

## Chapter 5

### INTRODUCTION

Composites are finding wider application in aerospace (namely the high speed civil transport (HSCT) airplane), civil infrastructure and ground transportation where both temperature and humidity profiles tend to be very aggressive. As they do so, the need to study the effects of sequencing moisture and temperature on the performance of these materials becomes increasingly important. The effects of temperature and humidity under isothermal aging are well understood and have been studied extensively for composites<sup>5.1-5.3</sup>. However, once a composite nears its saturation plateau the moisture uptake is much less predictable. One such observation is due to a phenomenon called the “reverse thermal effect” (RTE). This effect is essentially the inverse dependence of temperature on moisture absorption near saturation. In other words, some polymers/composites absorb *additional* moisture when they are placed in a *cooler* temperature water bath after they have been *saturated* at a relatively *higher* temperature. Several research groups<sup>5.4-5.6</sup> have reported similar results with epoxy resins and have offered explanations for the effect. Adamson<sup>5.4</sup> suggested a model that is based on free volume and states that free volume of a polymer in the truly glassy state does in fact increase with a decrease in temperature. El-Sa'ad, Darby and Yates<sup>5.5</sup> used the dilute solutions theory and treated water uptake by a polymer as an exothermic process. They went on to use Le Chatelier's principle to determine the trend of equilibrium water content in a polymer with temperature. Zeng and Morgan<sup>5.6</sup> offered an explanation based on moisture induced cavitation for the effect. Although all the above groups have contributed much to the field, the theories are extremely different and no agreement has been reached on this issue. In this paper we offer an explanation based partly on the theory detailed in<sup>5.5</sup>. Since properties of a composite can be highly dependant on moisture content, the RTE becomes particularly important to study, as equilibrium moisture content in a polymer/composite as a function of exposure temperature history becomes unpredictable.

In the past much work has been done in the area of moisture uptake and models including the Fick's law have been applied to try and predict the uptake profile. Shen and

Springer<sup>5.1</sup> used the Fickian model with great success to compute diffusion coefficients and predict uptake profiles for both polymers and unidirectional composites. However Loos et al.<sup>5.2</sup> observed deviations from Fickian behavior for composites under long term exposure. Micro damage that exists and accumulates in the composite during moisture exposure are usually identified as being the cause for this deviation. In fact, Whitney and Browning<sup>5.3</sup> have indicated that fiber architecture has a major influence on the extent of Non-Fickian behavior. Therefore understanding the moisture uptake phenomenon in composites can prove to be a particularly challenging task. The specific mechanisms of micro damage are not completely understood. Recently, Raman spectroscopy has been used to study the stress state in a single fiber composite under the influence of hydrothermal aging<sup>5.7</sup>.

In the present study, attention was focussed first on understanding the effects of moisture on the vinyl ester polymer, before trying to make a transition to composites. Moisture uptake data for the polymer were collected at four different immersion temperatures and Fick's law was used both to compute the diffusion coefficient and to model the uptake process. The temperature dependence of the diffusion coefficients was then plotted using a simple Arrhenius model and the activation energy calculated for the Derakane 441-400 resin.

In order to study the chemical structure both before and after aging (i.e. immersion in water), samples were aged to saturation at 66°C and removed. Fourier transform infrared (FTIR) tests were performed on them. Similar work done on both polyester and vinyl ester by Ghorbel and Valentin<sup>5.8</sup> has indicated a disappearance of bands at 1649 cm<sup>-1</sup>, 985 cm<sup>-1</sup> and 735 cm<sup>-1</sup> for the polyester composite after moisture exposure at 60°C which was attributed as being due to a loss of styrene. In addition, the band intensities at 1300 cm<sup>-1</sup> and 1250 cm<sup>-1</sup> were seen to change. The increase in the 1250cm<sup>-1</sup> peak followed by a widening was thought to be the formation of a phenol δ(OH) because of hydrolysis. A similar decrease in styrene content was also seen in the case of the polyester resin, but no indications of hydrolysis were observed. Similar work performed on the vinyl ester system indicated changes that were difficult to quantify for the resin. In the case of the composite, significant hydrolysis was observed through changes in the shape of the peak at 1450cm<sup>-1</sup>, which was attributed to a stretching

vibration of the  $\nu(\text{CO})$  and to the bending of the primary alcohol  $\delta(\text{OH})$ . In addition, a dehydration reaction following hydrolysis was observed above 3000 hours of exposure at  $60^\circ\text{C}$  through an increase in the intensities of bands at  $1250\text{cm}^{-1}$  and  $950\text{cm}^{-1}$ .

In addition to FTIR, dynamic mechanical analysis (DMA) tests were also performed to analyze  $T_g$  (glass transition temperature) as a function of moisture content. This was attempted to assess if there was a substantial change in  $T_g$ , which might in turn have implications on  $\alpha$  (coefficient of thermal expansion) for the polymer. Mijovic' and Lin<sup>5,9</sup> observed changes in  $T_g$  of almost  $100^\circ\text{C}$  during moisture uptake in the case of TGDDM/DDS epoxy. The change in glass transition temperature was explained in terms of two theories, the lubricity theory and the gel theory. Yet, another polymer plasticization theory was offered by Kessenikh et.al.<sup>5,10</sup> based on concepts such as intrabundle and interbundle plasticization. The plasticizer that causes intrabundle (molecular) plasticization enters the crosslinked regions of the polymer, swells it and reduces the glass transition temperature. The interbundle plasticization stays outside the highly crosslinked regions and has little effect on the glass transition of the polymer. In the present system however, small changes in  $T_g$  were observed and the inherently low moisture content was thought to be the cause.

## **MATERIALS USED AND EXPERIMENTAL PROCEDURE**

The resin used for the present research was Derakane 441-400 vinyl ester. The Dow Chemical Company supplied the resin in the form of a clear casting 3.18 mm. thick. Specimens used for the aging study were 40 mm long, 6.54 mm wide and 2.54 mm thick. The specimens were cut and surfaces ground to assure dimensional consistency. The specimens were then dried and placed in a dessicator for one week. Moisture uptake experiments were performed in four Fisher Scientific ovens that were equilibrated at the desired temperatures. Specimens were placed in small vials and then placed in the oven. Both oven and water temperatures were closely monitored throughout the test. Periodic weight measurements were made by removing the specimens from the vial, patting them dry and weighing them on a Mettler AE200 microbalance. Before the samples were weighed, they were kept on the table for five minutes in order to allow the sample to cool

down. Data collection was rapid initially in order to help determine the diffusion coefficient and were then spaced out as saturation was being approached.

Strongwell supplied an E-glass/vinyl ester composite. This is a commercially pultruded product marketed under the name EXTREN<sup>®</sup>. The lay up consists of alternating layers of both unidirectional rovings as well as continuous fiber random mat. The surfaces have a nylon chopped fiber veil cloth. The composite specimens were 152 mm long, 25.4 mm wide and 3.18 mm thick. The dimensions were so chosen in order to perform quasi-static tension tests. The specimens were aged in a large beaker filled with water, placed on a Corning stirrer/hotplate. An Omega temperature controller controlled the temperature of the water. Weight measurements were made in a similar manner as mentioned above.

Dynamic Mechanical Analysis (DMA) tests were performed on the neat resin using a TA Instruments model number 950 instrument. The tests were performed in flexure mode at 1 Hz. The temperature ramp was from 35°C to 165°C at a heating rate of 1°C/min. Several tests were run under different conditions however the one mentioned above gave the cleanest data in terms of signal noise. Samples with dimensions mentioned above, were transported in their environments and were removed only at the time of testing.

Fourier Transform Infrared (FTIR) analysis were performed on the neat resin films both before and after aging. The tests were run on a Nicolet Impact Model 400 instrument and multiple scans were taken on the material.

