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## **Using Quartz Crystal Microbalance/Heat Conduction Calorimetry To Monitor The Drying And Curing Of An Alkyd Spray Enamel**

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Chemical processes occurring in a thin film can be characterized using quartz crystal microbalance/heat conduction calorimetry, (QCM/HCC), a new technique that simultaneously measures small mass changes, heats of reaction, and viscoelastic changes in films. Published viscoelastic data obtained from quartz crystal microbalances are shown to be consistent with the WLF formalism of polymer viscoelasticity. Another data set from the literature is used to show how the loss compliance  $J''(t)$  of the film can be calculated from the motional resistance of the film which, in turn, can be measured directly by instruments such as the Masscal G1. Measurement principles of QCM/HCC are presented, and the technique is illustrated with a study of the drying and curing of a commercial alkyd spray enamel. By monitoring the process in alternating atmospheres of nitrogen and oxygen, it is possible to measure separately the drying of the film and its oxidative curing.

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## Drying and Curing of Coatings

When an organic coating is applied to a surface, a complex set of chemical and physical changes occurs before that coating can be useful in its intended environment. Further, the effectiveness of the final product can depend strongly on the properties determined by the competition and interaction of these reactions. It is helpful to categorize the two main types of processes as *drying* and *curing*, even though the two usually occur at the same time. Sliva (1) has summarized test methods used to determine drying, curing, and film formation of organic coatings. For the purposes of this article, we define *drying* as the physical evaporation of organic solvents and other volatile components present during the initial application of the film to a surface. Theoretical models have been developed to predict the drying behavior of polymer films on inert substrates (2) and these models contain no reaction chemistry. Miranda (3) has reviewed the process and the measurement of curing, and he defines *curing* as the cross-linking of polymeric systems. In all organic coatings except lacquers, cross-linking of the polymers introduce desirable properties such as increased hardness, durability and resistance to solvents. Cross-linking can be produced by oxidative, reactive, or catalytic means (3).

Heat and mass are two of the basic variables measured in experimental thermodynamics. From a thermodynamic point of view it should be straightforward to develop a method of distinguishing between the drying and the curing of a finish at constant temperature. In the drying process, the fluid coating (resin + solvents + pigments+ propellants + catalysts) loses mass by evaporation, an endothermic process requiring heat to be absorbed by the coating. The curing process, on the other hand, may involve either gain or loss of mass, for example as oxygen diffuses into the coating to generate the radicals inducing cross-linking, but the formation of chemical bonds in cross-linking is always exothermic. As the coating dries and cures it changes from a viscous fluid to a viscoelastic solid, and the film's mechanical properties, as measured by its modulus, change dramatically. Kaye and coworkers have defined many terms related to the "nonultimate mechanical properties of polymers" (4), including the loss compliance in simple shear deformation. Dynamic mechanical analysis (DMA) is the principal technique used to determine viscoelastic properties of polymer systems. DMA has been used to characterize the rates of cross-linking in thermoset polymers (5).

## Quartz Crystal Microbalance/Heat Conduction Calorimetry (QCM/HCC)

QCM/HCC is a new measurement technique uniquely positioned to measure the critical properties of films described above. QCM/HCC has been demonstrated to simultaneously measure the small mass changes, heats of reaction, and viscoelastic changes in films held in an isothermal environment and subjected to changes in gas composition (6-8). The Masscal G1™ Nanobalance/Microcalorimeter incorporates a quartz crystal resonator in intimate thermal contact with a sensitive heat flow sensor. The resonator is coated with a thin film sample (0.001-10 μm), and three quantities are monitored as the film is exposed to a programmed controlled gas mixture: (a) the mass  $m(t)$  (to ± 2 ng), (b) the thermal power  $P(t)$  (to ± 500 nW), and (c) the motional resistance  $R_{mot}(t)$ . We show below that in the thin film limit, the difference in motional resistance  $\Delta R_{mot}$  of the coated and uncoated resonator is proportional to  $\rho^2 h^3 J''$ , where  $\rho$  is the density,  $h$  is the thickness, and  $J''$  is the shear loss compliance of the coating. Thus, the Masscal G1 provides simultaneous real-time gravimetric, calorimetric, and dynamic mechanical monitoring of a single thin film sample such as a coating.

