Correlation of dynamic dielectric properties to reaction kinetics and changing mechanical properties of epoxy resins during cure

Yunfei Wang
College of William & Mary - Arts & Sciences

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CORRELATION OF DYNAMIC DIELECTRIC PROPERTIES TO REACTION KINETICS AND CHANGING MECHANICAL PROPERTIES OF EPOXY RESINS DURING CURE

A Dissertation
Presented to the Department of
Applied Science (Polymer Track)
The College of William and Mary in Virginia

In Partial Fulfillment
of the Requirements for the Degree of
Doctor of Philosophy

by
Yunfei Wang
January, 1997
Approval Sheet

This dissertation is submitted in partial fulfillment
of the requirements for the degree of

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Abstract

The principal objective of this paper is to describe how complex impedance, obtained from frequency dependent dielectric sensing technique, can be used as an effective diagnostic tool for in situ real-time investigation in the fabrication of thermoset structures.

Two epoxy systems (Pr500 from 3M and My720 from Ciba Geigy) with different functionality are characterized in terms of their dielectric, thermal, and rheological behavior. It is observed that there is a one to one relationship between Tg and conversion which is independent of cure temperature. The chemical kinetics of the reaction is satisfactorily described by an autocatalyzed reaction mechanism. The chemical rate constant has the usual Arrhenius form, whereas the diffusion rate constant is assumed to be given by a modified form of the Williams-Landel-Ferry (WLF) equation. The overall reaction rate constant is modeled by a combination of the chemical rate constant and the diffusion rate constant. The ability of the frequency dependent dielectric sensing technique to monitor the progress of curing reaction, build up in glass transition temperature, viscosity and to detect the time of occurrence of gel during thermoset cure are explored. The temperature dependence of the dielectric relaxation time, ionic conductivity and viscosity are described by the modified WLF equation. This approach provides a common framework for describing and comparing different related properties.
CORRELATION OF DYNAMIC DIELECTRIC PROPERTIES TO REACTION KINETICS AND CHANGING MECHANICAL PROPERTIES OF EPOXY RESINS DURING CURE
Introduction

Epoxy Resins have been widely used as a thermoset matrix in fiber reinforced composites because of their excellent physical, chemical and mechanical properties. Information related to the thermal and rheological properties of epoxy resins is a critical need in optimizing process conditions and product quality. The basic parameter governing the state of the material is the reaction conversion. Therefore reliable reaction kinetic models, gel detection models and viscosity models are required by manufacturers. For better control of fabrication processes, it is desirable to monitor thermal and rheological behavior on-line during part fabrication. Since direct, in situ thermal-rheological measurements are not feasible, indirect methods must be used. The recent development of microsensor dielectric measurement systems by Senturia and Kranbuehl is a promising technique. The frequency dependent electromagnetic sensing (FDEMS) technique is able to make continuous uninterrupted measurements of the curing process of a thermoset. In this method, the frequency dependent real and the imaginary parts of the complex permittivity are used to determine the ionic and dipolar mobility parameters. However the conversion of these two parameters to processing properties has not been well
established. The goal of this investigation is to develop a fundamental understanding of the relationships between dielectric properties and macroscopic processing properties such as build-up in viscosity, glass transition temperature and degree of cure. This goal was accomplished by the following steps. First, a series of thermal, rheological and dielectric experiments were conducted individually. Following the experimentation, models and correlations were established with respect to their ionic and dipolar properties. Finally the free volume based WLF equations were extended to connect the degree of conversion and viscosity to dipolar and ionic mobility.
Chapter I

Epoxy Resins

Introduction

The materials used in this study are high performance epoxy resins. In a broad sense, the epoxy resin refers to a chemical group containing one or more epoxides, which are three-membered rings of one oxygen atom and two carbon atoms\(^1\)\(^2\)\(^3\) (Fig 1.1).

\[ \text{Figure 1.1 Epoxide structure} \]

The neat or unreacted epoxy resin is a low molecular weight organic liquid. The polymerization (curing) of the epoxy resin transforms the low molecular weight liquid to a high molecular weight network by adding certain amounts of a catalytic or a curing agent. Generally the curing agents have available active hydrogen atoms. For example, amines, anhydrides, carboxylic...
acids. Epoxy resins offer great versatility. The basic properties may be modified in many ways: by selection of the resin type and curing agents, by the use of modifiers and fillers and by different processing methods. Epoxy resins have been used in a wide range of industries because of their versatility, good chemical resistance, low shrinkage, good electrical insulation and outstanding adhesion. High performance epoxy resins, which can withstand temperatures of 180°C or higher, are primarily used as matrix materials in the aerospace composite industry. An aromatic diamine which acts as a comonomer is used as a curing agent in the polymerization reaction of this type of resin. Epoxies cured with aromatic amines usually have a longer working life than those cured with aliphatic amines.