Quasi-static tension tests were performed using an Instron testing machine. Specimens with sandpaper at the ends were gripped in screw operated grips and tested at a crosshead speed of 1.5 mm/sec. An extensometer was used to measure strain. The extensometer was fastened to the specimen via rubber bands. Computer controlled data acquisition was used to collect the data. No mechanical tests were performed on the neat resin.

## **RESULTS AND DISCUSSION**

The results in the following sections will be divided into three broad categories, (i) Derakane 441-400 vinyl ester resin, (ii) CH<sub>3</sub>-GMA model resin, and (iii) EXTREN<sup>®</sup>

composite. This is done in order to assure clarity in presentation of data and to focus on the different tests that were performed on them and the results obtained therefrom. The topic of moisture absorption in a composite is not straightforward; complications by poor interfaces between fiber and matrix, residual stresses that are created during manufacturing, voids that tend to exist in almost all composites, reinforcement architecture and lay-up make studying the matrix polymer imperative. A thorough understanding and characterization of the polymer will enable us to understand the composite problem better. Before we discuss the specifics of this work, it is important that we appreciate and understand the various regions that are involved during the moisture uptake process in a polymer/composite. There are at least 3 regions that need to be clearly distinguished,

- (i) Initial absorption process, which is linear, is characterized as being a quick process. In terms of diffusion, this is the region during which the concentration gradients are equilibrating and therefore this is a “diffusion controlled” region. Any changes to the environment, for example changing the temperature of the aging water bath will result in a corresponding change in diffusion coefficient and therefore, the rate of uptake will either increase or decrease depending on the direction of temperature change. In terms of free volume, this is a region that is controlled by the “filling up” of the free volume of the polymer. Therefore much of the research papers that focussed on measuring strain during moisture uptake noticed little strain being experienced by the polymer during this region.
- (ii) The second region is the non-linear region in the Fickian uptake curve. This region is marked by the long time equilibration of concentration gradients. The end result is a stage in which the moisture content essentially remains unchanged over a long period of time. This region therefore marks a transition from the conventional diffusion controlled regime to a chemical equilibrium regime. The chemical equilibrium being established between the liquid phase and the polymer. If the chemical structure of the polymer allows for the existence of specific interactions (example hydrogen bonding) with water, then this region becomes extremely sensitive to external features such as temperature.

- (iii) The third region becomes important in the case of composites wherein upon saturation, additional moisture uptake is seen at longer exposure times. At very long exposure times, reinforcements such as glass can start degrading and this could allow room for further discrepancies.

### **Derakane 441-400 Vinyl Ester Resin**

The following are results from various tests performed on the vinyl ester resin. These range from moisture uptake characterization curves to DMA and FTIR.

#### **(a) *Isothermal Water Uptake Studies***

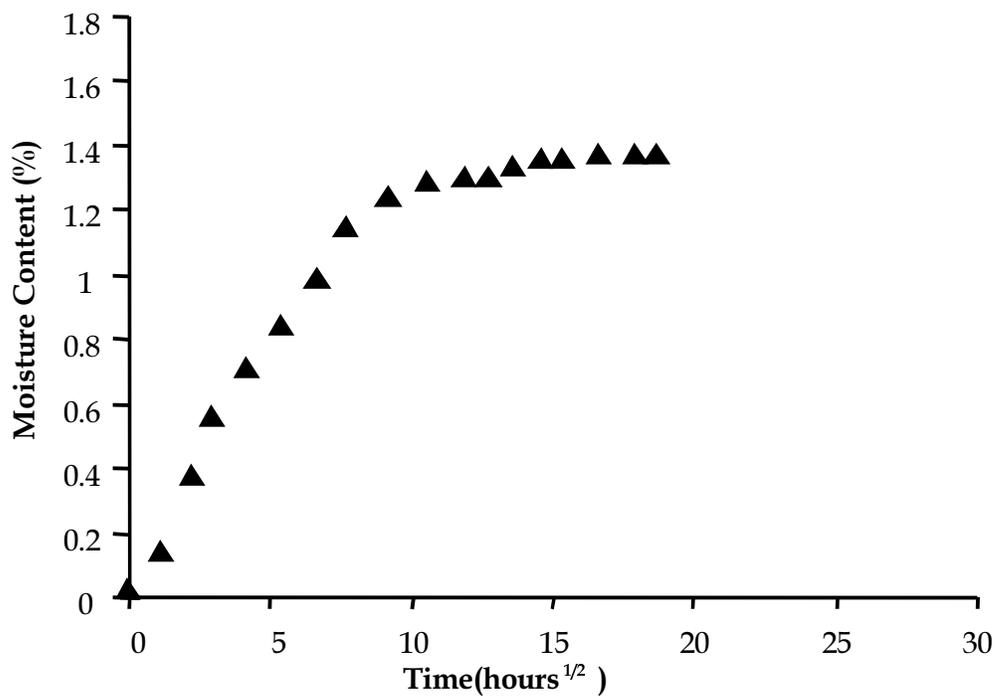
Isothermal moisture uptake experiments were performed on specimens at different temperatures. The specimen dimensions were as mentioned in the previous section. Water uptake was monitored by gravimetric changes in the polymer. Sample weight changes were plotted against time. A typical plot is shown in Figure (1). This is a moisture uptake plot for aging performed at 66°C.

The time axis on the plot has been intentionally plotted as hour<sup>1/2</sup> in order to comply with Ficks law. Three samples were run at this temperature and the standard deviation was found to be insignificant. Moisture content was determined using the following equation

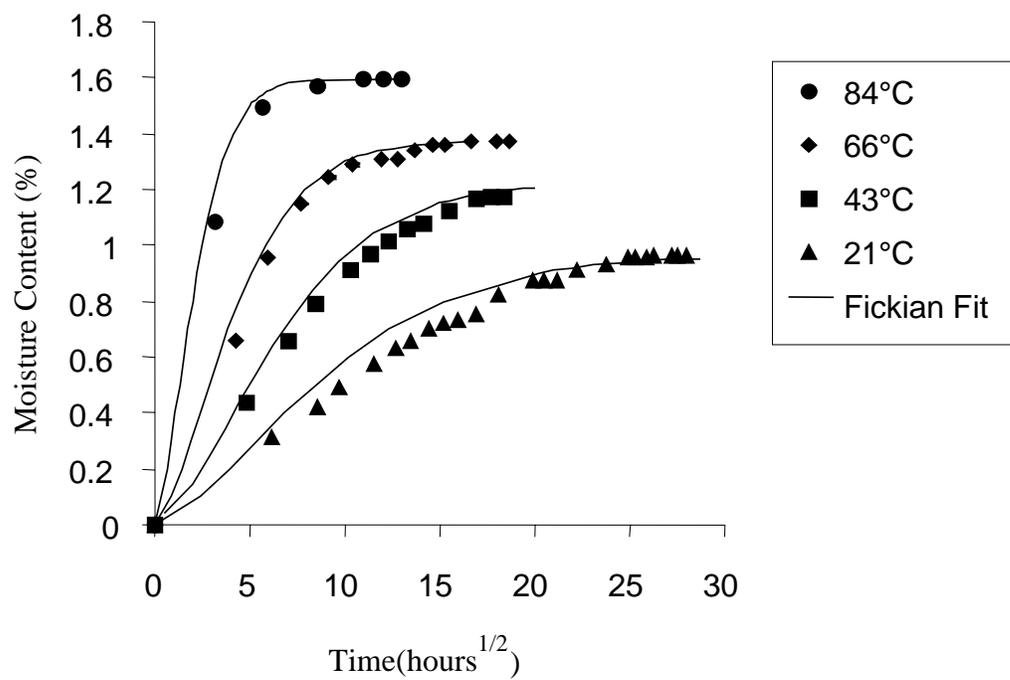
$$M(\%) = \left[ \frac{W - W_0}{W_0} \right] * 100 \quad (1)$$

where M(%), W and W<sub>0</sub> are the moisture content at a given time, weight of the sample at the time of the measurement and initial weight in grams respectively [5.1].

