CURE KINETICS AND PHYSICAL AGING OF
AN AMBIENT-CURING EPOXY RESIN

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Abstract
Epoxy resins employed in externally bonded fiber reinforced polymer (FRP) systems used for the repair and strengthening of civil engineering structures are typically cured under ambient temperature conditions. In the present investigation, the cure kinetics of a commercially available ambient-curing epoxy resin was studied using differential scanning calorimetry (DSC). The isoconversion map technique was followed to develop a graphical means of predicting degree of cure for a given temperature history. The isoconversion map was used to conclude that no progress in chemical cure occurred in the resin cured and aged at 22°C beyond the first 7 days of curing. DSC results also established that physical aging took place in the resin and that the rate of physical aging increased with the aging temperature (below the T_g). To study the kinetics of physical aging, specimens were aged at 30°C, 35°C and 22°C beyond the first 7 days of cure at 22°C. The T_g evolution at different aging temperatures was measured using DSC. Based on the T_g measurements, an extent-of-aging parameter was defined to parameterize the extent of physical aging and evolution of the resin towards equilibrium at the aging temperature. This information is useful for understanding the thermomechanical behavior of the epoxy resin.

Keywords: chemical curing, epoxy resin, fiber reinforced polymer, glass transition temperature, isoconversion map, physical aging.

1. Introduction
Fiber reinforced polymer (FRP) composites are widely used in the repair and strengthening of structures [1-2]. These applications typically involve the installation of FRP material using a hand layup technique which is done at ambient temperature. Curing temperature affects the mechanical properties and elevated temperature capability of the epoxy resin used as matrix and adhesive in FRP strengthening systems. The elevated temperature capability of an FRP strengthening system is dependent on the glass transition temperature (T_g) of the resin. Epoxy resin also undergoes a process of slow equilibration when aged at temperature below its glass transition temperature which is known as physical aging. Physical aging also affects the properties of the polymer. The chemical cure kinetics and physical aging thus can impact the
T_g evolution and creep behavior of epoxy resin and FRP laminates. Hence, it is important to understand and model the phenomena of chemical cure and physical aging in the resin system.

The kinetics of polymerization reactions in epoxy resins has been studied by several authors [3-5]. For this purpose, several techniques such as differential scanning calorimetry (DSC), infrared spectroscopy, dielectric spectroscopy and dielectric thermal analysis have been used. Isothermal and non-isothermal DSC are the most commonly used techniques for modeling epoxy cure kinetics. Ruiz et al. [5] describe the “isoconversion map” technique which uses DSC measurements to graphically predict the degree of cure in thermosetting polymers for varied thermal histories. In the present investigation, the “isoconversion map” technique has been adopted to model the cure kinetic behavior of an ambient-curing epoxy resin system used for strengthening existing structures with FRP composites. The phenomenon of physical aging has been comprehensively reviewed and discussed by several authors [6-8]. The term physical aging was first used by Struik [6] to describe the gradual evolution of glassy polymer towards equilibrium. Physical aging affects several experimentally measurable properties such as specific volume, enthalpy, elastic modulus, creep response, and dielectric properties of the polymer. In the present investigation, the objective is to model the advancement of chemical cure and physical aging in the epoxy resin used in FRP repair and strengthening systems.

2. Experimental Program

The experiments for studying kinetics of chemical cure and physical aging were done using DSC on an ambient-curing commercial resin mainly consisting of bisphenol-A epoxide and isophoronediamine curing agent. The experimental procedures are discussed in the following sections.

2.1 Chemical Cure Kinetics

The investigation on cure kinetics was done by using DSC to study the progress of chemical cure by heating freshly mixed epoxy resin at different heating rates. The enthalpy of reaction between epoxide and amine group was measured using DSC scans with different heating rates. By studying the progress of the chemical reaction at different heating rates, a model to predict the degree of cure (α) after a given thermal exposure can be developed. In the present study, Perkin Elmer’s DSC 8500—a power compensated DSC—was used. Large volume stainless steel pans of 60 µL capacity with a lid and rubber seal capable of sustaining high internal pressure were used in the scans. DSC scans were done at 3°C/min, 5°C/min, 8°C/min and 10°C/min from 0°C to 200°C. A specimen mass of around 5 mg was used in all scans.

2.2 Physical Aging Kinetics

To study physical aging kinetics, DSC was utilized. In these experiments, the DSC scans were done at 3°C/min from 0°C to 80°C as the interest was in studying the phenomena of glass transition and endothermic relaxation peak near the T_g to characterize physical aging.