Mechanism of Epoxy-Amine Reaction

The mechanism of the curing reaction of epoxy resins with diamine has been analyzed and reviewed by many investigators. The simplified versions of reaction possibilities are illustrated in Fig 1.2.

In the primary reactions the amine opens the epoxy ring and then adds onto the oligomer to form a secondary amine and a hydroxyl group. The secondary amine formed can react with other epoxides to form a tertiary amine and a new hydroxyl group. As secondary hydroxyl groups accumulate in the reaction, the epoxy-amine curing proceeds autocatalytically. The hydroxyl...
groups are known to promote the reaction between the amine and epoxy groups through the formation of a trimolecular transition state as shown in Fig 1.3. This allows the epoxide to become more susceptible to nucleophilic attack by the amine curing agents.

Side reactions such as etherification and homopolymerization sometimes occur in certain conditions. However the specific conditions under which these side reactions become important for a specific epoxy-amine cure are still unresolved and have continuously attracted considerable scientific efforts because of the contradictory findings in the literature\textsuperscript{12,13,14}.

In the etherification reaction the secondary hydroxyl groups formed add onto the epoxide oligomers to form an ether linkage and a new hydroxyl group, which is then available for further reaction. Experimental evidence indicates for stoichiometric mixtures of epoxy resins with aliphatic diamines that the cure takes place at room temperature or at low temperatures in a relatively short time. Therefore, the etherification reaction may be neglected\textsuperscript{15}. However, many aromatic diamines are solid and must be melted into the epoxy. They require moderate or higher temperatures to cure. The reactivity of the secondary amine with respect to the primary amine is lower. There is evidence of the presence of the etherification reaction especially when there is an excess of epoxy with respect to amine\textsuperscript{16}.

The homopolymerization of epoxy groups may be initiated by impurities present in the resin. It requires the presence of Lewis bases (i.e., tertiary
amines), inorganic bases (i.e., NaOH), or Lewis acid catalysts (i.e., F₃B complexed with an amine).

(1) \[ \text{Primary amine} + \text{Epoxide} \rightarrow \text{Secondary Amine} + \text{Hydroxyl} \]

(2) \[ \text{Secondary Amine} + \text{Epoxide} \rightarrow \text{Tertiary Amine} + \text{Hydroxyl} \]

(3) \[ \text{Hydroxyl} + \text{Epoxide} \rightarrow \text{Ether} + \text{Hydroxyl} \]

(4) \[ \text{Epoxide} \rightarrow \left\{ \text{ether} \right\}_{n} \]

Figure 1.2 Schematic representation of epoxy-amine reactions

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During the curing process, the state of the resin is transformed from a low molecular liquid to an infinite network of amorphous solid. The basic parameter governing the state of the material is the chemical conversion (degree of cure). Initially, all molecules are finite. As the extent of reaction increases, the glass transition temperature increases due to an increase in the molecular weight. After the gel point (incipient formation of an infinite molecular network), the system is transformed into a rubber state. Finally, the material reaches vitrification (corresponding to the glass transition temperature (Tg) rising to the cure temperature). The material changes into a brittle glassy state.

A schematic representation of a crosslinked epoxy resin is shown in Fig. 1.4.
Fig 1.4 Schematic of a cross-linked epoxy resin.

The properties of a cured epoxy resin depend primarily on the crosslink density (spacing between successive crosslink sites). In general, the higher the crosslink density, the higher the glass transition temperature, the better thermal stability as well as chemical resistance. Factors that control the crosslink density are the chemical structure of the starting materials and the curing conditions. For example, the number of epoxide groups per molecule and the spacing between them, functionality of the curing agent, curing time and temperature control the crosslink density. The curing time and temperature to complete the polymerization reaction depend on the type and the amount of the curing agent.