In order to get an estimate of the diffusion coefficient at this temperature as well as diffusion coefficient as a function of exposure temperature, experiments were run at four different temperatures namely 84°C, 66°C, 43°C and 21°C. Figure (2) shows a plot of moisture uptake at all four temperatures. It is evident from the plot that as temperature increases, the rate of moisture absorption increases and so does the maximum moisture content. In order to compute the diffusion coefficient one has to review the transport problem that exists. It is a combined thermal and moisture transport problem involving both Fourier and Fick's law respectively. However upon examination of the two transport processes, it becomes obvious that the thermal process is extremely fast



**Figure 1:** Moisture uptake at 66°C for Derakane 441-400 vinyl ester resin.



**Figure 2:** Temperature dependence on moisture absorption in Derakane 441-400.

compare to the moisture transport problem. Mathematically this is represented as follows [5.1],  $(K/\rho C)/D$  which is the ratio of the thermal to the moisture transportation speeds is approximately  $10^6$ .  $K$ ,  $\rho$ ,  $C$  and  $D$  are the thermal conductivity, density, specific heat and diffusion coefficient respectively. Therefore we tend to concentrate only on the moisture diffusion problem and neglect the temperature transport problem.

If one assumes the diffusion coefficient to be independent of position then one can write a one-dimensional approximation of Fick's second law as follows,

$$\frac{\partial c}{\partial t} = D_x \frac{\partial^2 c}{\partial x^2} \quad (2)$$

where  $c$ ,  $t$ ,  $x$  and  $D_x$  are the concentration, time, position and diffusion coefficient respectively.

In order to compute diffusivity, the semi-infinite solution to equation 2 is used with the following boundary conditions.

$$c=c_i \text{ at } 0 < x < \infty \text{ and } t \leq 0$$

$$c=c_m \text{ at } x=0; x=\infty \text{ and } t > 0$$

The result of the equation is changed to represent mass instead of concentrations by using the following equation

$$m = \int_0^t -AD_x \left( \frac{\partial c}{\partial x} \right)_{x=0} dt \quad (3)$$

where  $A$  is the cross sectional area. The equation in it's final form is as follows

$$F = \frac{W_t - W_0}{W_\infty - W_0} = 4 \left( \frac{Dt}{l^2} \right)^{1/2} \left( \frac{1}{\pi^2} + 2 \sum_{n=0}^{\infty} (-1)^n \operatorname{erfc} \left( \frac{nl}{2(Dt)^{1/2}} \right) \right) \quad (4)$$

The above equation can be used to compute the diffusion coefficient from the slope of the early part of the moisture content (%) versus time<sup>1/2</sup> plot. The initial slope of the curve is then put into the following equation,

$$D = \left( \frac{\pi}{16} \right) \left( \frac{F}{(t^{1/2} / l)} \right)^2 \quad (5)$$

The diffusion coefficients determined for the above mentioned four exposure temperatures are summarized in Table 1.

**Table 1:** Calculated Diffusion Coefficients for Derakane 441-400

Exposure Temperature (in °C)	Maximum Moisture Content (%)	Diffusion Coefficient, $D_z$ (in $\text{cm}^2/\text{sec}$ )
84	1.60	2.03E-07
66	1.37	5.37E-08
45	1.17	2.50E-08
25	0.97	1.18E-08

The above information can then be used to get an activation energy for the diffusion process by using a Arrhenius type equation that describes the temperature dependence of the process. This equation is of the following type,

$$D = D_0 \exp(-E_d / RT) \quad (6)$$

Where  $E_d$ ,  $D_0$ ,  $R$  and  $T$  are the activation energy for diffusion, constant coefficient, universal gas constant and temperature in degrees Kelvin respectively. This equation can then be reduced into a linear form by taking natural log on both sides. The equation then takes the following form and is plotted to acquire the slope and the intercept.

$$\ln(D) = \ln(D_0) - \left(\frac{E_d}{R}\right) \frac{1}{T} \quad (7)$$

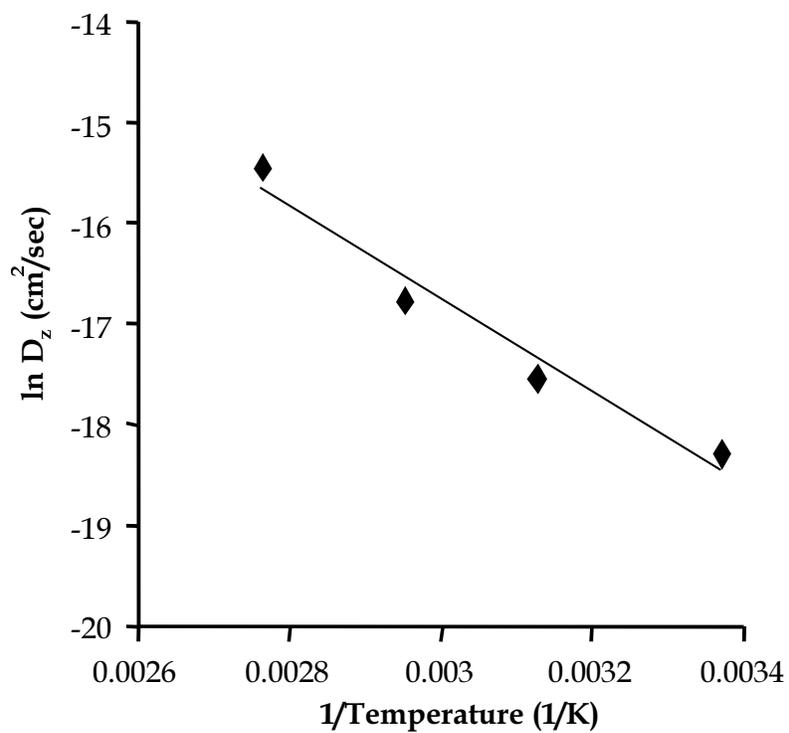
Figure (3) shows a plot of the above equation indicating the expected linear correlation. Note the change in temperature scales from Celsius to Kelvin. The constants of the equation are  $E_d/R=4620$  and  $D_0=0.052$ .

The other solution to Fick's law is one that is suitable for long times. It is particularly useful in trying to predict the uptake profile for a given exposure temperature knowing the diffusion coefficient and the maximum moisture content. The applied boundary conditions are,

$$c=c_i \text{ at } 0 < x < h \text{ and } t \leq 0$$

$$c=c_a \text{ at } x=0; x=h \text{ and } t > 0$$

where  $c_i$ ,  $c_a$  and  $h$  are the initial concentration, instantaneous equilibrium concentration at the surface and thickness of specimen respectively. A solution to the



**Figure3:** Arrhenius plot of diffusion coefficients for Derakane 441-400

above equation can be found in terms of a concentration profile that can then be converted in terms of weight as follows

$$F = \frac{W_t - W_0}{W_\infty - W_0} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{n=\infty} (2n+1)^{-2} \exp\left[\frac{-D(2n+1)^2 \pi^2 t}{l^2}\right] \quad (8)$$

The solid lines in Figure (2) are the predictions based on equation (8) for the uptake at different exposure temperatures. As one can see the moisture uptake for Derakane 441-400 does obey Fick's Law.

