

MONITORING THE DURABILITY OF PPS, NYLON, AND PVDF USING IN SITU FDEMS SENSING FOR EXTENDED USE IN THE FIELD

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SUMMARY: This report describes recent work on the use of dielectric and tensile-torsional measurements to monitor aging in thermoplastics during use in the field. Particular thermoplastics being studied are polyphenylene sulfide, (PPS), graphite tape, along with polyamide-11, (PA-11), and polyvinyl difluoride, (PVDF), which are used for flexible composite pipe to transport oil-gas in an offshore subsea environment. Current life monitoring work focuses on characterizing the chemical and physical processes occurring during aging, using frequency dependent dielectric measurements, FDEMS, to monitor the aging rate and state of the polymer, and integrating the sensor output with a model for predicting the remaining service life and state of the structure. The model predictions are periodically updated through the in situ online sensing measurements. This report will also discuss work on developing a fundamental understanding of the relationship of the sensor measurement of the ionic and dipolar mobility to the macroscopic properties of polymeric materials.

KEYWORDS: ageing, degradation, sensing, durability, dielectric-mechanical-chemical properties, in situ

INTRODUCTION

The use of polymeric materials in extended use structures such as airplanes, bridges and pipelines, where the expected lifetimes are 20 to 40 years and where failure can be catastrophic, is rapidly expanding. As such, there is a clear need to develop in situ health monitoring capabilities. This paper describes the progress toward the development of a frequency dependent dielectric measurement sensor (FDEMS) which is capable of detecting the change in the physical and chemical state of a polymeric material in situ during use in the field environment and during processing-fabrication.

FDEMS provide a sensitive, automated, in situ sensing technique for monitoring durability and degradation of polymers during use as well during intelligent processing. FDEMS in situ sensing can be designed and calibrated to monitor changes in mechanical service life properties of polymer materials during use in the field environment as well as in processing properties. The FDEMS sensor output already has been shown and used to monitor changes in viscosity, degree of cure and T_g during cure.[1-14] With a proper understanding of the type of polymer and the use environment, the FDEMS sensor can be used to monitor

modulus, maximum load and elongation at break during use. Monitoring degradation in these performance properties is the reversal of monitoring cure during which there is a buildup in mechanical properties. The FDEMS technique has advantages over other monitoring techniques in that it is: nondestructive, sensitive, in situ, remote, and automated.

This paper will discuss recent work on the use of FDEMS to monitor aging during field use of a flexible composite pipe designed to transport oil-gas in an offshore subsea environment. Current life monitoring work focuses are: characterizing the chemical and physical processes occurring during aging; determining the state of the polymer; using FDEMS sensing to monitor the aging rate.

BACKGROUND

Frequency dependent dielectric measurements, made over many decades of frequency, Hz-MHZ, have already been shown to be a sensitive, convenient automated means for characterizing the processing properties of thermosets and thermoplastics.[1-14] Using a planar wafer thin sensor, measurements can be made in situ in almost any environment. Through the frequency dependence of the impedance, this sensing technique is able to monitor changes in the molecular mobility of ions and dipoles. These changes in molecular mobility are then related to chemical and physical changes which occur during use or during processing. The FDEMS techniques have the advantage that measurements can be made both in the laboratory, in situ in the fabrication tool and in situ during use. Few laboratory measurement techniques have the advantage of being able to make measurements in a processing tool and in the field in a composite, in an adhesive bond line, of a thin film or a coating. It can be used at temperatures exceeding 400 EC and at pressures of 100 atm, with an accuracy of 0.1% and a range in magnitude of over 10 decades. It is difficult for most other in the field techniques to attain this level of sensitivity in harsh processing environments.

At the heart of dielectric sensing is the ability to measure the changes at the molecular level in the translational mobility of ions and changes in the rotational mobility of dipoles in the presence of a force created by an electric field. Mechanical properties reflect the response in displacement on a macroscopic level due to a mechanical force acting on the whole sample. The reason why dielectric sensing is quite sensitive is rooted in the fact that changes on the macroscopic level originate from changes in force displacement relationships on a molecular level. Indeed, it is these molecular changes in force-displacement relationships which dielectric sensing measures as the resin cures and ages. They are the origin of the resin's macroscopic changes in mechanical performance properties, during use and processing properties during procedure.