The first part of this section is an abbreviated version of the theory presented in Smith and Shirazi (8), a reference that also contains diagrams of the apparatus. A flat quartz disc with electrodes on both surfaces can be forced to oscillate in a transverse acoustic mode (motion parallel to the surface) by an RF voltage applied at the acoustical resonance frequency of the plate. This device is called a *transverse shear mode (TSM) quartz plate resonator*. TSM quartz plate resonators have been used as sensitive microbalances for thin adherent films since the late 1950's, following the pioneering work of Sauerbrey (9). A TSM resonator whose frequency is continuously monitored when sample is deposited on its surface is known as a quartz crystal microbalance (QCM). The resonant frequency of a quartz TSM resonator of thickness  $h_q$  is

$$f_0 = (\mu_q/\rho_q)^{1/2}/2h_q \quad (1)$$

where  $\mu_q$  and  $\rho_q$  are the shear modulus and density of quartz. The shift in frequency due to deposition of a thin, stiff film is proportional to the deposited mass per unit area of the film,  $\Delta m/A$ :

$$\Delta f = -(2f_0^2 / (\mu_q \rho_q)^{1/2}) \Delta m/A = -(2f_0^2 / (\mu_q \rho_q)^{1/2}) h_f \rho_f = -C h_f \rho_f \quad (2)$$

where  $h_f$  and  $\rho_f$  are the thickness and density of the film. For a 5 MHz crystal,  $C = 56.6 \text{ Hz}/(\mu\text{g}/\text{cm}^2)$ .

The width of the resonance for an uncoated 5 MHz resonator is 10-20 Hz, and the mechanical damping within the quartz that gives rise to this broadening can be determined by measuring the *motional resistance* R of the resonator, typically ~ 10 ohms. When thin, stiff films are deposited on the QCM surface the increase in R is small, but softer, thicker films (i.e., rubbery polymers 5-10 microns thick) can increase R by hundreds of ohms. The impedance of a TSM resonator damped by a finite viscoelastic film can be described as the sum of the impedance of the quartz and the impedance of the film. Theoretical predictions for the mechanical response of a model quartz crystal microbalance with a thin sample layer in a fluid bath have been given by White and Schrag(10). The film impedance is a function of four film parameters: the thickness  $h_f$ , the density  $\rho_f$ , the shear storage modulus  $G_f'$ , and the shear loss modulus  $G_f''$ . Shear moduli must be determined at the TSM resonant frequency (5 MHz). In the theory of viscoelastic solids, the *compliance* can be used instead of the *modulus* to quantify storage and loss behavior. The shear storage compliance is defined as

$$J' = \frac{G'}{(G'^2 + G''^2)} \quad (3)$$

and the shear loss compliance is defined as

$$J'' = \frac{G''}{(G'^2 + G''^2)} \quad (4)$$

An important step in any analysis of motional resistance data for polymeric coatings is to recognize how  $G'$  and  $G''$  are related to each other and to independent variables such as temperature, measurement frequency, and film composition. The basis for understanding these relationships is the Williams-Landel-Ferry theory of polymer viscoelasticity (11,12) and the time-temperature superposition principle. Key concepts in this formalism are as follows:

- (1) Master curves of  $G'$  and  $G''$  versus reduced measurement frequency  $f_{red}$  can be constructed for any polymer, and these curves are similar in shape from one polymer to another.
- (2) The reduced frequency is proportional to the actual frequency  $f$  at which the moduli are measured,

$$f_{red} = f a_T, \quad (5)$$

where  $a_T$  is called the shift factor. The shift factor depends on the free volume of the polymer.