An important quantity in the Fick's law is maximum moisture content. Equilibrium between liquid and solid phase is characterized by an equivalence in fugacity.

$$f_l = f_s \quad (9)$$

where  $f_l$  and  $f_s$  are the fugacities of the water in the bulk liquid phase and the water dissolved in the polymer respectively.

The fugacity of the liquid phase can be rigorously calculated from the following equation,

$$f_l = VP \ \varphi_l \ \exp\left(\int_{VP}^P \frac{v_l}{RT} dP\right) \quad (10)$$

where VP is the vapor pressure at the test temperature,  $\varphi_l$  is the fugacity coefficient for the saturated vapor and  $v_l$  is the molar volume of water<sup>5.11</sup>.

At low pressures,  $\varphi_l$  and the exponential term are approximately equal to 1. This then reduces the above equation to

$$f_l = VP \quad (11)$$

The fugacity of the water dissolved in the polymer can be approximated for low moisture contents as a linear function of moisture content and given as

$$f_s = Hx_w \quad (12)$$

where H is a constant that is a strong function of temperature and a weak function pressure and  $x_w$  is the weight fraction of water in the polymer.

Using equation 9 along with equations 11 and 12, we obtain the modified Henry's Law

$$H = \frac{VP}{x_w} \quad (13)$$

The temperature dependence of vapor pressure is defined by the Clausius Claypron equation which is a thermodynamic approximation valid only for temperatures close to the triple point. It is given as follows,

$$p = p^* \exp\left(\frac{-\Delta H_{sub}}{R} \left(\frac{1}{T} - \frac{1}{T^*}\right)\right) \quad (14)$$

where  $p^*$  and  $T^*$  are the triple point reference pressure (i.e. 6.1 mbar) and temperature (273.1 K) respectively.  $\Delta H_{sub}$  is the heat of sublimation (i.e. +51.06 KJ/mole). Values for vapor pressure at the test conditions are then inserted into equation 13 to compute the modified Henry's Law constant,  $H$ . Table 2 lists the values.

**Table 2:** Calculated Henry's Law Constants for Derakane 441-400

Exposure Temperature (in °C)	MaximumMoisture Content (%)	Henry's Law Constant, H (in bar)
84	1.60	75.96
66	1.37	35.51
45	1.17	12.53
25	0.97	4.17

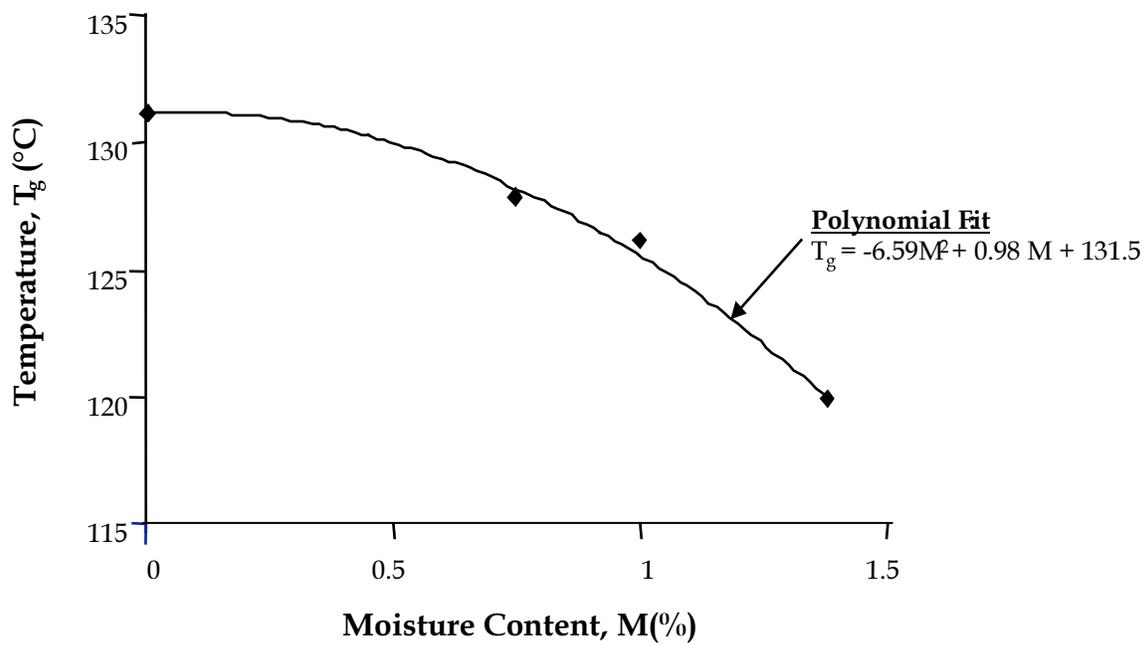
**(b) Physical and Chemical Characterization and Effects of Thermal Spiking**

In order to monitor changes that occur both physically as well as chemically during short term moisture uptake, the glass transition of the polymer was studied as a function moisture uptake. Four samples were aged isothermally at 66°C and were removed periodically and tested in a dynamic mechanical analyzer (DMA). The glass transition temperature was found to decrease with increase in moisture content. Figure (4) shows a plot of the  $T_g$  drop.

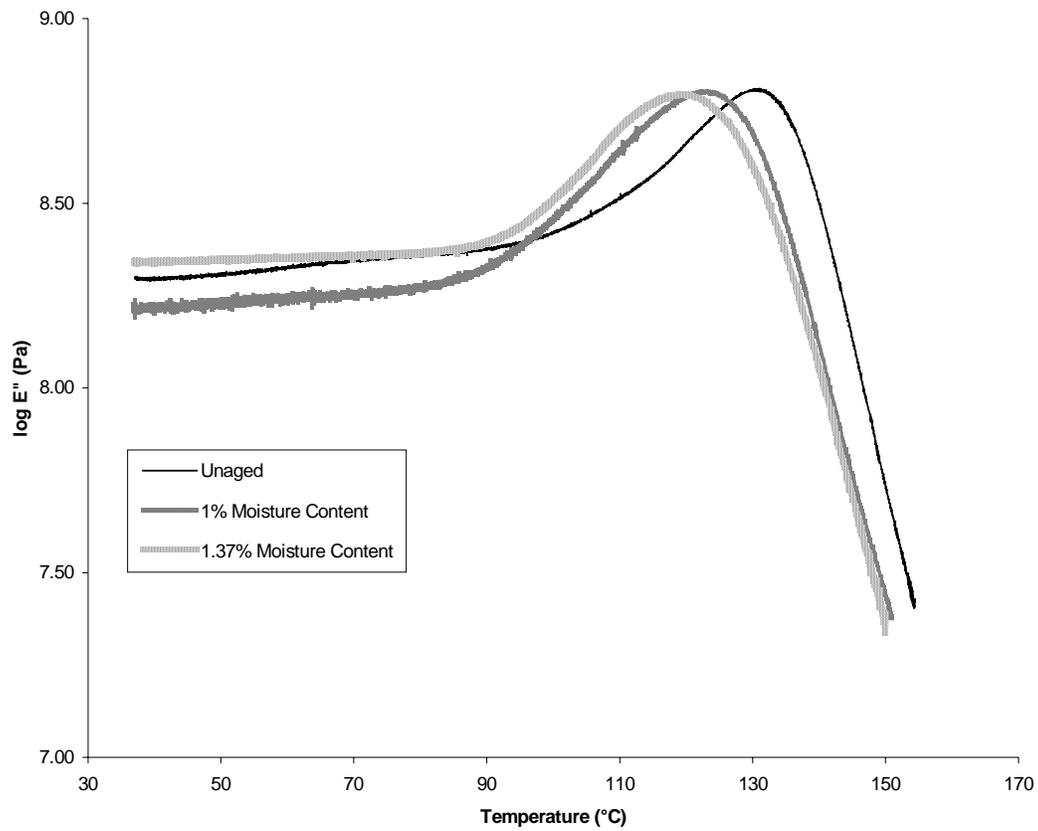
A second order polynomial fit can be applied to the curve as indicated in the plot, however the curve must be interpreted with some caution as the maximum moisture content for this particular experiment (i.e. exposure at 66°C) is limited to 1.35%. The drop in  $T_g$  does seem to be gentle in the beginning and then escalates as moisture content increases. This is in agreement with the popular lubrication and gelation theory for plasticization that has been mentioned in the literature [5.9]. Figure (5) shows the actual loss modulus  $E''$  curves from DMA runs performed at three different moisture contents.