INSTRUMENTATION

Frequency dependent complex dielectric measurements are made using an Impedance Analyzer controlled by a microcomputer.^[1-3] In the work discussed here, measurements at frequencies from Hz to MHZ are taken continuously throughout the entire cure process at regular intervals and converted to the complex permittivity, $\tilde{\epsilon}^* = \epsilon' - i\epsilon''$. The measurements are made with a geometry independent DekDyne microsensors which has been patented and is now commercially available. This system is used with either commercially available impedance bridges or specially built marine environmental bridges for use on offshore oil platforms as well as subsea. The system permits multiplexed measurement of several sensors.

The sensor itself is planar, 2.5 cm x 1.25 cm area and 5 mm thick. This single sensor-bridge microcomputer assembly is able to make continuous uninterrupted measurements of both ϵ' and ϵ'' over

decades in magnitude at all frequencies. The sensor is inert and has been used at temperatures exceeding 400EC and over 60 atm pressure.

THEORY

Frequency dependent measurements of the materials' dielectric impedance as characterized by its equivalent capacitance, C , and conductance, G , are used to calculate the complex permittivity, $\hat{\epsilon}^* = \epsilon' - i\epsilon''$, where $\omega = 2\pi f$, f is the measurement frequency and C_o is the equivalent air replacement capacitance of the

$$\epsilon'(\omega) = \frac{C(\omega) \text{ material}}{C_o}$$

$$\epsilon''(\omega) = \frac{G(\omega) \text{ material}}{\omega C_o}$$

sensor.

This calculation is possible when using the sensor whose geometry is invariant over all measurement conditions. Both the real and the imaginary parts of $\hat{\epsilon}^*$ can have a dipolar and ionic-charge polarization

$$\epsilon' = \epsilon_{d'} + \epsilon_{i'}$$

$$\epsilon'' = \epsilon_{d''} + \epsilon_{i''}$$

components.

Plots of the product of frequency (ω) multiplied by the imaginary component of the complex permittivity $\epsilon''(\omega)$ make it relatively easy to visually determine when the low frequency magnitude of ϵ'' is dominated by the mobility of ions in the resin and when at higher frequencies the rotational mobility of bound charge dominates ϵ'' . Generally, the magnitude of the low frequency overlapping values of $\omega \epsilon''(\omega)$ can be used to

$$S(\text{ohm}^{-1} \text{cm}^{-1}) = \epsilon_o \omega \epsilon_{i'}(\omega)$$

$$\epsilon_o = 8.854 \times 10^{-14} \text{C}^2 \text{J}^{-1} \text{cm}^{-1}$$

measure the change with time of the ionic mobility through the parameter σ where

The changing value of the ionic mobility is a molecular probe which can be used to quantitatively monitor the viscosity of the resin during cure. The dipolar component of the loss at higher frequencies can

$$\epsilon_{d''}(\omega) \text{ dipolar} = \epsilon''(\omega) - \frac{S}{\omega \epsilon_o}$$

then be determined by subtracting the ionic component.

Peaks in $\epsilon_{d''}$ dipolar (which are usually close to the peaks in ϵ'') can be used to determine the time or point in the cure process when the *mean* dipolar relaxation time has attained a specific value $\hat{\tau} = 1/\omega$, where $\omega = 2\pi f$ is the frequency of measurement. The dipolar mobility as measured by the mean relaxation time $\hat{\tau}$ can be used as a molecular probe of the changing value of the glass transition temperature T_g . The time of occurrence of a given dipolar relaxation time as measured by a peak in a particular high frequency value of $\epsilon''(\omega)$ can be quantitatively related to the attainment of a specific value of the polymer's T_g . Finally,

the changing value of $\frac{d\mathbf{e}''}{dt} / \mathbf{e}''$ can be used to monitor in situ during processing the buildup in degree of cure and related end-use properties such as modulus, hardness, etc., during the final stages of cure or post cure in situ during fabrication in the mold. Correspondingly the changes in $\frac{d\mathbf{e}''}{dt} / \mathbf{e}''$ or $\frac{d\mathbf{e}'}{dt} / \mathbf{e}'$ can be related to changes in performance properties during use, that is life monitoring of polymeric structures while in use in the field.

