedance. At 45 min most of the measured frequencies are no longer experiencing electrode blocking. At 90 and 125 min, electrode blocking is essentially non-existent. At 300 min, only the left portion of the semicircle can be seen because of the measurement limits of the impedance analyzer. Another detail to note with this data is that as time progresses, the intercept of the semi-circle, corresponding to the zero frequency limit impedance, goes to larger and larger impedance values (or lower conductance values).

Figure 6 shows a typical drying plot for a latex floor polish film dried at 27% relative humidity and 24°C. It is a log-log plot of the bulk conductance calculated using the Cole-Cole analysis discussed previously. The thickness of the measured film after drying is about 70 microns.

These data clearly show three different regions. The first region is marked by the lack of measurable conductance. This is because the sample is experiencing blocking effects in the entire range of measured frequencies. This induction period occurs when the ions are most mobile and therefore can quickly pile up at the electrodes. Eventually the ion mobility decreases to a point where blocking is not a problem for at least some of the frequencies. This region is labeled as stage 1 drying following a power law decrease in conductance with time ($\sim t^{-10}$). The boundary between the induction region and the stage 1 drying region is a function of the electrode geometry and does not necessarily indicate any physical transition. Finally, the drying curve shows a transition to a much shallower slope, termed stage 2 drying. This second stage of the drying process also obeys a power law ($\sim t^{-2}$). The transition from stage 1 to stage 2 drying is indeed a physical event, not an artifact of the measurement apparatus.

This curve shows the same behavior that Dissado et al.¹⁸ observed in a study of the drying of latex paint. They observed a rapid drop in conductance followed by a slower power law decay. The initial rapid drop occurred over only a data point or two in their data. However, for the floor polish data, shown in Figure 6, the initial stage clearly goes on for a long time and also obeys a power law. It is possible that in stage 1, the faster drying rate is from open capillaries. As the water evaporates, the undeformed latex particles begin in point contact and deform into polyhedra. Under this mechanism, the transition into stage 2 occurs when the latex particles have deformed enough to begin sealing off the capillaries and trapping the mobile ions in the interstices. When the interstices have been sealed off, the evaporation of water is a diffusion limited process. This is similar to the mechanism proposed by Dissado et al., but the reader should be cautioned that this mechanism can be verified only with additional experiments.

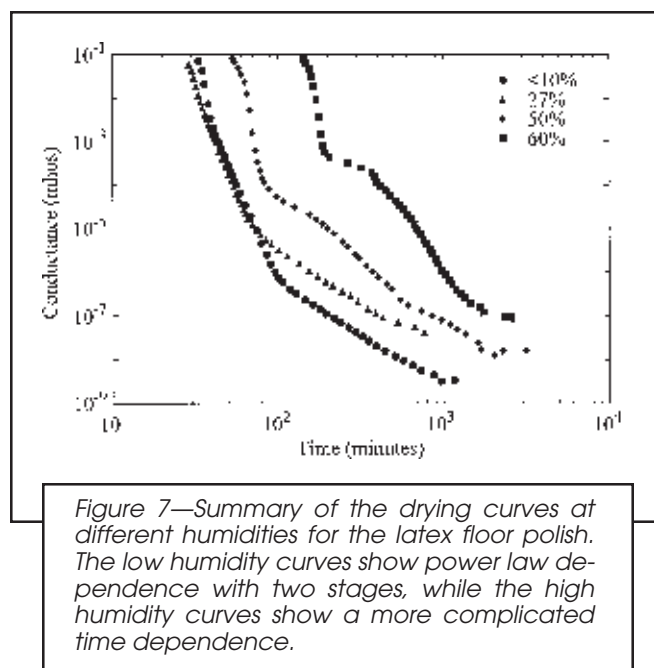
It is important to consider the effects of environmental conditions on the drying mechanism. Temperature, for example, is important because it determines the softness of the latex polymer, and, therefore, the ability of the particles to deform and flow into a continuous film. Humidity is another important variable, and its effect is