- (3) The temperature dependence of the shift factor is given by

$$\log a_T = -c_1^g (T - T_g) / (c_2^g + T - T_g), \quad (6)$$

where  $T_g$  is the glass transition temperature, and the “universal” constants  $c_1^g$  and  $c_2^g$  have the values  $c_1^g = 17.44$  and  $c_2^g = 51.60$ . Equation (6) is often referred to as the WLF equation.

- (4) Since free volume depends both on temperature and on the mass fraction of absorbed vapor, changes in both  $G'$  and  $G''$  can thus be related to these independent variables.
- (5) For a glassy polymer (i.e., measurement temperature less than the glass transition temperature,  $T_g$ ), the loss modulus  $G''$  is much less than the storage modulus  $G'$ .
- (6) At  $T_g$  the shear and loss modulus become comparable, and the loss tangent  $\delta = \tan^{-1}(G''/G')$  is a maximum.
- (7) Above  $T_g$  both  $G'$  and  $G''$  decrease with temperature.

Two convenient measurements of the film properties obtainable by QCM/HCC are (a) the difference in resonant frequency  $\Delta f = f(\text{crystal} + \text{film}) - f(\text{crystal})$ , and (b) the difference in motional resistance  $\Delta R = R(\text{crystal} + \text{film}) - R(\text{film})$ . Voinova et al (13) present equations for both quantities in a power series expansion in the thickness  $h_f$ . Utilizing equations (3) and (4), the result for  $\Delta f$  and  $\Delta R$ , to third order in  $h_f$ , is

$$\frac{\Delta f}{f_0} = \frac{\rho_f h_f}{\rho_q h_q} \left\{ 1 + \frac{4h_f^2 \pi f_0^2 \rho_f J'}{3} \right\} \quad (7)$$

and

$$\Delta R = \frac{2L_q}{3\pi Z_q} \omega^4 \rho_f^2 h_f^3 J'' \quad (8)$$

Thus, the motional resistance change is proportional to the square of the film density, the cube of the film thickness, and the loss compliance of the film. For a 5 MHz QCM, typical values for  $L_q$  and  $Z_q$  are 0.0402 Henry and  $8.84 \times 10^6$  Pa s/m, respectively. We demonstrate the correctness of Eq. (8) with the data of Lee, Hinsberg, and Kanazawa (14). They prepared a series of poly (n-butyl acrylate) films of thickness from 6 to 4000 nm and measured the motional resistance of the film in both air and water. Using the data from their Figure 5(a) for motional resistance in air, we plotted  $\Delta R$  versus the cube of the film thickness, as suggested by Eq. (8). The resulting plot is linear with an  $R^2$  of 0.9996. The slope is  $6.1 \times 10^{-9}$  ohm/nm<sup>3</sup>  $\pm$  5%. Using a value  $1.08$  g/cm<sup>3</sup> for the

density of poly (n-butyl acrylate), Eq. (8) gives a value for the loss compliance  $J''$  of  $5.0 \times 10^{-9} \text{ Pa}^{-1}$ . Lee et al (14) report values based on the Kanazawa relations for the shear storage modulus  $G'$  and shear viscosity  $\eta$  of  $3 \times 10^7 \text{ Pa}$  and  $0.13 \text{ Pa s}$ , respectively. With the relationship  $G'' = 2\pi f \eta$ , Eq. (4) yields a loss compliance  $J'' = 4.5 \times 10^{-9} \text{ Pa}^{-1}$  from these data, in good agreement with the value we derive,  $5.0 \times 10^{-9} \text{ Pa}^{-1}$ , from Eq. (8).

