In Situ Monitoring of Coating Polymerization, Cure and Aging Using Frequency Dependent Dielectric Monitoring

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INTRODUCTION

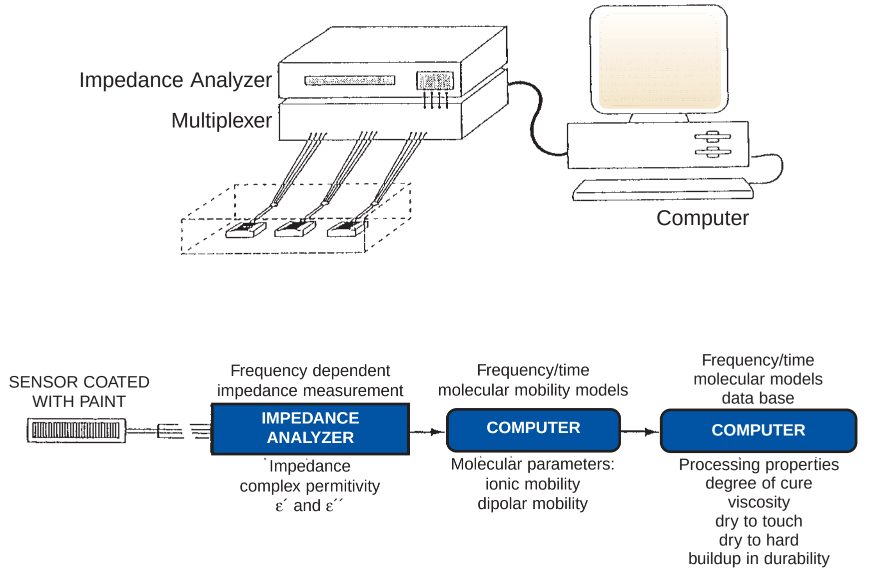
Frequency dependent dielectric measurements using in situ micro sensors, FDEMS, is a particularly useful technique for monitoring the changing state of a coating during synthesis, cure, and aging.[1] Measurements can be made in the laboratory to monitor the polymerization process in a flask, to monitor cure in an oven or under a UV lamp, and to monitor durability and aging in a weather controlled environmental chamber or other degradative environment. Equally important, the FDEMS in situ microsensor monitoring technique can be used to monitor reaction advancement in the pilot or production plant's batch reactor. Cure can be monitored in production ovens on the plant floor as well as outside, for example, on the surface of a ship in dry dock. Durability and aging can be monitored while the coated object is in use. Examples are a marine coating on a ship or the protective coating on the liner of an acid containing tank.

The FDEMS micro sensor technique ought to be more widely used, particularly in monitoring cure and degradation of a coating. One reason the planar micro sensor should be used more extensively is that it is ideally suited to monitoring coatings where only one side of a thin polymer film is exposed to the environment. This condition is difficult to duplicate in most rheological and calorimetric measurements. Coatings can be monitored using optical techniques. However, in optical and calorimetric techniques the sensitivity and accuracy decreases when one tries to detect changes during the final stages of cure, a point addressed later in this article. Further, remote, planar, micro dielectric sensors provide simple, in situ, accurate measurements of the progress of the reaction and changes in state during cure with a high degree of sensitivity regardless of the state of cure.

A probable reason why FDEMS is not used more widely is that there is a limited understanding by practitioners in the coating industry of the physical principles upon which the instrumental technique is based. Often there is a desire to cut short the importance of understanding the science behind the frequency dependence of dielectric measurements and to simply interpret changes in the shape of the instrument's signal. This simplified approach leads to misinterpretation and error.

The key to successfully using dielectric measurements to monitor changes in the state of a coating system during synthesis, cure, and use in the environment is to understand the frequency dependence of the complex permittivity ε^*, a force-displacement parameter similar to the complex modulus G^* or compliance J^* in rheological measurements. As in rheological measurements, the complex permittivity has two components as does G^* and J^* with their real G', J' and imaginary G'', J'' components. As in mechani-

Figure 1—Schematic diagram of the dielectric frequency dependent measurement system with an interdigitated sensor.



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cal properties, the real component of ε^* is ε' and its magnitude is a measure of energy storage, while the imaginary ε'' is a measure of energy dissipation. The difference is that dielectrics is a molecular force-displacement measurement, unlike rheology which is a macroscopic force displacement measurement. Therein lies its power as a technique to detect change. After all, most changes in performance properties originate at the molecular level. In dielectrics the applied force is an electric field and this force causes displacement in position, that is motion, of molecules with polar groups and charged, ionic species.

This paper initially discusses the physical science behind dielectric measurements, particularly the importance of understanding the frequency dependence of the two components of ε^*, ε', and ε''. It describes the equipment and some of the theoretical equations relating changes in ε' and ε'' as a function of frequency to molecular parameters characterizing mobility at the molecular level. Then changes in mobility are related to changes in the physical state of the resin. Finally, a range of applications from monitoring polyester synthesis, cure of a marine and a latex coating, and finally monitoring durability under environmental factors such as water and acid are described.

While FDEMS is an extremely powerful sensing technique for coatings, it is important to understand that it does not displace conventional rheological, calorimetric, and optical techniques. Rather, its ultimate power is that measurements of changes in ionic and dipolar mobility at the molecular level made in situ in the field can be correlated with conventional laboratory measurements and coating criteria such as dry to touch. Thereby, information about viscosity, buildup in T_g, extent of reaction advancement, rates of change, reaction completion, degradation, and useful life of a coating can be quantitatively monitored using the FDEMS sensor measured values of ε' and ε'' in the production or field environment.