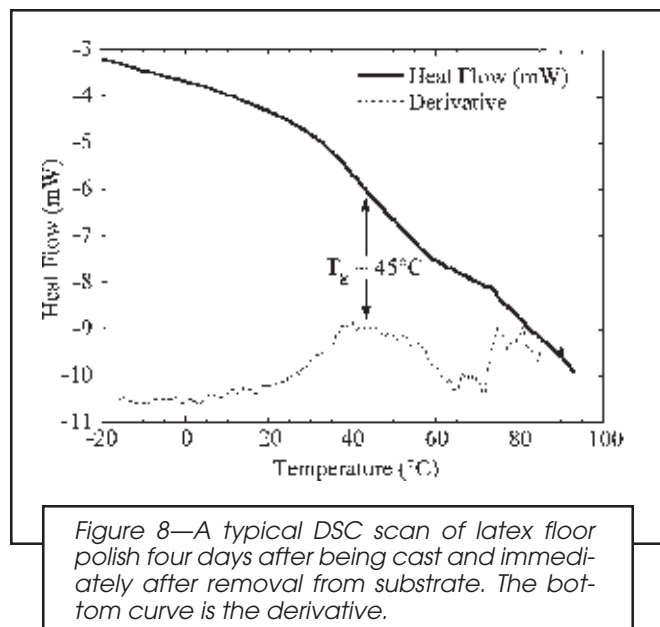


considered in the present work. Figure 7 summarizes the drying curves for the floor polish when dried at different relative humidities. The film thicknesses after drying varied from 50 to 70 microns, and the drying temperatures varied from 23 to 25°C.

The rate at which water evaporates from the latex is obviously dependent on the vapor pressure of the water in the air and, therefore, on the relative humidity. Harren²⁵ dramatically demonstrated the effect of ambient humidity conditions on the long term stability of a latex film by contrasting two samples: one painted under dry conditions and the other under humid conditions. Two years later the dry film cracked, while even after eight years, the humid film was still intact. Thus the humidity at drying is an important factor in determining the amount of coalescence of the film.

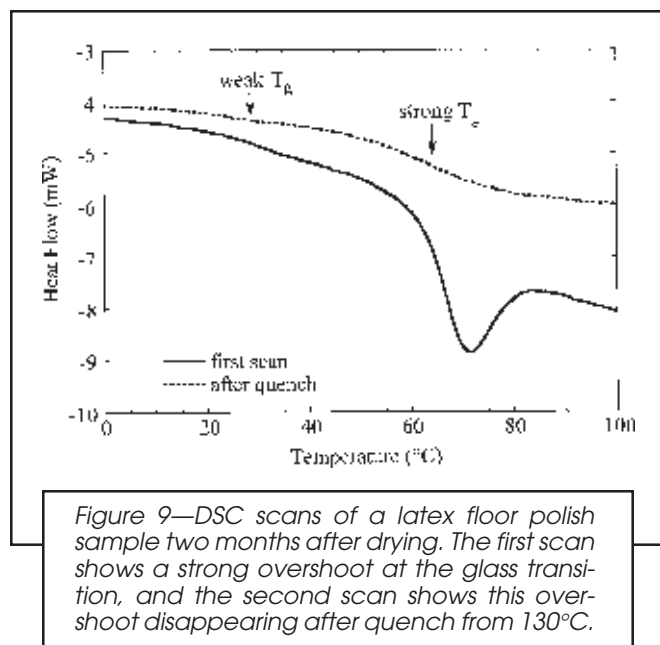
The data shown in Figure 7 clearly show the trend of increased drying time with increased humidity level. Of





greater importance, however, is that the data provide evidence that the film formation mechanism may also change with humidity. Specifically at the lower humidity levels, the drying curves follow a power law in both stages 1 and 2. However at the upper humidity levels, the curves are no longer linear so the power law assumption is not necessarily valid anymore. In fact, the higher humidity data show that there may be an additional stage of drying that is not present in the lower humidity data.

In the latex floor polish system studied here, it was found that even at very low humidities and fast drying rates, a continuous film was still formed. Conversely, at very high humidities (>75% RH) and long drying times, the film was found to crack and rupture. This is contrary to intuition. However, a possible explanation can be provided by the presence of the coalescing solvent. According to Hoy,¹⁵ the coalescing solvent is not necessarily



ily evenly distributed between the aqueous phase and the polymer phase in a latex, and the distribution is highly dependent on the proportion of water to solids in the system. His data for Carbitol, which is used in the present system, shows that a majority of it remains in the aqueous phase, and it does not migrate into the polymer phase until almost all the water is evaporated. The implication is that the Carbitol migrates into the polymer only when the latex particles are deformed to their greatest extent. At this point, the Carbitol softens the latex and further aids the deformation. It could be argued that even at the shorter drying times, there is enough Carbitol in the polymer to sufficiently soften it for formation of a continuous film.