RELATIONSHIP TO MACROSCOPIC PERFORMANCE AND PROCESSING PROPERTIES

The two parameter representation of the magnitude and phase relationship between the sinusoidal force, in this case electric, and the displacement-change in position of charge is the complex electric compliance $\hat{\alpha}^* = \mathbb{A} - i\mathbb{D}$. This quantity is directly analogous to the macroscopic mechanical property compliance $J^* = \mathbb{J} + i\mathbb{D}$ or its reciprocal $G^* = \mathbb{G} + i\mathbb{D}$. For all three complex compliance-modulus quantities ($\hat{\alpha}^*$, J^* , G^*) the real component represents energy storage and the imaginary component, energy lost. Thus measurements of the dielectric properties $\hat{\alpha}^*$ are directly analogous to mechanical measurements.

A major difference is that mechanical properties detect macroscopic displacement, while dielectric properties monitor changes in position, mobility, at the molecular level. The Maxwell- Voigt models are used to relate the frequency dependent macroscopic mechanical measurements of \mathbb{G} , \mathbb{D} , \mathbb{J} and \mathbb{D} to equivalent spring and viscous components. In dielectrics, the classic Debye (with its many modifications) and Einstein rotational and translational flow models (with their size and slip boundary modifications) can be used to relate measurements of \mathbb{A} and \mathbb{D} to conductivity σ and a relaxation time \hat{t} .

For large particles in a small molecule continuum the value of σ is equal to the product of the molecular translational mobility of the charged particles $\hat{\lambda}_i$ times their concentration N_i .

$$\sigma = \sum N_i \hat{\lambda}_i \quad (5)$$

The mobility is directly proportional to the viscosity, where for spherical particles with radius r ; in an ideal fluid.

$$\hat{\lambda}_i = \frac{6}{\zeta} r \quad (6)$$

The value of \hat{t} is proportional to the molecular rotational mobility of dipolar groups, which for spherical shaped particles can be related to viscosity from

$$\hat{t} = \frac{8 \pi r^3 \eta}{kT}$$

A general relation in a wide range of fluid to rubbery materials between translational mobility and viscosity of $\sigma \zeta^{-1}$ has been shown to be valid by several investigators. For polymers in a preglass state through this relationship, σ has been widely used to monitor viscosity during polymer resin cure.^[1-5, 7-14] As a material

goes into the rubbery-glass transition state, the ionic mobility persists and can be used to monitor changes in macroscopic performance properties through laboratory calibrations which relate these changes in molecular translational mobility of charge, σ , to the macroscopic performance property of interest. Once this relation is established in the laboratory, in situ dielectric measurements of ϵ'' and thereby σ can be used to monitor with the calibration, changes in the macroscopic performance property during fabrication or during use in the field.

The general relation between τ and viscosity is also well established in the fluid state where again τ , like σ , is monitoring a molecular viscosity and is proportional, in general, to the macroscopic viscosity as $\tau \propto \eta$. In the gel-glass transition region, it is well documented σ monitors changes in the glass transition temperature, T_g . Exact determinations of T_g from σ can be made using a VTF or WLF type molecular model. Again once the calibration constants relating σ and T_g are made from laboratory measurements, in the field measurements of ϵ'' dipolar and thereby σ can be used to monitor changes in T_g during cure or during use.

Finally the simple absence of change in $\epsilon''(\omega)$ indicates no change in either translational mobility of charge and rotational mobility of dipoles. This is a very strong indicator that there is no change in the material's performance properties. Clearly the structure itself could fail for other reasons than changes in the polymers material properties. A new material could be simply cut by a sharp object as one trivial example.