Next, water uptake studies were performed under dynamic aging conditions. A 65°C-room temperature (22°C)-65°C water temperature profile was adopted and changes in temperature were made only when the specimens had reached saturation at the previous temperature. Figure (6) shows the uptake curves for the above specified aging conditions. Although the initial, isothermal 65°C aging process follows the conventional Fickian diffusion profile, there seems to be somewhat of an anomalous increase in saturation water content when the temperature is lowered to 22°C. The other feature that seems to be striking about this second uptake is the very short time required for saturation. The process is however reversible as indicated by the third stage wherein increasing the water temperature back to 65°C results in very rapid desorption down to the previously attained saturation moisture content at 65°C. As indicated by the plot, repeated cycling of the temperature profile bears little or no effect on the saturation moisture contents.

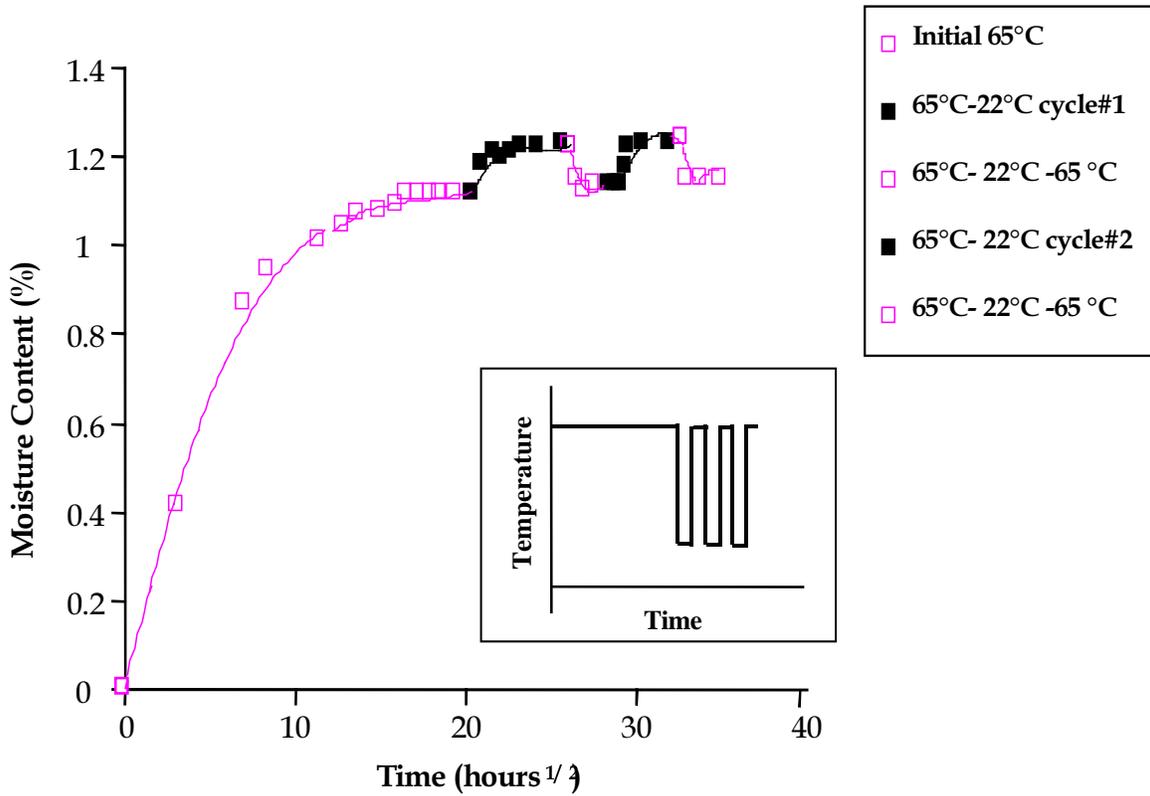
The obvious question that arises is "what really causes this anomalous behavior to occur at saturation, is it diffusion controlled (kinetic process) or does it have something to do with the chemistry of the polymer". It is clear that diffusion alone cannot explain this behavior and so understanding the state of water in the polymer becomes of great importance. In order to check the nature of the interactions of water with the vinyl ester polymer, fourier transform infrared (FTIR) tests were performed on samples that were cast to meet the dimensions mentioned earlier. FTIR runs were made both on the as prepared samples and on samples that were aged isothermally for 192 hours at 66°C. The



**Figure 4:** Changes in glass transition temperature as a function of moisture content.



**Figure 5:** Dynamic mechanical tests indicating change in loss modulus as a function of moisture content. Tests were performed at 1Hz fixed frequency and a heating rate of 1 $^{\circ}\text{C}/\text{minute}$ . Samples were aged to different extents in a 65 $^{\circ}\text{C}$  water bath prior to testing.

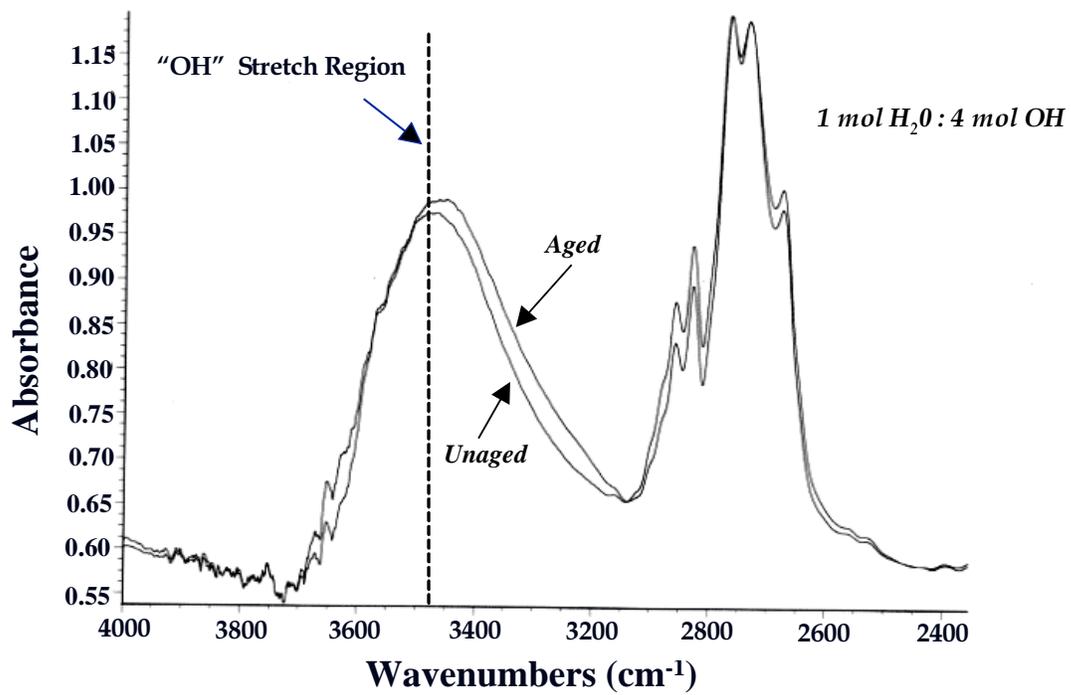


**Figure 6:** Moisture uptake curves for Derakane 441-400 resin subjected to a 65°C-22°C-65°C temperature cycle. Spikes in temperature were made only upon saturation at the previous temperature. Inset details the temperature history. Resin shows the presence of the reverse thermal effect (RTE) under repeated conditions, in this case 2 complete cycles.