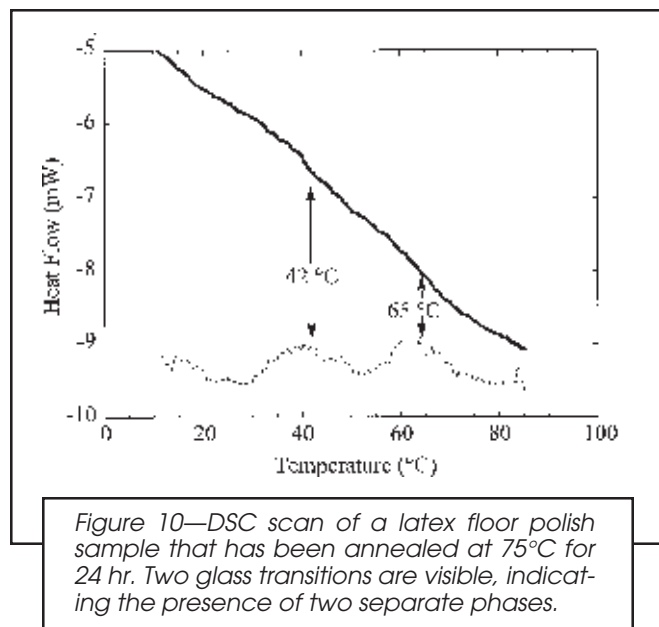
Hoy's work does not address the issue of solvent evaporation, however, this may be the cause of the film cracking at humidities >75%. Sullivan²⁶ found that the water and solvent evaporate simultaneously during film formation. In general the water evaporates faster than the solvent, so sufficient solvent remains in the system to allow the latex particles to deform. When the humidity level is sufficiently high, water evaporation is slow. Under these conditions, it is possible that the corresponding solvent evaporation rate is fast enough so at the critical time of maximum particle deformation, there is not enough solvent left to soften the polymer. Then internal stresses become sufficiently high to cause the film to lose integrity. In the latex polymer studied here, the glass transition of the polymer dried without additives is well above room temperature (see Figure 1). Thus, it is important that there is enough solvent in the polymer to lower its T_g for film formation. It should be pointed out that Dobler et al.,¹⁷ who also studied the effect of humidity on latex film formation, did not see this high humidity effect. However, their study did not address the effect of coalescing solvents.

Dobler et al.¹⁷ as well as Sheetz⁹ asserted that a continuous skin forms at the top of the latex film, through which water must then diffuse. However, evidence of this could not be detected with the dielectric apparatus. It is possible that this experiment was not sensitive enough to detect this. The drying did occur, however, in a moving front manner—from the outside edges toward the center of the sample. The dielectric response was an average over the entire film.

One final effect that might be important is that at some point during the process of particle deformation and coalescence, ionic crosslinks form. The presence of zinc ammonium carbonate (ZAC) presumably forms these ionic crosslinks. As a salt, the ZAC is readily dissolved in the water when the floor polish is formulated. Thus, it is probable that the ionic crosslinks form at the interfaces between latex particles and do not occur internally. How this impacts the film formation mechanism or dielectric response is not known.

Thermal Analysis Measurements

Along with the dielectric measurements made on the latex floor polish samples, some limited thermal analysis experiments were conducted. These other techniques provide further insights into the characteristics of the



floor polish system. They include differential scanning calorimetry (DSC) and thermomechanical analysis (TMA) measurements.

DSC experiments were conducted on dried films of floor polish. Figure 8 shows the typical DSC scan of a dried floor polish film. These particular data were taken with a 9 mg sample size. The derivative plot is also included on this figure, and it shows that the inflection point of the glass transition is approximately 45°C. This plot also indicates that the glass transition is quite broad even at the relatively fast temperature scan rate. Thus it is difficult to detect the glass transition of this material with the DSC technique. It should be noted that this sample was measured four days after it was cast and immediately after being peeled off the aluminum foil substrate, so there was probably a considerable amount of residual volatiles still in the film.

The DSC scan data in Figure 9 are for a dried latex floor polish film approximately two months after being cast. There are two scans pictured and several interesting aspects to this data should be noted. The first aspect is that the main glass transition is no longer at 45°C as in Figure 8 but has increased to around 65°C. This is likely caused by the slow diffusion and evaporation of volatiles from the film that occurs even long after its initial coalescence. The second aspect is that the first scan shows an overshoot at the main glass transition. This enthalpy overshoot disappears in the second scan which was done after a quench from 130°C. There are two possible explanations for this overshoot: stress relaxation and physical aging. That the film is undergoing stress relaxation is confirmed in TMA data shown later. It is particularly interesting that even after two months of drying, there is still a considerable amount of residual stress in this material. Physical aging could also be occurring, and it is possible that the residual stress in the dried film accelerates this aging. A third aspect to these data is the appearance of a second glass transition. These two DSC scans show a strong glass transition near 65°C, and a barely detectable weaker transition closer to room tempera-