Similarly, the rate of change in ϵ'' and ϵ' and its changing magnitude for complex rubbery to glassy materials, indicates change in the molecular mobility and hence change in the performance properties. The relation between these changes in molecular mobility and performance properties does not follow a simple single universal relationship. One reason that relating molecular change to macroscopic change is an extremely challenging topic is that the molecular structure of amorphous materials is far more complex than a crystal or gas. Theories of the structure of amorphous gel-solid materials are far from complete. Nevertheless careful laboratory measurement of the macroscopic property changes and the quantities ϵ'' and ϵ' can be made. These changes in ϵ'' and ϵ' due to changes in molecular mobility can then be related to changes in macroscopic force-displacement properties over time for a particular polymer material during use in the field and within given range of environmental conditions close to the laboratory conditions. This parallel between dielectric and mechanical measurements as one example was introduced 30 years ago in the book Anelastic and Dielectric Effects in Polymeric Solids by McCrum, Read, and Williams.

In summary, dielectric measurements are sensitive means to monitor changes in the state of a polymer material or resin both as it ages and during synthesis processing and cure. The reason dielectric sensing is so sensitive is the fact that changes in macroscopic material force-displacement properties such as modulus, elasticity, viscosity, T_g , etc. occur when there are changes in mobility at the molecular level. Dielectric sensor measurements of ϵ'' monitor molecular mobility. Equally important they can be made over many orders of magnitude, in harsh environments, continuously and in situ for polymeric composites, coatings, adhesives, in virtually any environment.

LIFE MONITORING

Three materials have been monitored using dielectrics to detect changes in their performance properties during use in an offshore oil-water environment; a polyamide nylon-11 (PA-11), polyvinyl difluoride (PVDF) and polyphenyl sulfide (PPS).^[15-16] The first two materials are already in use in metal-polymer flexible subsea oil-gas transmission pipes on oil platforms throughout the world. The PA-11 system is used as the oil-gas retention barrier in pipes with operating temperatures up to 80EC. The PVDF is a higher temperature polymer barrier used for oil-gas temperatures up to 130EC. The PPS material is being considered with graphite as an unidirectional tape for use as the axial wrap. It will replace steel bands and create a lighter, higher performance flexible pipe for extremely deep water and arctic environments. As the outer layer of the pipe, the PPS graphic tape is exposed to seawater. The nylon-11 and PVDF, on the other hand, serve as the inner fluid gas barrier and are exposed to the acidic H₂S, water, oil mixture coming up from the ground.

FDEMS sensors were embedded in all three material systems by heating the polymer to its glass transition temperature, placing the sensor between 2 pieces of the polymer and encapsulating the sensor in the center with pressure. The resulting material sensor system was approximately 1 cm thick. The embedded sensor material system and mechanical test dog bones of ASTM D638 specifications were then placed in the following aging environments. Nylon-11: 95% oil, 5% water, pH 4.6, 70E and 105EC. PVDF: 95% oil, 5% water, pH 4.6 130EC. PPS: 100% simulated sea water 90EC. Periodically FDEMS sensor data was taken and pieces were removed for mechanical testing.

LIFE MONITORING – RESULTS

For nylon, polyamide-11, PA-11, Figures 1-2 display the value of ϵ'' multiplied by the frequency at 100, 120, 10³, 10⁴ and 10⁵ Hz versus time in the 105E and 70E oil-water acidic aging environment. The results are on a log scale. They show a rapid very large rise, 10⁴, during the initial days as water diffuses into the polymer. This process occurs over 150 days at 70E, although a large fraction of this change occurs in the initial 30 days. At 105EC, the water diffusion process occurs over the initial 30 days. After water impregnation has occurred at 105E there is a gradual decline in ϵ'' . This drop of ϵ'' reflects the drop in molecular mobility with the gradual aging and approach to embrittlement of the PA-11.