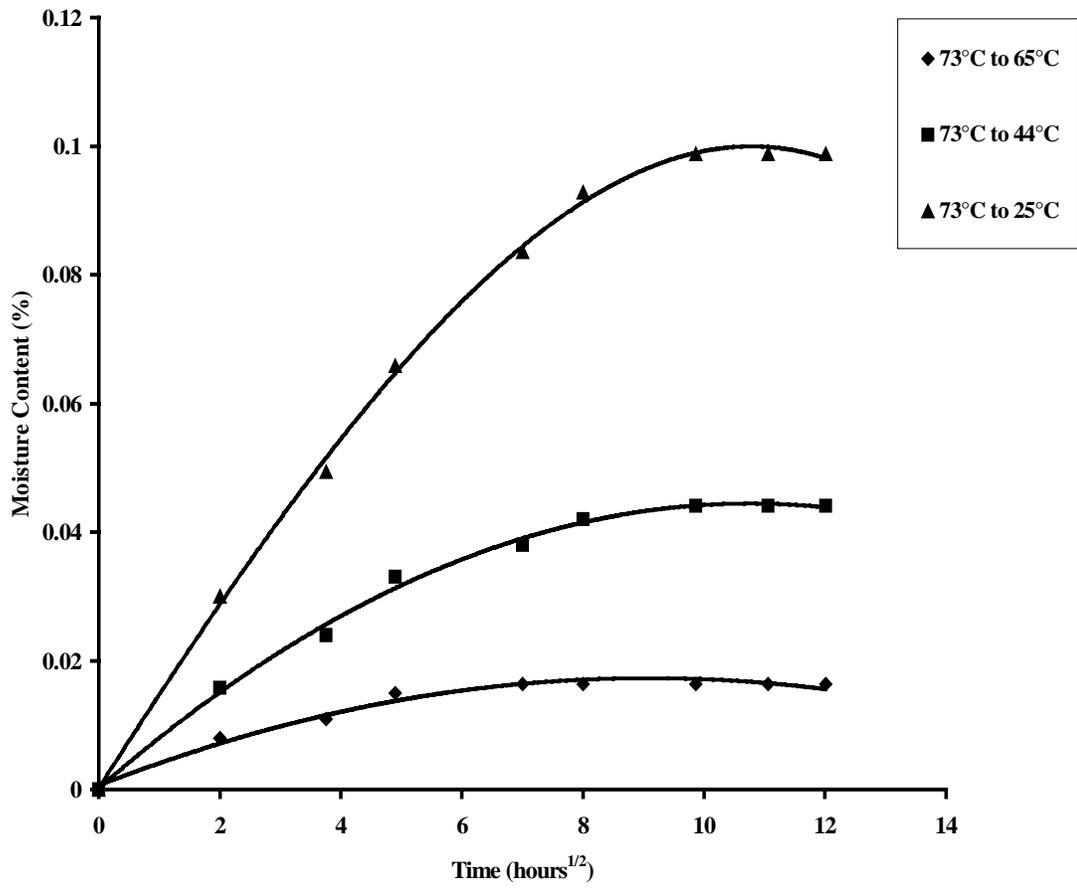
moisture content as measured by weight was approximately 1.3%. Although the overall spectra did not show significant shifting, an area close to  $3000\text{-}3800\text{cm}^{-1}$  did show a slight increase in area. Also, the peak at around  $3500\text{ cm}^{-1}$  corresponding to the  $\text{-OH}$  stretch did show a net change towards a lower wave number. This can be interpreted as being due to interference from the water molecule which, being polar, tends to exert its influence on the pendant  $\text{-OH}$  groups of the vinyl ester molecule. This would then manifest itself as being a stretch in the  $\text{-OH}$  bond resulting in lower frequencies (i.e. lower wave numbers) upon exposure to infrared light. Figure (7) shows the region of interest in the FTIR experiment for both the unaged and the aged samples. The slight shift in the spectra despite the extensive hydrogen bonding capability that vinyl ester has with water is because of two reasons. First, there is only 1.3 percent water in the system even at saturation at  $66^\circ\text{C}$  and secondly because there exists extensive internal hydrogen bonding in the resin by itself. The latter makes it extremely difficult to observe any significant contributions from the absorbed water. In spite of this, Figure (7) elucidates the state of water in the resin system. Existence of hydrogen bonding now makes the saturation moisture content extremely sensitive to exposure temperature. It is also well known that hydrogen bonding tends to become stronger as temperature decreases and vice versa.

This indicates that the ability to hydrogen bond exists in this polymer and that it increases as temperature decreases, which in turn results in an increase in the moisture content. The opposite would be true if the temperature were to be increased. Thus we believe that the reverse thermal effect is a manifestation of a type of specific interaction that the polymer has with water, in this case hydrogen bonding. Similar findings have been reported by Lefebvre et. al.<sup>5,12</sup>.

In order to check this hypothesis, we narrowed our attention down to the thermal spiking part of the experiment and studied the activation energy of the process. Six vinyl ester samples were immersed in a  $73^\circ\text{C}$  water container and allowed to saturate. Upon saturation, they were then divided and two samples each were subjected to three different thermal spikes namely,  $65^\circ\text{C}$ ,  $44^\circ\text{C}$  and room temperature (i.e.  $25^\circ\text{C}$ ). Figure (8) shows the RTE induced uptake plots for the above mentioned samples. Although the y-axis shows initial moisture content as zero, one must bear in mind that all samples have been