FUNDAMENTALS OF DIELECTRIC CURE MONITORING

The ability to monitor advancement and characteristics of reaction in actual processing environments is obtained through monitoring the changes in the magnitude and frequency dependence of the complex permittivity ε^*. As in rheology, complex permittivity has a real ε' and a loss ε'' component, where $\varepsilon^* = \varepsilon' - i\varepsilon''$ and ε' is a measure of energy storage and ε'' is a measure of energy loss.

Capacitance and Conductance

Fundamentally, dielectric measurements measure the voltage and current between a pair of electrodes in order to determine conductance and capacitance. Conductance is a measure of a material's loss or dissipation of energy, while capacitance is a measure of energy storage for a given potential difference. These values are dependent upon the geometry of the sensor involved in the measurement, the material, and the electrodes. In a capacitor sensor there are two sets of electrodes set a fixed distance apart. A voltage, V, is applied to the capacitor sensor.

In the presence of air, or technically a vacuum, the capacitance of this empty capacitor sensor is Co. Once a material is placed between the electrodes, the applied voltage polarizes the charge distribution of the material. Then the new capacitance increases to C as the result of orientation at the molecular level of polar and ionic species. The dielectric permittivity ε^* of a nonconducting material is simply $\varepsilon' = \frac{C}{Co}$, where there are no mobile ionic species. If the material does contain mobile ionic and/or polar species, which move on the same time scale as the frequency (time = 1/(2π frequency) of the applied voltage, the material has a loss or conductive component, ε''. In this case, the permittivity is "complex," represented by a real ε' and a ε'' loss component due to the polar and ionic conductive aspects of the material.

Dielectric Theory

Typically dielectric measurements are obtained using an in-situ microsensor and a multi-frequency impedance analyzer. The impedance of a material is measured over a range of frequencies, allowing the determination of the material's capacitance (C), energy stored, and conductance (G), loss of energy, due to movement of dipolar and ionic groups. Note, capacitance C and conductance G, the two components of a dielectric measurement, are analogous to the spring and dash pot of a macroscopic mechanical measurement. Knowing the value for Co, the air replaceable capacitance of a dielectric sensor, the material's geometry independent permittivity components, ε' and ε'', can be determined by measuring G and C. This is because the two components, ε' and ε'', are simply geometry independent measures of the real capacitive energy storage component and the conductance-loss component of the material. Since ε' and ε'' are the *geometry independent* manifestations of the material's C and G, then

$$\varepsilon' = \frac{C_{\text{material}}}{C_o} \tag{1}$$

and

$$\varepsilon'' = \frac{G_{\text{material}}}{C_o\omega} \tag{2}$$

The conductance G and thereby ε'' exists when dipolar groups or ionic species are able to move, along with the frequency of the applied field. In general, at low viscosities, low frequencies, and high temperatures, conductance due to ionic species such as salts or ionic ingredients in an uncured coating resin dominates the impedance of a material. In this case, the specific conductivity of the material is

$$\sigma = \varepsilon_o\omega\ \varepsilon'' \tag{3}$$

The value of σ, the specific conductivity, is in units of reciprocal ohm cm and ε_o is the relative permittivity of free space $8.854 \times .\ 10^{-14}C^2J^{-1}cm^{-1}$.

The ionic conductivity of a polymerizing material on a molecular level is a sum of the product of the number of ions present and their respective mobility.

$$\sigma = \sum Ni * \mu_i \tag{4}$$

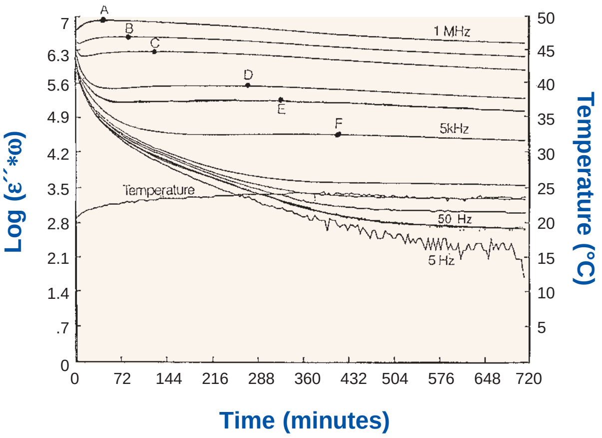
where μ_i is the mean mobility of the ion, and N*i* is the ion concentration of mobile ions. The relationship between viscosity and ionic conductivity has been studied. In general, the ionic conductivity is directly related to the inverse of the viscosity of a fluid by the Stokes Einstein relation.

$$\sigma = \eta^{-a} \tag{5}$$

Ideally, the exponent *a* equals one, but in practice the exponent generally is between 0.7 and 0.9.

Using this relationship it is possible thereby for a dielectric sensor to monitor changes in viscosity by measuring ε''

Figure 2—Decrease in the log of the product of ε'' times the frequency for a marine coating during cure at room temperature. Measurements of ε'' were made at a range of frequencies from 5 Hz to 1 MHz. The series of peaks in ε'' at the various frequencies are each associated with the attainment of a particular value of T_g. The overlapping values of ε'' times frequency values can be used to calculate σ.