Experimental work in our laboratory and recently reported by others has shown that the nylon is degrading due to hydrolysis.^[17,18] This is accompanied by a sudden loss in the tensile % elongation properties of the PA-11. This drop in almost like new properties to below 30% occurs as a critical molecular weight is approached. This is schematically shown in Figure 3. In the past tensile properties were used to monitor the life of the PA-11. Our work on measuring changes in molecular weight and the associated measurements of viscosity, size exclusion times, light scattering etc. has been shown to be a far better method to monitor the age and remaining life of PA-11 in use in an oil field. The method was subsequently patented as a service-life monitoring method for the PA-11 barrier in oil transport pipes.^[17]

The use of changes in molecular weight and % elongation make it possible to calibrate the long term changes in translational mobility as measured by \bar{D} with both the amount of life remaining (through correlation with molecular weight) and the desired mechanical performance properties (through correlation with % elongation).

By measuring the drop in the ionic translational mobility and the corresponding decrease in the value of \bar{D} , and then correlating this change in ionic mobility and \bar{D} with the molecular weight and % elongation of samples aged in the same environment for the same amount of time, it is possible to correlate and calibrate the change in \bar{D} with the change in molecular weight and % elongation. This is displayed in Figure 4 where the normalized decrease in $\bar{D}(t)/\bar{D}(\max)$ is plotted vs molecular weight. Note dielectric measurements are not monitoring molecular weight but the effect of the molecular weight aging process on molecular mobility. The corresponding % elongation at each time is also plotted. Again note, dielectric measurements are not measuring the macroscopic bulk tensile properties but rather changes in mobility at the molecular level which in time effect the macroscopic % elongation properties. In this manner, dielectric measurements of \bar{D} are able to provide continuous, in situ monitoring in the field operating environment measurements of the % elongation performance properties. Further by knowing the initial molecular weight and the critical value of molecular weight where the % elongation drops, it is possible to relate the \bar{D} correlation measurements of molecular weight to the extent of the aging and fraction of life remaining.

In another sensor service life monitoring experiment, the durability of a polyphenylene sulfide, PPS, graphite tape was examined over a 2 year period in a 90EC salt water environment. Unlike the polyamide PA-11 barrier which contains the oil-water mixture on the inner surface of the pipe, the PPS graphite tape is used as an axial armor wrapped around the outer surface of the pipe to allow the flexible pipe to be used at high pressures. Thus the PPS accelerated study was conducted in 90EC seawater.

Figure 5 shows the FDEMS output of \bar{D} , ionic mobility. Figure 5 indicates an absence of significant change, aging, of the PPS over this 2 year period at 90EC in saltwater. Mechanical tensile tests on the PPS tape torsion tests on the PPS tape and tensile tests on neat PPS all show the PPS has not changed its mechanical properties, in agreement with the dielectric, \bar{D} , ionic mobility measurements.

Finally, Figure 6 displays the FDEMS output of polyvinyl difluoride PVDF as it ages at 130EC in an oil water environment. The drop in molecular mobility over one decade tracks a significant decrease in the molecular mobility of charge within the PVDF. Mechanical measurements show the tensile % elongation drops from around 80% to about 15%. During the 130°C oil-water aging chemical characterization data shows no change in molecular weight but a loss in plasticizer. Similar experiments in aromatic environments show a rise in the FDEMS output. This increase in molecular mobility reflects the strong plasticization of PVDF by aromatic hydrocarbons during which time a corresponding increase in the % elongation properties is observed. The role of deplasticization and replasticization in PVDF is known to be one critical mechanism in its possible failure. More work needs to be done but the FDEMS sensing of molecular mobility does appear to be a good means to monitor these changes in PVDF's mechanical tensile properties.