**Figure 7:** Fourier Infrared (FTIR) scans on unaged and aged Derakane 441-400 films

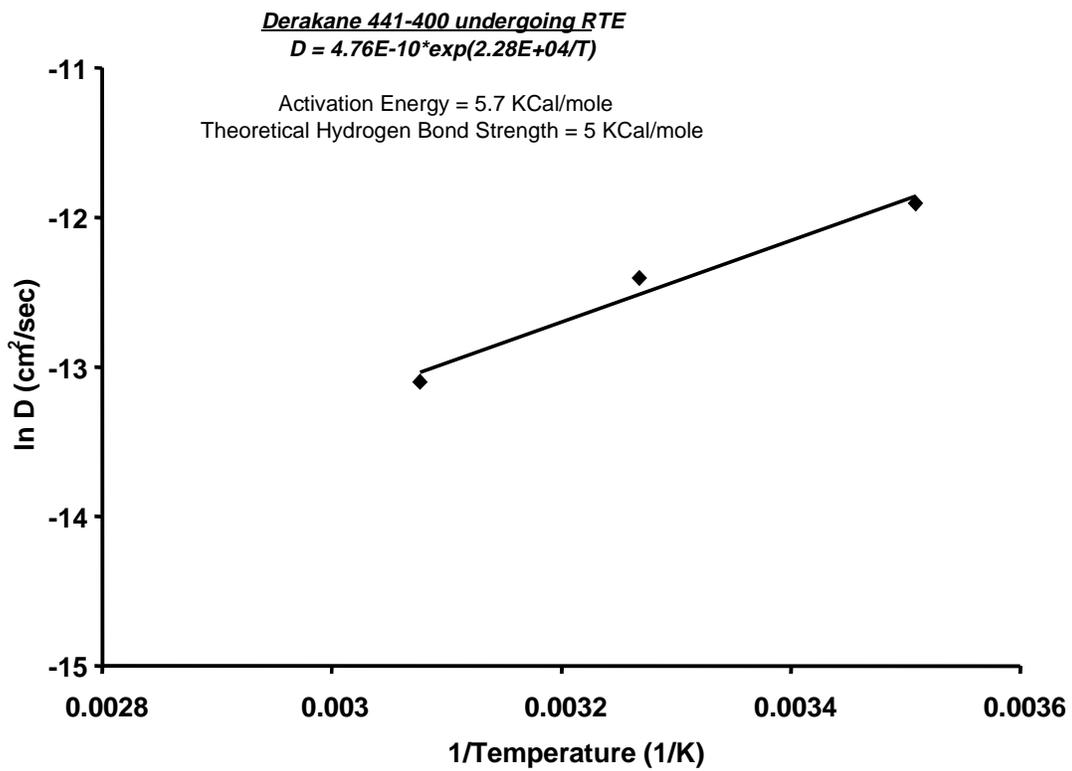


**Figure 8:** Uptake curves for specimens subjected to three different temperature spikes.

saturated in a 73°C water bath. Using equation 5, the diffusion coefficients for the different temperature drops were calculated. They were then used in equations 6 and 7 respectively to obtain the activation energy for the process. Figure (9) shows the Arrhenius plot for the second stage. As shown in the figure the activation energy works out to be 22.8 KJ/mole. A typical hydrogen bonding energy number is 20 KJ/mole. It is therefore quite clear that the chemistry of the vinyl ester does support specific interactions in the form of hydrogen bonding under short term aging conditions and that the above mentioned results support our findings through FTIR. In order to further confirm the hydrogen bonding hypothesis, experiments were performed on a polymer that did not possess any -OH sites. This polymer has been labeled as the Model Resin.

### **Model CH<sub>3</sub>-GMA Resin**

Having gained an understanding of the exact nature of the interactions between water and the polymer under short term exposure times, efforts were directed towards carrying out similar experiments on a model resin system that had virtually the same chemical structure as that of the vinyl ester but lacked the presence of the -OH groups. The chemical structure of such a monomer is shown in Figure (10) and is compared to that of the standard bis-GMA (i.e. vinyl ester resin precursor) monomer. The only structural difference is the presence of the methyl (CH<sub>3</sub>) groups instead of the OH. This unique system presented a simple yet elegant way of reconfirming the hydrogen bonding theory postulated earlier. Figure (11) shows FTIR scans that were run on both the unaged and aged specimens. The testing conditions were similar to the ones explained earlier. As expected the peak in the 3000-3800cm<sup>-1</sup> disappeared due to the absence of the OH groups. However a vertical shift was noticed in the aged specimen and this was likely due to the existence of water in the specimen that does not interact with the polymer. Having eliminated the possibility of hydrogen bonding between the matrix and water, the same cyclic water uptake study namely 65°C-room temperature (22°C)-65°C was performed on the polymer. Figure (12) shows the water uptake curve for the different exposure temperatures. Interestingly, this time when the specimens were transferred from the 65°C to the 22°C water bath, no additional water uptake was noticed. In fact the polymer achieved a new saturation moisture content that was lower than that at 65°C



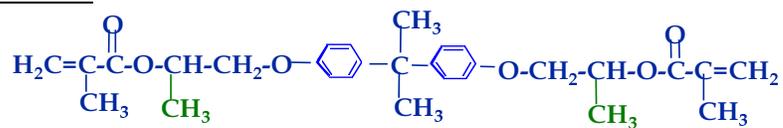
**Figure 9:** Activation energy plot for the reverse thermal process conducted at three different temperatures after pre-saturation of specimens in a water bath at 73°C.

### Bis-GMA



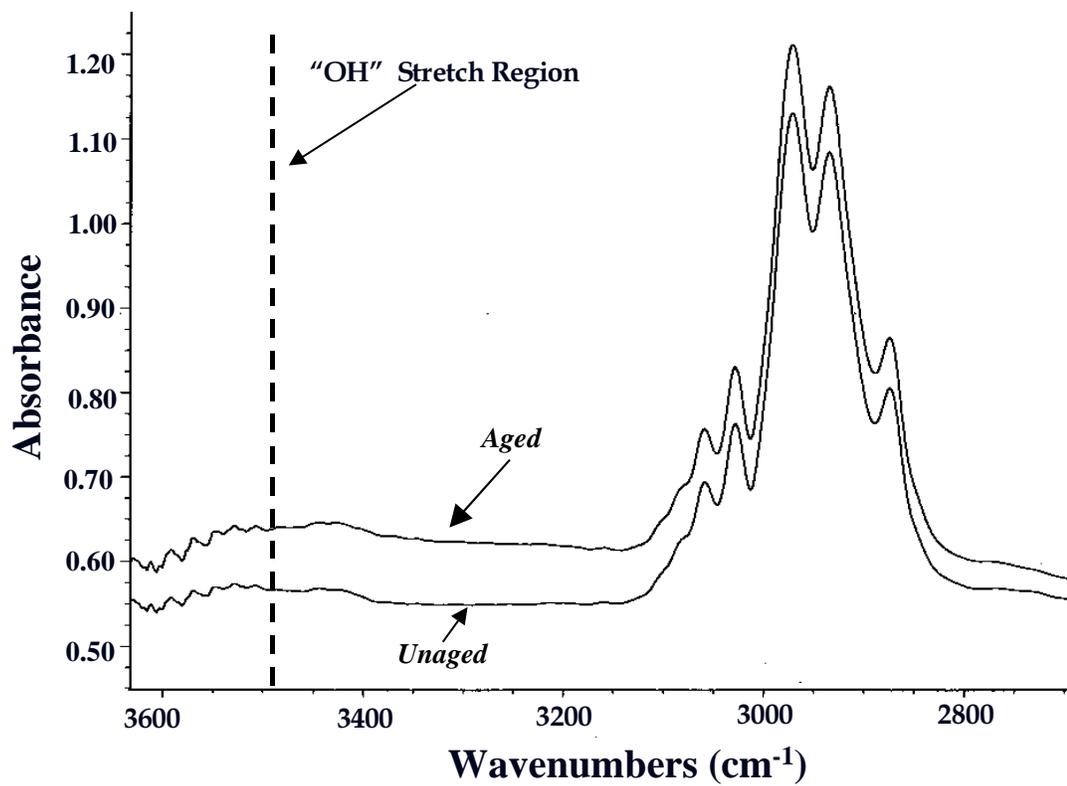
$T_g = -6^\circ\text{C}$  and  $\eta = 1,200,000$  cps at  $25^\circ\text{C}$