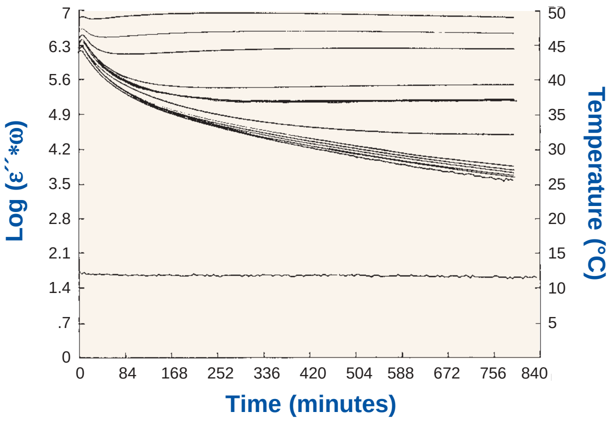
from which σ and the viscosity can be calculated using equations (3) and (5).

EXPERIMENTAL

Dielectric cure monitoring measurements are usually made at frequencies in the Hz to MHz range. They are taken continuously throughout the entire cure process or periodically while the material is in use and converted to the complex permittivity, $\varepsilon^* = \varepsilon'' - i\varepsilon''$. As previously described like rheological measurements, the complex permittivity has two components similar to G* and J* with their real G′, J′ and imaginary G″, J″ components. The real component of ε^* is ε' and its magnitude is a measure of energy storage while the imaginary ε'' is a measure of energy dissipation. Dielectric measurements are made with a commercially available impedance analyzer which creates a frequency dependent electric field, the force. Measurement taking is usually automated by connecting the bridge to a computer. Usually in measuring coatings the coating is put on to a geometry independent inter digitated planar microsensor. This type of dielectric sensor is planar, about 2 × 1 cm in area and several mm thick. A diagram of an inter digitated planer sensor is shown in *Figure* 1.

The micro sensor can monitor changes during synthesis of a coating resin, cure of the coating, and degradation of the coating while in use. First, in order to monitor the progress of a polymerization reaction, a dielectric sensor can be inserted into the reaction vessel during synthesis of the coating resin. Second, the coating resin can be spread as a film onto the planar sensor which is already placed on the application surface. Then the cure of the coating can be monitored under the actual environmental conditions in a laboratory drying oven or in the field environment such as the side of a ship. Finally, the sensor can be cured with the coating on top of it and this cured sensor system placed in the environment either as part of the structure or as a witness coupon to monitor the coating's durability and changes-degradation in its performance properties over time.

Figure 3—Cure of the same coating at 11°C.



Changes in ε' and ε'' occur due to changes in the molecular mobility of dipoles and ions. Thereby, changes in ε' and ε'' are monitoring changes in the state of the material. Clearly, these changes during synthesis, cure, and use must be previously calibrated with conventional laboratory measurements. This step is needed to correlate conventional coating criteria to changes in the magnitude of ε' and ε''.

There are many advantages to ε' and ε'' dielectric sensor measurements once they have been correlated with conventional coating terms and other measurement properties. A typical sensor-bridge PC computer assembly is able to make continuous uninterrupted measurements of both ε'' and ε' over 10 decades in magnitude of ε'' and ε' at all frequencies. Measurements can be made remotely at distances of several hundred feet away from the computer-bridge system. Automated measurements can be made simultaneously on several sensors at differing locations or inserted during application into differing layers of multiple coatings through multiplexing. Thereby, for example, laboratory samples can be compared side-by-side simultaneously under identical ambient conditions of humidity, air flow, light flux, temperature, etc. In the field, cure at different positions can be evaluated. Further, the effect of a second coating on the first can be evaluated using an embedded sensor in the first coating.

A detailed description of the equipment and procedures used to monitor cure has been published.[1,2] A schematic is shown in *Figure* 1. The impedance bridge computer system records frequency dependent measurements of the materials' dielectric impedance as characterized by its equivalent capacitance, C, and conductance, G. These values are used to calculate the complex permittivity, ε', ε'', and σ as previously defined in equations (1–3) over a range of frequencies. Note, σ is the limiting steady state conductivity at those low frequencies where the value of σ is independent of frequency. Thus σ is calculated from those frequencies where ε'' times frequency is constant. This is seen in equation (3).

Both the value of ε' and the loss factor ε'' can have an ionic and dipolar component.

$$\varepsilon'' = \varepsilon''_d + \varepsilon''_1 \qquad \text{and} \qquad \varepsilon' = \varepsilon'_d + \varepsilon'_1 \qquad (6)$$

The dipolar component ε_d arises from rotational diffusion of molecular dipole moments or bound charge. The ionic component ε_1 arises from the translational diffusion of charge, ionic species. The dipolar term is generally the major component of ε' and ε'' of the dielectric signal at high frequencies and in highly viscous media. The ionic component dominates ε' and ε'' at low frequencies, low viscosities, and/or higher temperatures.

The dipolar component generates a peak in ε'' when the time scale of the measurement, which is the reciprocal of the frequency, is comparable to the rotational rate of the dipole's mobility. At this point, $2\pi f = 1/\tau$ where τ is the mean rotational relaxation time. As a coating cures, the time τ for rotation increases. This results in a series of peaks in ε'' in a plot of ($\varepsilon''*2\pi f$). The peaks occur with increasing time at decreasing values of f as the rotational time increases due to the cure advancing. The increase in τ reflects the reaction advancement and the gradual increase in the coating's T_g. Thus, the time of occurrence of a peak in ε'' at a particular frequency monitors the time of attainment of both a particular T_g and a specifc degree of reaction advancement. If the user wants to use in situ remote measurements of ε'' to directly monitor T_g and extent of the reaction, the dielectric output must be correlated with DSC and T_g measurements in the laboratory. This is done by running all three measurements on the material using the same temperature-time cure cycle.