CONCLUSIONS

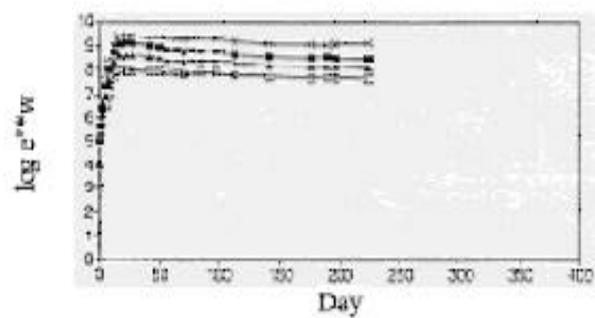
Dielectric properties monitor molecular mobility. This is a critical initial molecular step that causes changes in macroscopic material mechanical properties. Molecular mobility is not directly linked to molecular weight but rather the consequences of the changes in molecular weight as well as changes as plasticizer moves in and out. Both cause changes in molecular weight and plasticization effect molecular mobility first and eventually a change in the mechanical properties. Could changes in the dielectric mobility occur that do not effect or would mislead an absolute interpretation-measurement of aging? Yes. This is why multiple independent sensor measurements are needed.

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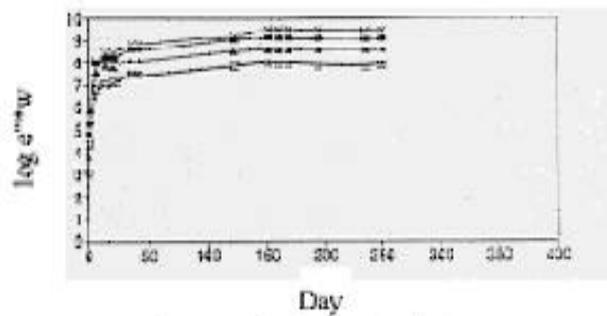
Nylon Sensor in 105C 5% ASTM Oil 95% Water