Two sets of measurements of the shear storage modulus and the shear loss modulus of a thin film with a TSM resonator exist in the literature. Lucklum et al (15,16) measured  $G'$  and  $G''$  for a polyisobutylene film as a function of temperature, determined at 15 MHz using coating thicknesses of from 0.2 to 1.0  $\mu\text{m}$ . Their data are shown in Figure 1. Katz and Ward (17) measured  $G'$  and  $G''$  at 5 MHz for a 9.25  $\mu\text{m}$  polystyrene film as a function of the mass fraction of adsorbed 2-chlorotoluene vapor at 25°C. Their data are shown in Figure 2. Polystyrene is a glassy polymer at room temperature; Ferry (11) gives  $T_g = 97^\circ\text{C}$ . Although polyisobutylene is classified as a rubbery material at low frequencies ( $T_g = -70^\circ\text{C}$ ), the Lucklum data show that at a measurement frequency of 15 MHz the glass transition temperature (i.e. the temperature at which  $G'$  and  $G''$  are equal) is  $\sim 50^\circ\text{C}$ . This is consistent with the WLF theory, which states that the glass transition temperature increases with measurement frequency.

The data of Katz and Ward (Fig. 2) show that as the mass fraction of absorbed solvent in polystyrene increases,  $G'$  decreases substantially by over two orders of magnitude while  $G''$  first increases and then decreases. The point where  $G' \sim G''$  occurs at a mass fraction of 4%. Katz and Ward interpret this change to be due to rotational relaxation of the 2-chlorotoluene solvent. Another interpretation of the data of Katz and Ward is possible. It is well known that the addition of a diluent of low molecular weight to an undiluted polymer decreases the glass transition temperature  $T_g$ . Indeed, this is the basis for adding plasticizers to stiff polymers to make them more pliable. Ferry (11) describes a theoretical approach to predicting the shift in  $T_g$  by combining his shift factor  $a_T$  with a linear dependence of  $T_g$  on the weight fraction of the diluent:

$$T_g = T_{g2} - kw_1. \quad (9)$$

Here 1 is the diluent or solvent and 2 is the polymer,  $w_1$  is the weight fraction of solvent in the polymer, and  $k$  ranges from  $200^\circ\text{C}$  to  $500^\circ\text{C}$  for various solvents in polystyrene. Martin, Frye, and Senturia (18) extend these ideas of Ferry to derive a new equation for the dependence of the shift factor  $a_T$  on both temperature and vapor absorption. They say of this relationship, "This free volume treatment indicates the interchangeability of temperature and vapor absorption in determining film elastic properties."

It is not a coincidence that the polyisobutylene data of Figure 1 look similar in shape to the polystyrene data of Figure 2, even though the independent variable differs for the two plots. Either an increase in temperature or an increase in solvent volume fraction will decrease the shift factor  $a_T$  and thus move the frequency regime from high frequencies (glassy polymers) to lower frequencies (rubbery polymers). We used the data of Katz and Ward to compute the dependence of the shear storage compliance and the shear loss compliance on the mass fraction of 2-chlorotoluene absorbed in polystyrene. We find that  $J'$  remains constant at  $1.4 \times 10^{-11} \text{ Pa}^{-1}$  for  $0.02 < \text{mass fraction} < 0.08$ , increasing to  $4.4 \times 10^{-11} \text{ Pa}^{-1}$  at a mass fraction of 0.16. The results for  $J''$  are shown in Figure 3. Notice that as the 2-chlorotoluene mass fraction increases  $J''$  increases by three orders of magnitude. We compute from Eq. (7) that the error in using the Sauerbrey equation is only 0.13%. From Eq. (8) we calculate that the change motional resistance varies from 0.1 ohms to 447 ohms.

## **QCM/HCC Measurements on an alkyd spray enamel**

We present here an example of the application of the QCM/HCC technique to the drying and curing of Decrolon, a commercial aerosol spray enamel made by Sherwin-Williams. The resin in Decrolon is a vinyl toluene alkyd, and the volatile organic solvents are acetone (20%), toluene (13%) and light aliphatic naphtha (8%), plus propellants.