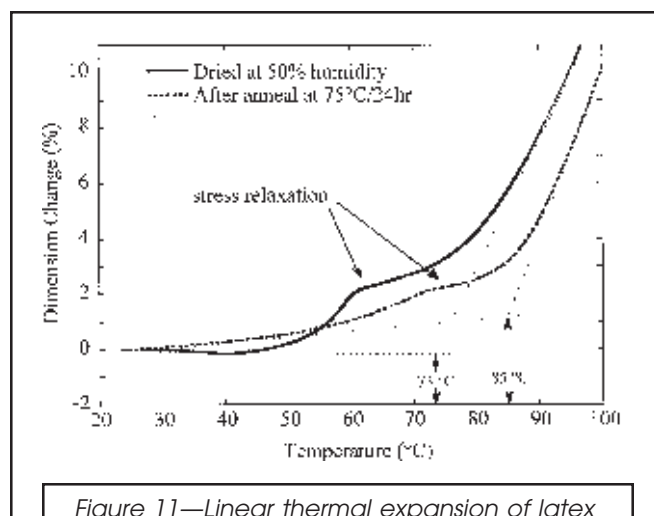
ture. Two glass transitions indicate the existence of two separate phases in the film. It may be that the second phase is caused by the lower molecular weight, water soluble resin that was part of this material, and this second phase formed in the interstices between the packed latex particles as they coalesced. However, the DSC scan of the pure polymer shown in Figure 1 shows the existence of this second phase already in the pure latex polymer, so it is possible that this is the source of the weak T_g .

The DSC scan in Figure 10 also shows the existence of two glass transitions. This particular sample was annealed at 75°C for 24 hr before this scan. The derivative curve is plotted in this figure to show the inflection points of the transitions. It should be pointed out that the possibility exists for migration of the plasticizer, tributoxethyl phosphate, because of unequal solubility in the two phases. This could also contribute to the separation between the temperatures of the two apparent glass transitions.

A TMA experiment was conducted on a dried film specimen to measure the linear thermal expansion coefficient and the glass transition. These data are shown in Figure 11. The latex floor polish film used in these tests had been dried for two months so these data are comparable to Figures 9 and 10. Figure 11 confirms the DSC data in showing a much higher T_g value (73 and 85°C in this case) for films that are two months old. In addition, the curves show sudden decreases in thermal expansion coefficient during the glass to rubber transition, confirming the existence of residual stress.

CONCLUSIONS

Real-time characterization of the coalescence of a polymer latex film has been carried out using dielectric analysis. In this technique, the sample film is cast on an interdigitated comb electrode, and scans of complex im-



pedance versus frequency are made as the film dries. These data are reduced to give the zero frequency or bulk conductance, and this bulk conductance is plotted as a function of time in a log-log plot. The drying curves show that at ambient temperatures the drying mechanism varies as a function of humidity with the trend that as humidity is increased, water evaporation is slowed, and drying times are lengthened.

When drying at low humidities, the conductance as a function of time shows two distinct regions with two distinct, but constant, slopes. The drying follows a power law in these two regions. The difference between these two regions is interpreted as the difference between open capillaries between the latex particles with fast evaporation and closed capillaries with diffusion limited evaporation. At higher humidities, the power law approximation breaks down, and the drying curves become more complicated, showing that there may be an additional stage in the film formation mechanism. An additional effect was seen at very high humidities, which was the loss of integrity of the latex film. This rupture was caused by the internal stresses which became sufficiently high. An explanation for this is that at the slow drying times of these high humidity films, there was sufficient time for the coalescing solvent to evaporate, thereby increasing the modulus of the latex particles. Hence, the coalescent plays an extremely important role in the film formation mechanism.

In addition to the dielectric measurements, more traditional thermal analysis experiments were conducted to better characterize what happens as the material forms a film. The first characteristic noted is that the glass transition of the film covers a broad temperature range. Second, there was evidence that as the film dried over long time periods, the glass transition increased from room temperature to much higher temperatures ($>65^{\circ}\text{C}$). In addition, a second glass transition appeared near ambient temperature that indicates some phase separation in the film. Third, there was also strong evidence that a considerable amount of residual stress remained in the film, even after a two-month period.

Latex film formation is a surprisingly complicated process which still sees much controversial discussion. Latexes used in practical applications contain additives that further complicate the drying mechanisms. This work has demonstrated that dielectric techniques can be used to measure the effect of various variables on the film formation. It has also helped to characterize a latex formulation that is typical of those used in practical applications.

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