APPLICATIONS

Treatment of Data

Plots of angular frequency times the loss factor where $\omega\varepsilon''(\omega)$ where $\omega = 2\pi f$ make it relatively easy to visually determine when the low frequency magnitude of ε'' is monitoring ionic translational motion and when dipolar rotational motion dominates. A detailed description of the frequency dependence of $\varepsilon^*(\omega)$ due to ionic, dipolar, and charge polarization effects has been previously described.[1-8] If we avoid charge polarization effects, which are usually small at frequencies above 10 Hz, the magnitude of the low frequency overlapping values of $\omega\varepsilon^*(\omega)$ can be used to monitor the conductivity [equation (3)] and the resulting ionic mobility which changes with the viscosity [equation (5)]. The time of occurrence in a peak in a particular $\varepsilon''\omega$ line (i.e., at a particular frequency) can be used to monitor the buildup in T_g and thereby extent of reaction. Together the ionic and dipolar mobility can be used to monitor the occurrence of critical cure points such as dry-to-touch, dry-to-hard, and the achievement of end-use durability.

Figure 2 shows a typical plot of log($2\pi f\varepsilon''$) vs time which is monitoring the polymerization of a commercial Seaguard 151 marine epoxy-polyamide polymer coating during the first 12 hours after the application under normal conditions, i.e., 24°C and 45% RH. The cure is dominated by ionic diffusion for the first 100 minutes at the lower frequencies as indicated by the overlapping $2\pi f\varepsilon''$ lines. Note the changing magnitude of $2\pi f\varepsilon''$ in this region. These overlapping values for differing frequencies can be used to calculate σ [equation (3)] and thereby to monitor the buildup of viscosity [equation (5)]. The rapid decrease in the signal monitors the decrease in the mobility of the ions reflecting a rapid buildup in viscosity. In general, the overlapping $2\pi f\varepsilon''$ lines are proportioned as discussed previously to the inverse of the macroscopic viscosity where $2\pi f\varepsilon'' = A\left(\frac{1}{\eta}\right)^a$. At the time of application, the coating is in the "wet" stage. In this stage the viscosity is very low and solvent evaporation occurs rapidly. Solvent loss from the coating was measured by thermogravimetric analysis (TGA) in a pan of approximately the same film thickness. The "wet" stage of solvent loss was seen in the rapid

Figure 4—Similar measurement of coating cure where a second coat is applied at 144 min into cure.

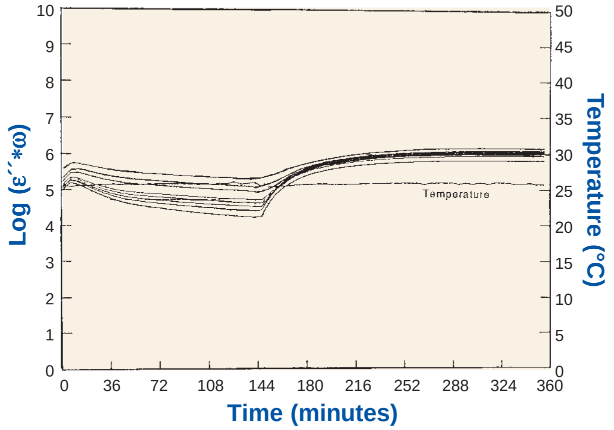


Figure 5—Similar measurements of coating cure where second coat is applied after 26 hr.

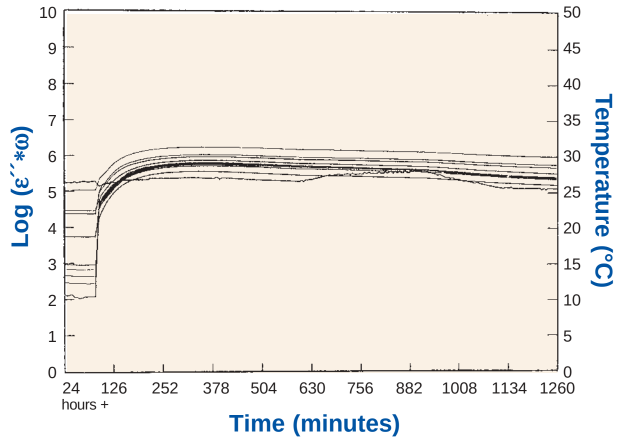


Figure 6—Use of log (ε'' times frequency) to monitor cure of a latex coating at room temperature.

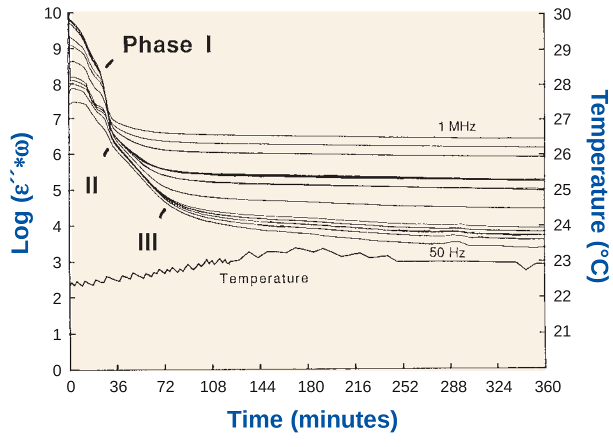


Figure 7—Use of log (ε'' times frequency) at 5 kHz to monitor the rapid cure with UV radiation.