### **Short-term drying of enamel**

An uncoated QCM crystal was characterized by weighing on a 5-place balance and then measuring its resonant frequency and motional resistance in a Masscal G1 nanobalance/calorimeter. The larger gold electrode of this crystal was then sprayed with a thin coat of Decrolon. Within three minutes the crystal was installed in the Masscal G1 sample chamber at  $30.0^\circ \text{C}$  and purged briefly with  $\text{N}_2$  so as to arrest any air-induced curing. Ten minutes into the experiment, a  $5 \text{ std cm}^3/\text{sec}$  flow of dry  $\text{N}_2$  was established; the resulting heat flow, mass change and motional resistance are shown in Figure 4. Evaporation of the solvents causes the large negative thermal power peak, the loss in mass of the film, and the decrease in motional resistance or loss compliance. At the end of all experiments on this film, the QCM crystal was reweighed. The mass of the film was  $250 \pm 30 \text{ } \mu\text{g}$ . From the difference in frequency of the crystal before and after coating and the area of the coating ( $1.6 \text{ cm}^2$ ), the film mass was calculated to be  $252 \pm 5 \text{ } \mu\text{g}$  using the Sauerbrey equation. Assuming a film density of  $1.5 \text{ g/cm}^3$ , the film thickness is  $1.08 \text{ } \mu\text{m}$ . The loss in mass per unit area shown in

Figure 4 is  $40 \mu\text{g}/\text{cm}^2$ , and the area of the sprayed film was  $1.6 \text{ cm}^2$ . Thus the evaporative mass loss of the solvents was  $64 \mu\text{g}$ , or 26% of the original film mass.

### **Toluene uptake and loss in uncured and air-cured enamel**

As long as the alkyd enamel film remains under the nitrogen flow, no oxidative cross-linking can occur. We refer to a film in this state as *dried* but *uncured*. To examine the uptake and release of toluene vapor from such a film, two mass flow controllers were used to control the flow of a variable mixture of pure  $\text{N}_2$  and of  $\text{N}_2$  saturated with toluene vapor into the sample chamber of the Masscal G1. The toluene bubbler chamber temperature was  $28.9 \text{ }^\circ\text{C}$ . The system was programmed to provide five 900 second steps of increasing toluene vapor pressure from 0 to 3600 Pa followed by five steps of equivalent decreases. A complete cycle thus took 9000 seconds, and a single run included two cycles. The data collected are shown in Figure 5. The top panel shows the partial pressure of toluene produced by the flow program, and the remaining three panels show the variables measured as the Decrolon film was exposed to the toluene vapor. All thermal power measurements have been corrected for the heat dissipated by the oscillating crystal, a function of the motional resistance of the crystal. Details of this correction will be presented elsewhere.

After the run was completed, the QCM crystal was removed and allowed to cure in air for 3 days. It was reweighed on the 5-place balance and then was then reinserted in the G1, and the same flow program protocol was followed. The raw data were similar to those of Figure 5 but with a smaller mass of toluene absorbed. Analysis of the QCM/HCC data, construction of sorption isotherms and determinations of sorption enthalpies follows the methodology introduced in the study of water and ethanol sorption in an aliphatic polyurethane(7). The prompt changes in mass and motional resistance and the peaks in thermal power produced whenever the partial pressure of toluene changes indicates that this film of Decrolon quickly absorbs and desorbs toluene vapor and that the rate of sorption is not significantly limited by the rate of diffusion of toluene in the resin. The sorption isotherms of toluene in Decrolon calculated from the data of Figure 5 and from the data on the air-cured Decrolon film are shown in Figure 6. Notice that the air-cured film absorbs less toluene than the dried but uncured film.

To determine the sorption enthalpy of toluene in Decrolon, the integral  $\int P dt$  of the thermal power over one step of constant toluene activity yields the integrated heat,  $Q$ , associated with that sorption or desorption process. The change in mass of the film for that step is equated to the mass of toluene vapor

adsorbed or desorbed,  $m_{\text{toluene}}$ . Finally, the enthalpy of sorption is calculated for each step by the relationship  $\Delta H_{\text{sorption}} = Q/(m_{\text{toluene}}/MM_{\text{toluene}})$ , where  $MM$  is the molar mass of toluene. The average of all steps shown in Figure 5 give  $\Delta H_{\text{sorption}} = -21.2 \pm 2.8$  kJ/mol. Since the molar enthalpy of condensation of toluene is  $-38.0$  kJ/mol at  $25^\circ\text{C}$  (19), we can conclude that the interaction of toluene with the alkyd resin is weaker than the interaction of toluene with itself in the pure liquid state.