Experimental Materials

There are two epoxy-amine systems with different functionality used in this study.
I. Pr500 Epoxy Resin

Pr500 purchased from 3M, a premixed one-part high performance resin which combines both the epoxy and curing agent in one part. The resin was created with high viscosity at low temperature so that the components were unable to react\(^\text{18}\). The high performance capabilities of this resin are due to the highly rigid structure of the epoxy oligomer. It is based on the diglycidyl ether of fluorene Bisphenol (Fig 1.5). Four aromatic benzene rings in the backbone enhance the strength and thermal stability. Pr500 contains 30-40% epoxy resin C.A.S # 1675-54-3, 1-10% epoxy resin C.A.S. # 5026-74-4, 35-50% non-MDA-aromatic amine curative, and 10-20% aromatic diglycidyl ether. The exact structures of the epoxy and catalyst or curing agent are not disclosed for proprietary reasons\(^\text{19}\).

Figure 1.5 Diglycidyl ether of fluorene bisphenol

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II. My720 Resin and DDS

The second high performance epoxy system used in this study was composed of Ciba-Geigy's My720 (lot#10109), which contains basically the tetraglycidyldiaminodiphenylmethane molecule (TGDDM), and diaminodiphenylsulfone (DDS) hardener from Aldrich (lot#05706HW) (Fig 1.6). Both ingredients were used as received. The ratio of My720 to DDS was 100/28 by weight (a common ratio used in the composite industry). The mixtures were prepared by mixing the epoxy and amine at room temperature and stirring it by hand for about 3 minutes. Afterwards, the mixture was put in an air-circulated oven set at 120°C and stirred continuously until a clear mixture was formed. The total mixing time was approximately 10 minutes. After that, they were quenched in a freezer (-21°C). The composition of My720 and DDS are listed in Table 1.1

Table 1.1

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Weight (g)</th>
<th>Molecular weight (g)</th>
<th>No. moles</th>
<th>Functionality</th>
</tr>
</thead>
<tbody>
<tr>
<td>My720</td>
<td>10</td>
<td>422</td>
<td>.0237</td>
<td>4</td>
</tr>
<tr>
<td>DDS</td>
<td>2.8</td>
<td>248</td>
<td>.0113</td>
<td>4</td>
</tr>
</tbody>
</table>
Figure 1.6 The structures of TGDDM and DDS
References to Chapter I


18. 3M Aerospace Materials Department, "Material Safety Data Sheet".
Chapter II

The Characterization of Thermoset Cure Behavior by DSC

The thermoset curing process is crucial in making structural composites, coatings and adhesives, etc. The basic parameter governing the state of the material is the chemical conversion. Therefore, knowledge of the kinetic rate of curing and how the curing rate is affected by the curing temperature is very important and useful for predicting the chemical conversion achieved after a cure schedule. DSC is the most powerful tool in studying the reaction kinetics of thermosetting resins. In this investigation both chemical and diffusion controlled reaction kinetic models have been established for Pr500 and My720 systems by the DSC method.

DSC Instrumentation

The differential scanning calorimeter (DSC) is a widely used tool of thermal analysis. It is composed of two calorimetric cells. One is the sample cell, the other is for reference. In DSC measurements the same programmed temperature in each cell is maintained and the difference in the amount of heat
supplied to the sample and reference is recorded. DSC produces a thermogram of the rate of heat absorption, \( \frac{dH}{dt} \), as a function of temperature and time. Thermal events in the sample appear as deviations (a characteristic change in heat flow) from the baseline in either an endothermic or exothermic direction depending upon whether more or less energy has to be supplied to the sample relative to the reference material.\(^1,2,3,4\)

Fig 2.1 Schematic of DSC cells.\(^5\)

DSC provides a wide range of information such as thermal transition temperature, specific heat capacity, heats of transition and reaction, and extent of crystallinity.\(^1,2,3,4\)

Curing Study by the DSC

DSC is the most effective method of obtaining both qualitative and quantitative information during cure. Applying this technique to the polymerization studies of thermosets has been investigated by many...
authors\textsuperscript{6,7,8,9,10,11}. During the thermoset curing process, the low molecular weight liquid is transferred to a highly crosslinked insoluble network by chemical reaction. The DSC thermogram obtained during an isothermal run represents the heat flux, dH/dt, from the sample as it cures. It is assumed that this heat evolution is directly proportional to the reaction rate d\alpha/dt.