3. Results and Discussion

This section presents the results of the investigation of chemical cure kinetics and physical aging kinetics for the epoxy resin under study.
3.1 Model for Prediction of Degree of Cure

The results for DSC scans on freshly mixed epoxy at rates of 3°C/min, 5°C/min, 8°C/min and 10°C/min are shown in Figure 1. The DSC scans have tilted baselines, as the baselines were not subtracted in the data shown. Figure 1 shows a double peaked cure exotherm for the epoxide-amine reaction. A B-spline function was fitted as the baseline. The area under the DSC curve was calculated by numerical integration to evaluate the heat of reaction at different heating rates. The reaction enthalpy value was, on an average, 312 J/g.

\[ \Delta H = 317.6 \text{J/g} \]

\[ \Delta H = 322.3 \text{J/g} \]

\[ \Delta H = 337.5 \text{J/g} \]

\[ \Delta H = 270 \text{J/g} \]

(a) (b) (c) (d)

Figure 1. DSC scans and heat of reaction value of freshly mixed resin at (a) 3°C/min (b) 5°C/min (c) 8°C/min and (d) 10°C/min.

DSC scans at different heating rates were used to calculate degree of cure ($\alpha$) versus time using Eq. (1)

\[ \alpha(t) = \frac{A_t}{A_{total}} \]

where $A_{total}$ corresponds to the total area under DSC curve and $A_t$ is the partial area under DSC curve up to time $t$. Figure 2 shows the degree of cure versus time plot for different heating rates.
The isoconversion modeling technique reported by Ruiz et al. [5] was followed to develop the model for degree of cure. The method is called the iso-conversion technique because it evaluates points with same degree of cure on DSC curves but at different curing times and heating rates and then uses this data to predict the time-dependent variation of degree of cure at different heating rates or at different isothermal conditions. The time-heating rate function for constant degree of cure ($\alpha$) can be expressed as

$$\log \frac{t}{\phi} = \log \frac{P}{\phi} + Q$$

where $t$ is time (min), $\phi$ is the heating rate in °C/min, and $P$ and $Q$ are two constants that depend on $\alpha$. From the degree of cure versus time plot (Figure 2), curing time values corresponding to constant degrees of cure from 0.02 to 0.95 were picked and are plotted in Figure 3. Equation (3), which is obtained by rearranging Eq. 2, was used to fit the experimentally obtained discrete points (also shown in Figure 3).

$$\frac{t}{\phi} = 10^{P / \phi}$$

The dependence of parameters $P$ and $Q$, on $\alpha$ is shown in Figure 4 and in Eqs. (4a) and (4b).

$$P = 0.08915 + 0.0035 \alpha$$

$$Q = 2.08915$$
Since the thermal scans were done at a constant temperature ramp rate, the temperature ($T$) and heating rate ($\phi$) can be related according to Eq. 5.

$$T = T_i + \phi t$$  \hspace{1cm} (5)

where $T_i$ is the initial temperature, which in the current case is 0°C. Also, using Eq. 3 to eliminate $\phi$ from Eq. 5, cure temperature $T$ (°C) can be expressed in terms of curing time $t$ (minutes).

$$T = (\frac{T_0}{1-\alpha})\alpha 0$$  \hspace{1cm} (6)

Equations 3 and 4 can be used to generate a series of curves relating heating rate and time for fixed values of $\alpha$. Similarly, Eqs. 6 and 4 can be used to generate a series of curves relating cure time and cure temperature for fixed values of $\alpha$. These two set of curves together constitute the isoconversion map, which can be used to predict the degree of cure of epoxy for a sequence of temperature ramp and isothermal dwell. The isoconversion map developed using the technique discussed above is shown in Figure 5. For a given duration of time, the degree of cure can be predicted for a certain temperature ramp rate using the isoconversion curves shown in red (lower and left axes). Likewise, for a given time, the degree of cure can be predicted for a selected isothermal temperature using the isoconversion curves shown in black (upper and right axes).

To draw conclusions regarding the progress of chemical cure of epoxy resin cured and aged at 22°C, a 7-day-old sample was studied using the DSC technique. As seen in Figure 6, the residual enthalpy of reaction was calculated to be 64 J/g. Hence, the degree of cure of the material calculated using Eq. 1 is (312-64)/312 or 0.79. From the isoconversion map shown in Figure 5 it can be seen that practically no change in degree of cure of a material with degree of cure of 0.79 can take place by aging it isothermally below a temperature of approximately 70°C. So it can be concluded that, for a 7-day-old epoxy resin that is cured at 22°C, no progress in chemical cure takes place at room temperature (22°C). Hence, any change in $T_g$ of this epoxy resin with aging time at less than approximately 70°C cannot be attributed to progress in chemical cure.
The usefulness of the isoconversion map can also be realized in developing a post-curing thermal scheme to advance the degree of cure. Consider a case where the degree of cure is to be enhanced from 0.8 to 0.9 by maintaining it isothermally at a temperature for some duration of time. Using Figure 5, it is seen that the resin would need to be subjected to a temperature of 80°C for roughly 2000 minutes (1.4 days) to advance $\alpha$ from 0.8 to 0.9.