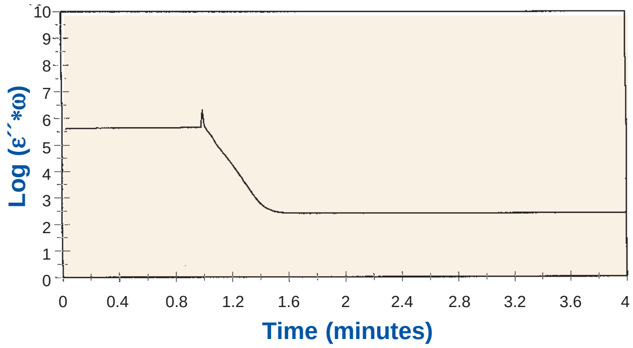
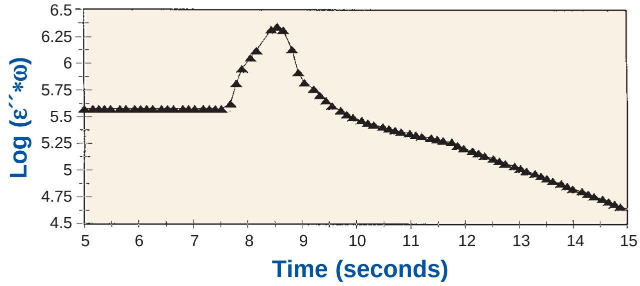


Figure 8—Expansion of *Figure* 7 showing each measured point during application of the UV pulse.



weight loss in the first 144 min. The evaporation slows down markedly after six hours when the change in weight is barely noticeable. Thus, a combination of solvent loss and crosslinking of the resin rapidly increases the viscosity of the film. This process is monitored by the decreasing value of $2\pi f\varepsilon''$ in *Figure* 2. At 100 minutes into the run the coating reaches its set-to-touch point as defined by ASTM D1640-83 guidelines. At this point the sensor output is $\log(2\pi f\varepsilon'') = 4.2$. Using the 50 Hz line to monitor the initial cure, one observes by ASTM criteria that the dielectric sensor calibration value for dry-to-hard occurs when $\log(2\pi f\varepsilon'') = 2.8$. Achievement of these values in the sensor output can be used as an in situ means of detecting and monitoring when dry-to-touch and dry-to-hard have occurred in any environment of differing temperature or humidity.

The high frequency values of ε'' show peaks in *Figure* 2 and monitor the α relaxation process. This is generally a cooperative relaxation process involving many molecules. It is seen both in dielectric relaxation and dynamical mechanical measurements. The time of occurrence of peaks in ε'' at each frequency can be used to monitor the attainment of the T_g value associated with the relaxation peak at that frequency as previously described, as well as the extent of buildup in corresponding final use properties of the curing coating. The peaks in the 5 kHz to 1 MHZ $2\pi f\varepsilon''$ lines, points A–F, indicate the time when the characteristic relaxation time for dipolar relaxation $\tau = 1/2\pi f$ has occurred in the Seaguard 150 coating. Thus, point A, 15 min, marks the cure time when $\tau = (2\pi \times 10^6)^{-1}$ sec and point F, 400 min, marks the time when the rotational relaxation time has slowed to $\tau = 1/(2\pi^* 5 \times 10^3)$ sec. The relationship between the value of τ and the value of T_g or any other use property can be quantitatively determined by correlating measurements of τ with measurements of T_g or the use property of interest. Either using a correlation plot and/or using a mathematical WLF type function such as $1n\ \tau = A/(B - (T - T_g))$, the FDEMS output can be used to continuously monitor the buildup in an end-use property such as T_g in situ under the actual cure conditions.

Monitoring Cure of Coatings

FDEMS output similar to *Figure* 2 can be used to monitor the variation in cure rate with temperature, humidity, airflow, pigment loading, catalyst concentration, thickness, age, batch, etc. For example, it was thought that epoxy-polyamide coatings would cure at temperatures as low as 10°C (50°F), even though the time required to reach a given stage is at least double that required at 22°C.[4] To examine the effects of decreased temperature, the polymerization process was monitored in an environmental chamber, and held at 11°C and 30% RH, for three weeks. *Figure* 3 shows a plot of $\log(e''{*}2\pi f)$ measured with the planar FDEMS sensor. The time to set-to-touch was 420 min. Dry-to-hard occurred at 695 min. The value of $\log(\varepsilon''{*}2\pi f)$ at set-to-touch was 4.1 and at dry-to-hard was 2.9 compared to 4.2 and 2.8 in the 24°C measurement. The drop in $\varepsilon''{*}2\pi f$ is much slower than at 24°C. The sample continued to cure as seen by the continual drop in ε'' even during the third week since application. After 500 hr at 11°C, the 50 kHz line still has not reached the degree of polymerization that the same coating does in 48 hr at 24°C and the rate of cure as monitored by the change in ε'' is relatively flat, indicating a very slow cure rate at 11°C.

These FDEMS results clearly indicate that below 10°C, the curing is greatly retarded and full cure is not achieved. More importantly, this epoxy-polyamide will not reach full cure until the temperature rises. Although the partly-cured film may feel dry, poor resistance to abrasion, moisture, and chemicals results.

It is interesting to demonstrate that the sensor can monitor the extent to which the first coating of the Seaguard epoxy polyamide is softened by the second for varying elapsed times since the initial coat's application. *Figure* 4 displays the softening of the first coating by the second when the second coating has been applied 144 min after the first for the epoxy-polyamide system shown in *Figure* 2. The initial coating's values of $\log(\varepsilon''\omega)$ have only dropped from 5.5 to 4.5. Upon application of the second coating the values rise to 6.0 after 60 minutes as the second coat resoftens the first layer.