### CH<sub>3</sub>-GMA

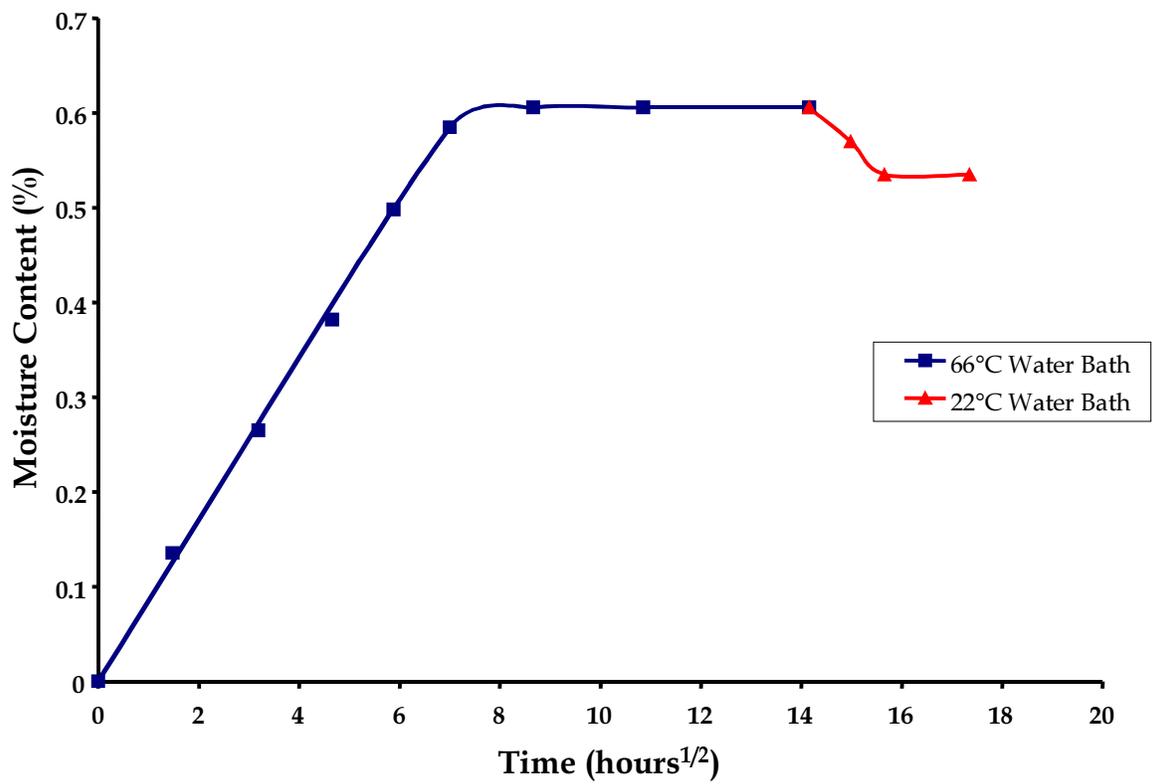


$T_g = -27^\circ\text{C}$ ,  $\eta = 300$  cps at  $25^\circ\text{C}$

**Figure 10:** Comparison of monomer chemical structure between vinyl ester and model resin system, CH<sub>3</sub>-GMA.



**Figure 11:** Fourier Infrared (FTIR) scans on unaged and aged CH<sub>3</sub>GMA films. Aging was performed in a 65°C water bath.



**Figure 12:** Moisture uptake curve for CH<sub>3</sub>GMA resin, subjected to reverse thermal aging conditions. Solid line does not represent a fit and is merely a connection between the data points.

which coincides with previous observations made wherein saturation moisture content increases with increase in temperature.

### **Vinyl Ester/ glass fiber composite, EXTREN<sup>®</sup>**

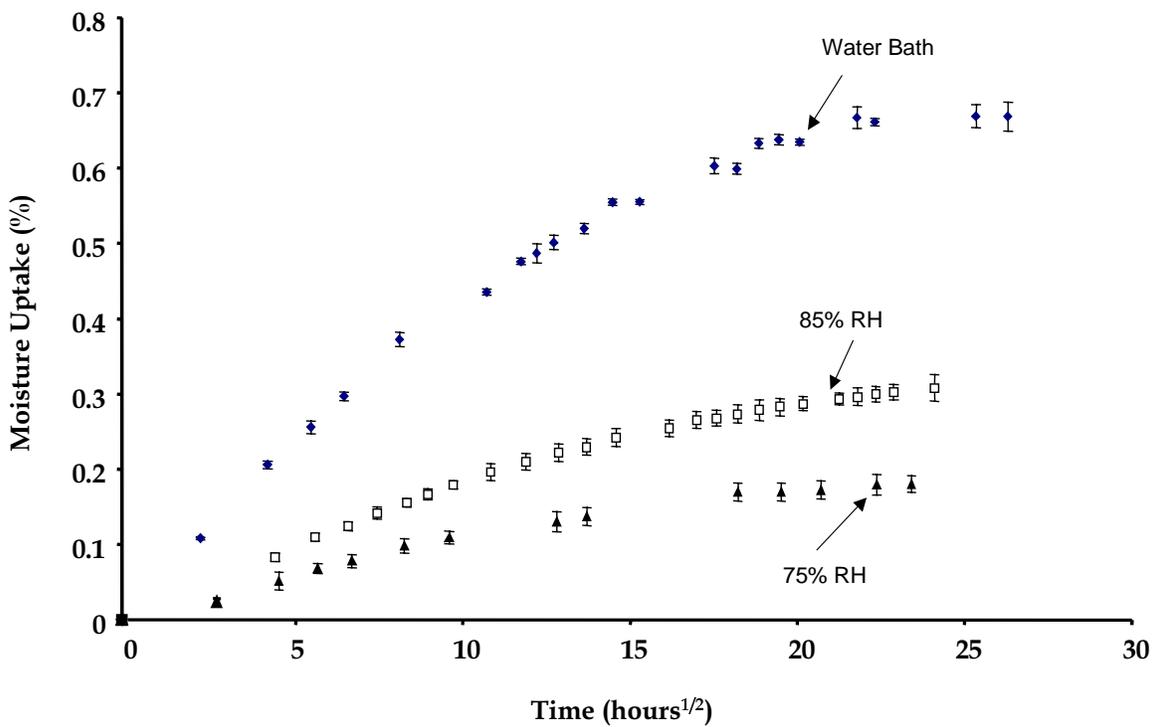
Similar studies were also performed on composites. Efforts were made to not only study the effects of aging temperature on saturation water content but also to study the effects of relative humidity (RH) on the same. Figure (13) shows the uptake curves obtained from three different relative humidities. Clearly both rate of uptake and saturation moisture content depend on the relative humidity of the environment, both increasing with RH. A power law fit was used to characterize the moisture content with RH. The equation is given by

$$M = a (RH)^b \quad (15)$$

where M is the maximum moisture content (%), RH is the fractional relative humidity and 'a' and 'b' are the constants of the fit. For EXTREN<sup>®</sup> 'a' and 'b' work out to be 0.653 and 4.3 respectively. The reverse thermal effect much like the case of the pure resin was found to exist in the composite too. In order to assess the changes in mechanical properties of the composite when subjected to RTE, specimens were removed at different saturation stages and tested in quasi-static tension mode. Figure (14) shows a plot of the tensile strength, stiffness and strain to failure as a function of saturation moisture content. The plot indicates that strength is a strong function of the moisture content and is not dependent on the path by which the moisture content was achieved.

### **CONCLUSIONS**

It has been observed that vinyl ester and polymers with similar chemistry (e.g. epoxy etc.) are capable of entertaining specific interactions when in contact with absorbed water. The specific interaction in this case is hydrogen bonding. The presence of such interactions, can have significant effects on the saturation moisture content especially under temperature sequencing conditions. These interactions can alter the state



**Figure 13:** Plot of moisture uptake in EXTREN<sup>®</sup> as a function of relative humidity (RH) of the environment. Plot indicates both a dependence of rate of uptake and maximum moisture content on the RH.

of the occupied water in the polymer. As long as they remain as interactions, the process is fully reversible. However, if these interactions over long times reduce to chemical reactions, such as hydrolysis, then this process could become irreversible. In the present case of short term aging, the process seemed to be fully reversible thereby indicating only the presence of interactions.

The ability to distinguish between the different regimes of a typical water uptake curve also becomes key in determining how water exists in the polymer and/or composite either during isothermal aging conditions or under temperature sequencing especially near saturation. Since some composite properties were seen to be very dependent on the moisture content, this capability then becomes an extremely useful input for commercial life prediction packages that are used to predict composite life/durability in service applications and environments.