### 3.2 Physical Aging Evolution Model

An investigation of physical aging was done on resin cast and aged at 22°C for 10 days and then subjected to 40°C for variable amounts of time. As can be seen from Figure 7, the $T_g$ monotonically increases from an initial value of 44°C to a maximum value of 64°C with aging times of up to 240 hours at 40°C. Over the same exposure period, the residual heat of enthalpy ranges between 66 and 72 J/g, corresponding to a degree of cure between 0.79 and 0.76. The non-monotonic fluctuation in heat of enthalpy is believed to be due to material variability or uncertainty in fitting the baseline to the DSC data. It is therefore concluded that exposure to 40°C did not advance the chemical cure. It can also be concluded by logical extension that no progress in chemical cure takes place for a 10-day-old epoxy resin stored at 22°C. This fact is also supported by isoconversion map predictions discussed earlier.
Since Figure 7 supports the argument that the increase in \( T_g \) occurring with aging at 22°C is due to physical aging and not advancement of cure, a measure of physical aging was sought. Based on DSC experiments, the evolution of \( T_g \) at three different aging temperatures following an initial curing period of 7 days at 22°C was determined (Figure 8). In this graph, the time axis pertains to the time after the initial curing period. Experimental data points for the 22°C case represent the average and range of specimens taken from three different batches of resin tested at the ages of 7, 30, and 100 days. For ease of comparison, all experimental data points were slightly shifted vertically (±2°C) so that the \( T_g \) value at the common starting point (age of 0 days) was equal to the average of all experimental data at that age. Mathematical functions fitted to the data (shown as solid lines in Figure 8) were used to characterize an “extent of aging” parameter, as explained later. Figure 8 shows that the rate of \( T_g \) change in the first week was very low at 22°C in comparison to that at 30°C and 35°C. At temperatures of 30°C and 35°C, the evolution of \( T_g \) decelerated markedly after the first 14 days of aging as the epoxy approached different equilibrium conditions at the two aging temperatures. This is evidence of an accelerated structural relaxation process at aging temperatures approaching, yet still below, the \( T_g \) [6].

According to Eq. 6, an “extent of aging” parameter, \( \beta \), is defined as the ratio of \( T_g \) at the instantaneous time at temperature \( T \) to the \( T_g \) at infinite aging time at temperature \( T \).
The “extent of aging” value of 1 means that the polymer has reached its equilibrium condition at the particular temperature. Smaller fractional values of $\beta$ imply that the polymer is farther away from equilibrium. The mathematical functions for the evolution of $\beta$ with time, $t$, for three different aging temperatures, $T$, are given in Eqs. 7a, b and c.

\[
\beta = \frac{T_g}{T_{g\infty}} \left( \frac{\alpha}{\alpha_{\infty}} \right)
\]

\[\beta_2: c = \frac{40.46 + 11.5^\circ\alpha_{\infty}}{52 + 273} \]

\[\beta_3: c = \frac{55.58^\circ\alpha_{\infty}}{56 + 273} - \frac{15.56}{e^{0.2421t} + 2.73}
\]

\[\beta_4: c = \frac{59.9^\circ\alpha_{\infty}}{60 + 273} - \frac{19.77}{e^{-0.4609t} + 2.73}
\]

Once again, time $t$ in Eqs. (7) pertains to aging time beyond the initial 10 day period at 22°C. From these functions and Figure 8, it can be seen that the projected $T_g$ values at infinite time at aging temperatures of 22°C, 30°C, and 35°C are 52°C, 56°C, and 60°C, respectively.

4. Conclusions

The cure kinetics of an ambient-curing epoxy resin used for infrastructure repair and strengthening was studied using DSC scans on freshly mixed resin at different heating rates. The “isoconversion map” technique was followed to develop a map to predict degree of cure ($\alpha$) for a given thermal history. The isoconversion map was used to conclude that no progress in chemical cure occurs in epoxy resin cured and aged at 22°C beyond the first 7 days of curing. For resin cured 7 days at 22°C, a minimum temperature of 70°C is required to advance the degree of cure. The map is useful in developing a thermal program to post cure the epoxy resin to a desired degree of cure. DSC scans on a 10-day-old resin sample, cured at 22°C for 10 days and aged at 40°C thereafter, showed an evolution of glass transition temperature, $T_g$, from 44°C to 64°C without any change in residual reaction enthalpy, which provides evidence of physical aging without post-curing. To study the kinetics of physical aging, specimens were aged at 22°C, 30°C, and 35°C beyond the first 7 days of cure at 22°C. The $T_g$ evolution at different temperatures was measured using DSC. An “extent of aging” parameter ($\beta$) was defined to characterize the evolution of epoxy resin towards equilibrium at the aging temperature. The projected $T_g$ values at infinite time at aging temperatures of 22°C, 30°C, and 35°C are 52°C, 56°C, and 60°C, respectively.

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6. References