Next, the FDEMS sensor is used to examine the extent of softening of the first coat if 24 hr elapse before the second coating is applied. *Figure* 5 shows that after 24 hr, the first coat has decreased its low frequency values of $\log(\varepsilon''\omega)$ to around 2. The application of the second coat on the next day resoftens the first coat and $\log(\varepsilon''\omega)$ returns back to 5.5. Hence 24 hr has little effect on the resoftening ability of the first coat by a second coat for this paint system.

The ability of the FDEMS sensor to monitor cure in a proprietary latex coating is shown in *Figure* 6. Initially, there is a rather rapid decay in the $\log(\varepsilon''\omega)$ overlapping ionic lines from 10 to 8.5 over 30 min. This is followed by a rapid drop of over 2 decades from 8.5 to 6.2 in several more minutes. One can ascribe the initial 30 min to phase I packing of the latex

Figure 9—Comparison of UV cure of three different resin formulations designed to achieve full cure rapidly.

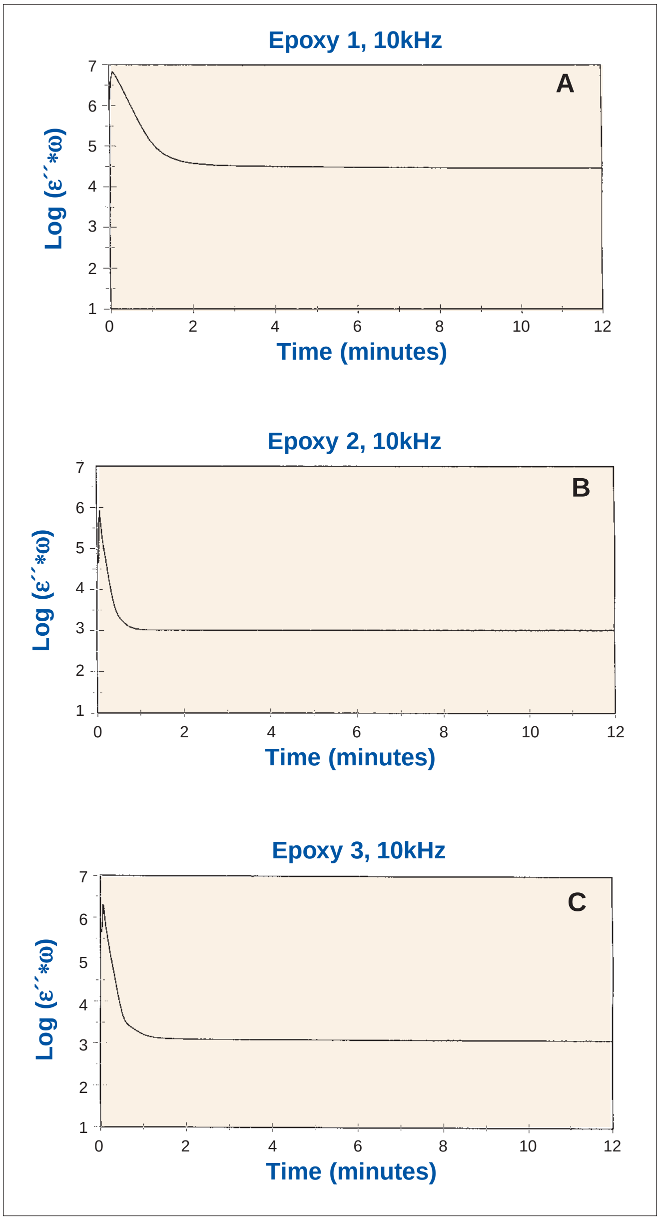
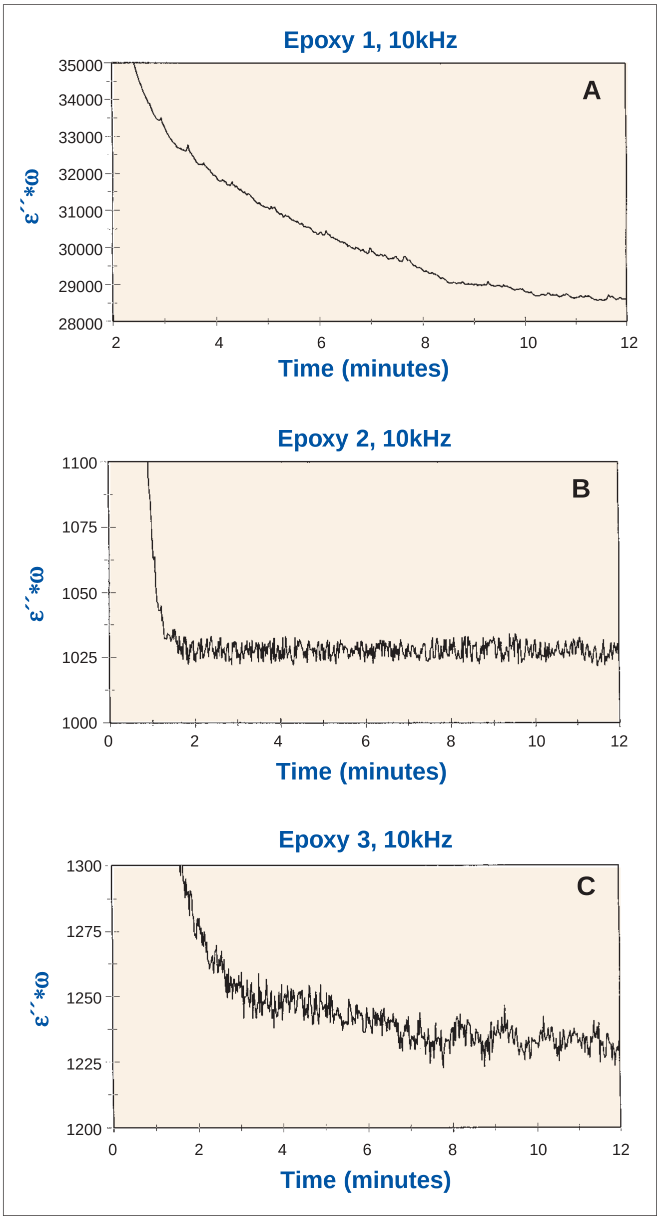