The motional resistance data for the uncured (Figure 5) and cured Decrolon film are converted to loss compliance using Eq. (8) and plotted in Figure 7 as a function of the mass of toluene per gram of film. Notice that the loss compliance of the cured film is lower than that of the uncured film for all values of the toluene content of the films. Since lower loss compliance is generally correlated with greater stiffness of a polymer film we can conclude that these data are consistent with the fact that curing increases the stiffness of the resin coating.

### **Monitoring the O<sub>2</sub>-induced curing of enamel with the QCM/HCC.**

A second, thicker Decrolon film was prepared on another QCM crystal and installed within a few minutes of its deposition in the sample chamber of the Masscal G1. The mass of this film was  $1.33 \pm 0.11$  mg and its thickness was calculated to be  $4.9 \mu\text{m}$ . The film was dried for four hours within the Masscal G1 under a  $5 \text{ cm}^3/\text{min}$  flow of nitrogen. Two mass flow controllers were used to provide a variable mixture of nitrogen and oxygen to the sample chamber. The flow controller software was programmed to alternate between  $5 \text{ cm}^3/\text{min}$  of  $\text{N}_2$  and  $5 \text{ cm}^3/\text{min}$  of  $\text{O}_2$  at 10 minute intervals, and a 12-hour experiment was recorded. We call this mode of operation “modulated environment chemistry”, because it is only during the presence of oxygen that air-curing of the alkyd enamel can occur. If drying was not complete in the first four hours, the mass and motional resistance might still decrease slowly under  $\text{N}_2$  flow as the film dries, but  $\text{O}_2$ -initiated cross-linking cannot occur. The resulting data are shown in Figure 8.

There is much detailed information of interest in the data shown in this Figure, and a complete analysis, particularly of the rapid short-term changes, must wait for another publication. But the long-term trends in mass, motional resistance, and thermal power show clearly the onset of a slow chemical process at about 6 hours into the run, well beyond the expected drying period of the thin film. A more exothermic process begins in the thermal power curve at 6 hours and reaches its maximum amplitude at 8.5 hours; this is consistent with the exothermic process expected in cross-linking. By 10 hours, the mass of the film

has increased by 0.37% and the loss compliance has decreased by 50%. As can be seen from Figures 2 and 3, a decrease in loss compliance of a film below its glass transition temperature is consistent with the stiffening of a glassy film due to cross-linking. An extension of the run shown in Figure 8 for the next several days produced a film whose loss compliance was only 20% of its value at the beginning of exposure to O<sub>2</sub>. We interpret the changes in all three signals starting at 6 hours to be the onset of the curing of the alkyd resin induced by the O<sub>2</sub>. These long-term trends clearly show that the QCM/HCC can separate the measurement of the drying process from that of the curing process.

## Conclusions

In this chapter we have described briefly how a new measurement technology, quartz crystal microbalance/heat conduction calorimetry, has the capability to simultaneously measure three critical properties for understanding thin film reactions: thermal power, mass, and motional resistance. We have explained the connection of the measured motional resistance to the loss compliance of the film and we demonstrate that viscoelastic properties of polymers measured at 5 MHz with the Masscal G1 nanobalance/calorimeter can be understood in terms of the WLF theory of polymer viscoelasticity. As an illustration of the measurements, we present data on the drying and curing of an alkyd enamel spray finish. The data demonstrates the usefulness of making these measurements in real time under controlled changes in environment, not only to determine reaction properties under different gases but also to be able to separate the changes related to drying and curing. The measurements made were highly sensitive to changes in the film and we believe the information provided by this technology will enable coatings researchers both to monitor and to control the drying and curing process. Watching paint dry is not boring if you have the right perspective.