Frequencies from top to bottom:
100, 10, 1, .12, .1 kHz

Figure 1

Nylon Sensor in 70C 95% ASTM Oil 5% Water



Frequencies from top to bottom:
100, 10, 1, .12, .1 kHz

Figure 2

Percent Elongation vs Mw

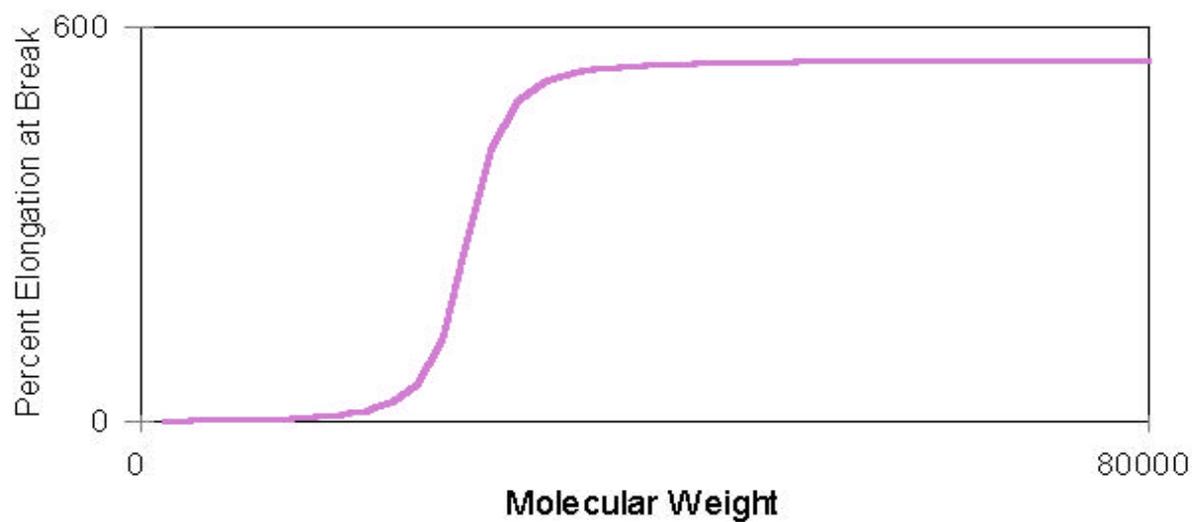


Figure 3

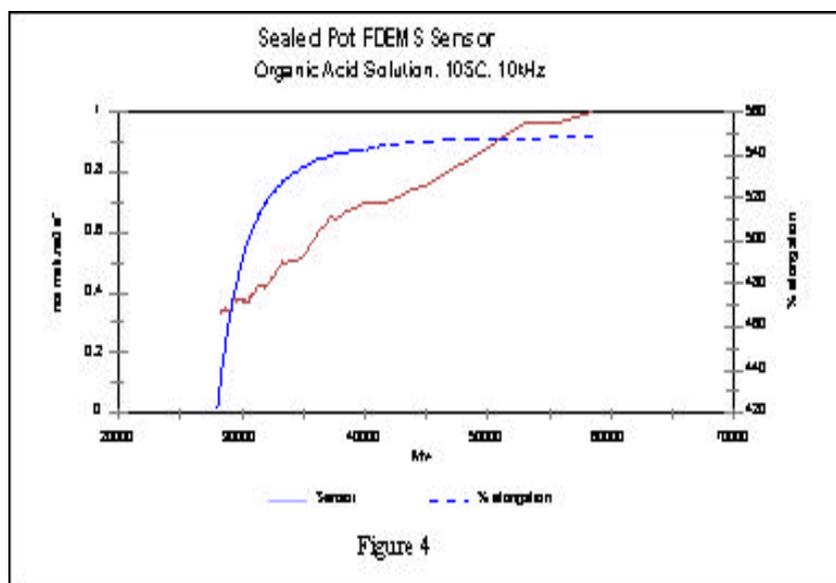


Figure 4

PPS Sensor in 90C Seawater

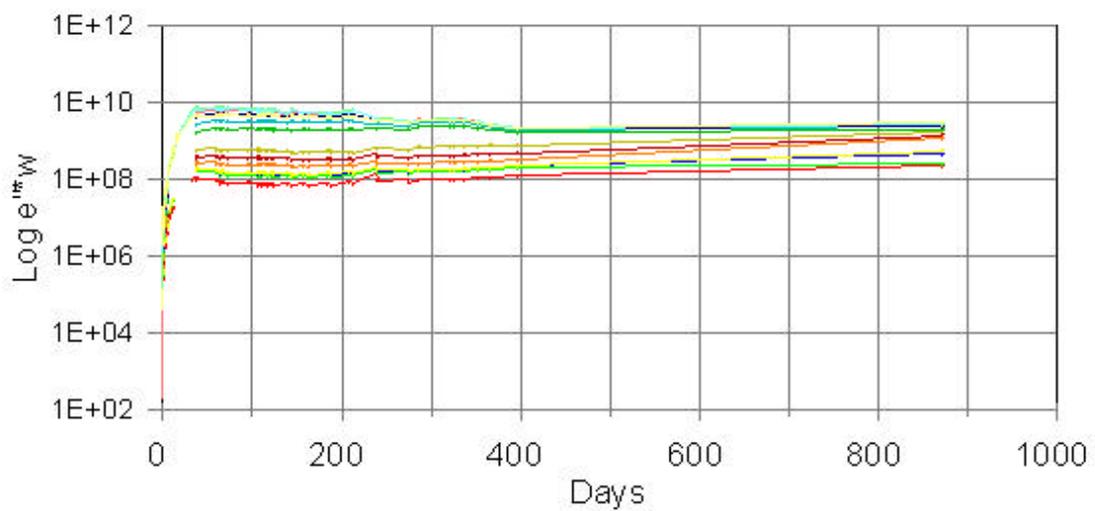


Figure 5

PVDF in 130C 95% ASTM 5% Water

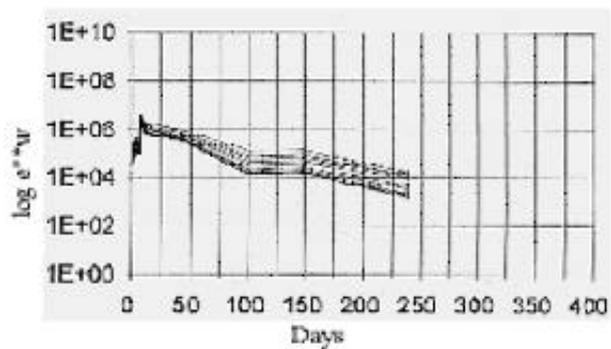


Figure 6