Figure 10—Non log expansion of Figure 10 to evaluate the achievement of full cure in the 2–12 min period after UV irradiation.



spheres. There is a loss of volatiles to the point where the latex spheres touch. After this point water is no longer the continuous medium, the latex spheres rather than the suspending fluid are the conducting medium. This transition point generated the large drop in $\varepsilon''\omega$. The rapid drop is then followed by a gradual decrease in log($\varepsilon''\omega$) which is ascribed to phase II deformation of the latex spheres. There appears to be another shift in the slope around 72 min. This shift in the rate of the drop of log($\varepsilon''\omega$) at 72 min is probably due to the transitions from what is described as a predominately phase II deformation and packing cure process to a phase III autohesion and diffusion cure process.

In Situ, On-Line Monitoring of Rapid Cure

Figure 7 displays the output of a FDEMS sensor which monitored UV cure of a specially formulated epoxy coating.[8] The data is taken at 1 kHz, one frequency, to give the maximum number of data points per minute. The sensor output clearly shows the point of the UV flash and onset of cure about one minute into the display. The output clearly shows the rapid drop in molecular mobility as monitored by ε'', of over three decades during the following 30 seconds.

Figure 8 displays the time interval during which the 5-sec UV pulse occurred. This picture shows the UV pulse was initiated at 7.5 sec. There is a 10-fold increase in the conductivity in the next second due to the formation of the protons generated by formation of the acid catalyst. One second later, at 8.5 sec, the cure reaction is initiated driving the viscosity down. The one-second delay may reflect either the diffusion kinetics and/or the fact that the FDEMS sensor sees the bottom portion of the epoxy

Figure 11—Monitoring the polymerization process of a polyester in the reaction vessel by the correlation of change in ε'' times frequency with the change in the acid number.

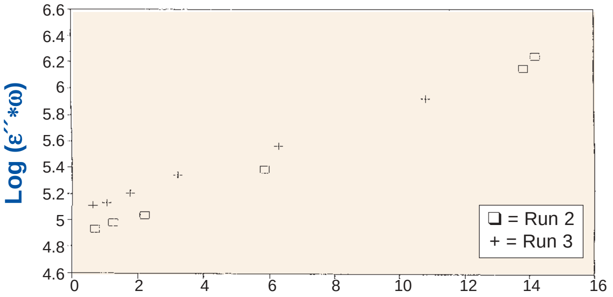


Figure 12—Monitoring the extent of water penetration into the coating when immersed in the 80° ASTM water blister test tank for a resin cured for four days.

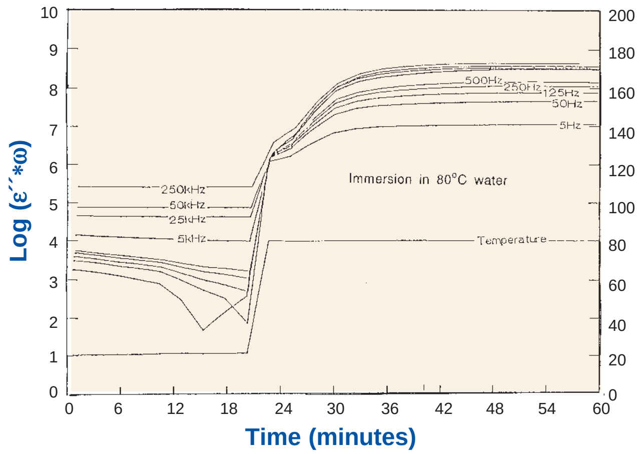
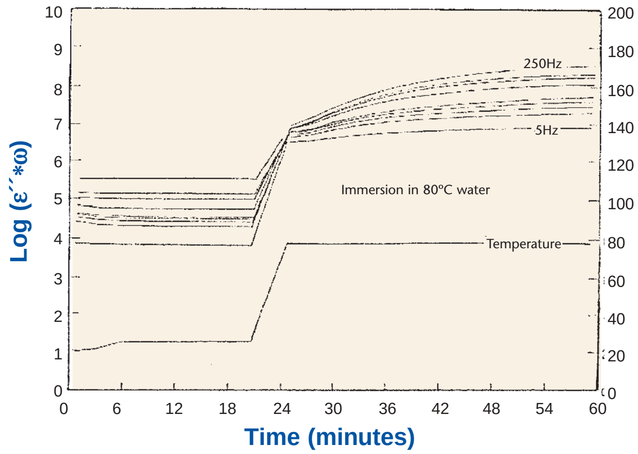


Figure 13—Monitoring the extent of water penetration into the coating when immersed in the 80° ASTM water blister test tank for a resin cured for 14 days.



coating. Throughout the 5-sec pulse, more catalyst is activated while the viscosity is building up. At 12 sec the rate of decrease in conductivity increases and follows a log decay. This marks the end of the pulse, actually 4.5 sec as monitored by the FDEMS system. At this point the sensor is tracking the buildup in viscosity which decreases the translational mobility of the ions.