## References

1. Sliva, T. J. Drying Time. In *Paint and Coating Testing Manual*; 14th Edition of the Gardner-Sward Handbook ed.; Koleske, J. V., Ed.; ASTM: Philadelphia, 1995; Vol. MNL 17; pp 439.
2. Alsoy, S.; Duda, J. L. *AIChE* **1999**, *45*, 896.
3. Miranda, T. J. Curing: The Process and Its Measurement. In *Paint and Coating Testing Manual*; Koleske, J. V., Ed.; ASTM: Philadelphia, 1995; Vol. MNL 17; pp 407.

4. Kaye, A.; Stepto, R. F. T.; Work, W. J.; Aleman, J. V.; Malkin, A. Y. *Pure and Appl. Chem.* **1998**, *70*, 701.
5. Nichols, M. E.; Gerlock, J. L.; Smith, C. A. *Polymer Degradation And Stability* **1997**, *56*, 81.
6. Smith, A. L.; Shirazi, H. M. *J. of Thermal Analysis and Calorimetry* **2000**, *59*, 171.
7. Smith, A. L.; Mulligan, S. R.; Shirazi, H. M. *J. Polymer Sci. Part B Polymer Physics* **2004**, *42*, 3893.
8. Smith, A. L.; Shirazi, H. M. *Thermochemica Acta* **2005**, *432*, 202.
9. Sauerbrey, G. *Z. Physik* **1959**, *155*, 206.
10. White, C. C.; Schrag, J. L. *J. Chem. Phys.* **1999**, *111*, 11192.
11. Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley: New York, 1980.
12. Weissman, P. E.; Chartoff, R. P. Extrapolating Viscoelastic Data in the Temperature-Frequency Domain. In *Sound and Vibration Damping with Polymers*; American Chemical Society, 1990; pp 111.
13. Voinova, M. V.; Jonson, M.; Kasemo, B. *Biosensors and Bioelectronics* **2002**, *17*, 835.
14. Lee, S.-W.; Hinsberg, W. D.; Kanazawa, K. K. *Anal. Chem.* **2002**, *74*, 125.
15. Lucklum, R.; Hauptmann, P. *Faraday Discussion* **1997**, *107*, 123.
16. Lucklum, R.; Hauptmann, P. *Electrochimica Acta* **2000**, *45*, 3907.
17. Katz, A.; Ward, M. D. *J. Appl. Phys.* **1996**, *80*, 4153.
18. Martin, S. J.; Frye, G. C.; Senturia, S. D. *Anal. Chem.* **1994**, *66*, 2201.
19. *CRC Handbook of Chemistry and Physics*, 80th ed.; CRC Press: Boca Raton, 1999.

### Figure Captions

1. Shear storage modulus  $G'$  and shear loss modulus  $G''$  for polyisobutylene. Data are from Ref. 15.
2. Shear storage modulus  $G'$  and shear loss modulus  $G''$  for polystyrene plasticized with 2-chlorotoluene. Data in this figure are from Ref. 17.
3. Shear loss compliance of  $J''$  polystyrene plasticized with 2-chlorotoluene. Data in this figure are from Ref. 17.
4. Short-term drying of uncured Decrolon film.
5. Sorption of toluene vapor in an uncured Decrolon film. (a) toluene vapor partial pressure; (b) net thermal power (Eq. 11); (c) motional resistance; (d) change in mass per unit area.
6. Toluene sorption isotherms for uncured and cured Decrolon.
7. Loss compliance of uncured and cured Decrolon as a function of toluene content.

8. Change in mass per unit area, loss compliance, and thermal power in a Decrolon film when exposed to alternate flows of  $N_2$  and  $O_2$  in 10 minute intervals.

### G' and G'' for Polyisobutylene