Figure 9a, an enlargement of *Figure* 7, displays the sensitivity of the FDEMS signal to monitor cure completion over the 0.5–2.5 min time period. This enlargement of *Figure* 7 on a non log scale demonstrates how the output can be used to monitor the approach to full cure as monitored by the approach to a constant value of the mobility, i.e., $\frac{d\varepsilon''}{dt}=0$. *Figures* 7 and 9a show that the major portion of cure is over after about 30 sec, and completely between 1.0 and 1.5 min.

Finally, *Figures* 9 and 10a–c display the ability of the FDEMS output to monitor and compare the cure properties of three different formulations. The three formulations were based on the cycloaliphatic epoxide ERL-4221 sold by Union Carbide. They contained different types and compositions of diols along with the triaryl sulfonium hexafluoro antiminate. Clearly, formulation 2 cures the most rapidly and formulation 1 is the slowest.

Monitoring Polyester Synthesis

The polyester synthesized for this application is used as a precursor for a number of coating formulations. It is a condensation reaction between two diols (neopentyl glycol and trimethylopropane) with two (diacids adipic acid and isopthalic acid). A drying agent was added to remove residual water. The reaction was carried out in the laboratory using a three-liter, fluted, round-bottom flask. The flask was outfitted with a packed column condenser, an air driven stir bar, an FDEMS sensor, and a glass stopper on the flask's flute for addition of ingredients. The same FDEMS sensor was later attached to a steel pipe for insertion into the pilot plant's reactor for monitoring production batches based on the calibration of the sensor output with extent of reaction from the laboratory experiments.

There are two issues of industrial significance which are usually monitored in a polyester synthesis: acid number and the refractive index of the distillate.

The acid numbers of the samples taken during the synthesis are germane because they establish the criteria for the termination of the reaction. In an industrial setting, when a sample has an acid number of a certain value, then the next stage of the synthesis would be undertaken. The problem with this technique is in the timing. Considering the reaction is continuous and the acid number titration technique takes about an hour to perform, any acid number data would be available at least an hour behind the actual reaction. These timing problems are considerable. There is a need to establish an in situ technique for the determination of end point criteria.

To accomplish this, samples were removed from the reactor and their acid numbers determined. Then, this acid number was correlated with the FDEMS sensor data at the time of sampling. The correlation of the absolute, on-line measurement of the ionic mobility, log $\varepsilon''*\omega$, against acid number is shown in *Figure* 11. *Figure* 11 shows that there is a good correlation of the sensor output with acid number. The data were normalized by taking the highest $\log(\varepsilon''*\omega)$ value of the synthesis, called the peak, and dividing the changing $\log(\varepsilon''*\omega)$ values by the value at the peak.

Monitoring Durability

Finally, we examine the ability of the FDEMS sensor to monitor buildup in durability.[9,10] Customarily, buildup in durability of a coating for marine systems is evaluated over a period of weeks and months by immersing the coating in an 80° water bath and monitoring the time to blistering as well as the number and size of the blisters based on the company's ASTM "Standard Method of Evaluating Degree at Blistering of Paints."[11] *Figures* 12 and 13 monitor the coating on a series of standard 8 × 10 inch steel panels over the initial 45 min after immersion in the 80° water bath. The coating which was immersed after four days cure at 24°C, 45% RH shows a rapid and large change in the values of $\log(\varepsilon''\omega)$ within 10 min. The coating which was cured 14 days under these conditions shows a much more gradual change over 45 min. The coating on the fourth day showed blistering based on medium ASTM blister frequency failure criteria on the thirty-eighth day. The 14-day cured coating showed failure on day 58. Clearly the FDEMS sensor can provide a much more rapid (1 hr vs 6–12 weeks) indication of the buildup in durability and end-use properties. The sensor output once calibrated for a particular paint system to the industries standard criteria offers a rapid instrumented indication of the time the coating has attained its desired end use properties.

In other experiments to monitor durability, the FDEMS sensor was placed on the metal liner of a tank and then a protective coating was applied before filling the tank with hydrochloric acid. The sensor displayed a constant reading until the acid had diffused over several weeks' time through the coating under accelerated aging conditions. The sensor's detection of the onset of HC1 reaching the steel housing was verified by inspection of the steel surface at various times.

CONCLUSIONS

It has been shown that dielectric, FDEMS, sensing provides a sensitive method for monitoring the cure of coatings, both for latex systems and epoxy polyamide coatings. FDEMS can track the varying cure rates which result from changing environmental cure conditions. The sensor output provides an instrumental means for monitoring buildup in durability under varying environments such as temperature and/or humidity. Good sensitivity can be attained with these sensor measurement techniques to detect differences in the coating formulation. Dielectric sensing can also be used to monitor reaction advancement during synthesis of a coating resin in the reactor environment. The FDEMS sensor output can monitor the buildup in durability and service life properties and the output can be correlated with ASTM service life tests such as time-to-blister failure. Finally, the FDEMS sensor coating system can be used for detection of end-of-useful life, that is, as a life monitoring sensor for a coating while in use.

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Errata

In the article "Industrial Paint Application Technology: An Overview" (April 2004 CoatingsTech, p. 50), under the section on Powder Coatings, it was stated, "According to Harry Lader . . . This need, combined with the increased cost effectiveness of powder coatings and improved recycling ability, has resulted in a shift to "spray-to-waste" techniques where the guns and lines are blown out after each color is used to clear them for the next." The statement should read: "According to Harry Lader, Ph.D., . . . This need, combined with the increased cost effectiveness of powder coatings and improved booth technology, has resulted in a shift to "spray-to-waste" techniques where the guns and lines are blown out after each color is used to clear them for the next."

JCT CoatingsTech apologizes for any inconvenience.