\[ \frac{d\alpha}{dt} = \frac{dH}{dt} \] \hspace{1cm} [2-1]

Thus \[ \alpha(t) = \frac{1}{H} \int_{t_0}^{t} (dH/dt)dt \] \hspace{1cm} [2-2]

Thus, DSC can monitor simultaneously the rate of reaction d\alpha/dt and extent of reaction \alpha over the entire course of reaction. However, there are some disadvantages. Near the apparent completion of the reaction at long times heat will be unrecorded if the reaction rate falls below the sensitivity of the calorimeter (it is not sensitive to high degree of conversion after vitrification). Significant instrumentation improvements may be required for high accuracy. In addition, the very small sample sizes used in a typical DSC experiment, although often an advantageous feature, may in certain cases present a sampling problem, such as for composite or foamed materials\textsuperscript{6}.

**Kinetic Analysis Methods**

All kinetic studies start with the basic rate equation that relates the rate of conversion, d\alpha/dt, at constant temperature to some function of the concentration
of reactants consumed after time $t$, $f(\alpha)$, through a rate constant $k$.

$$\frac{d\alpha}{dt} = k f(\alpha) \quad [2-3]$$

where $\alpha$ is the degree of conversion.

There are primarily two categories of kinetic models in the literature. One arises from the reaction mechanism proposed by Horie, et al$^8$. By assuming equal reactivity of primary and secondary amines in the diamine system, an autocatalyzed equation is simplified:

$$\frac{d\alpha}{dt} = (k_1 + k_2 \alpha)(1-\alpha)(B-\alpha) \quad [2-4]$$

where $k_1$ is a rate constant for the reaction catalyzed by groups initially present in the resin, $k_2$ is a rate constant for the reaction catalyzed by newly formed hydroxyl groups, and $B$ is the initial ratio of amine N-H bonds to epoxide rings. This equation does not account for the possibility of other reactions such as etherification as illustrated in Chapter I. There is evidence that etherification becomes significant when there is an excess of epoxy with respect to amine and/or when the cure is performed at higher temperatures.$^{12,13}$ Under these circumstances, the Horie approach is less valid. Recently there have been a few attempts to extend the Horie model to include the etherification reaction in this analysis. However different authors$^{14,15,16}$ have made different assumptions and approximations to study the kinetics and the effects of various parameters on the extent of etherification.

Generally, most commercial epoxies have quite complex curing mechanisms. For a primary reaction alone there are about 12 rate constants
involved (6-non catalytic values and 6-autocatalytic values). Fig 2.2 illustrates the kinetic scheme of the curing of a diepoxy with a diamine based on the assumption that the reactivities of epoxy groups are identical. $A_0$ represents an unreacted diamine. $A_i$ represents a diamine with number $i$ reacted amino hydrogen. "•" represents reacted amino H; "○" represents unreacted amino hydrogen.

Fig 2.2 Reaction scheme for the cure of a diamine with a diepoxide\textsuperscript{16}.

How the kinetic rate constants are related to each other has been the subject of many studies, but the problem is still unsolved. There is general disagreement in the literature concerning the values obtained.

Because of the complexity of the reaction mechanisms, usually only the kinetics of the overall reaction are determined when chemical reactions occur simultaneously. The focus of the other category is on determining whether the overall reaction kinetics can be fitted to general semiempirical kinetic models, although these models do not provide any information about the reaction path.
There are three basic equations used in this category:

(1) A simple nth-order kinetic expression governed by a single rate constant.

\[
d\alpha/dt = k^*(1-\alpha)^n \tag{2-5}
\]

(2) A general expression for an autocatalyzed reaction proposed by Kamal and coworkers\textsuperscript{17,18}.

\[
d\alpha/dt = k^*\alpha_m^\star(1-\alpha)^n \tag{2-6}
\]

(3) An autocatalyzed kinetic equation which accounts for a possible non-zero reaction rate at \( t=0 \).\textsuperscript{19}

\[
d\alpha/dt = (k_1 + k_2\alpha^m)(1-\alpha)^n \tag{2-7}
\]

The nth-order kinetic model failed to depict the auto-acceleration of the curing reaction and the maximum cure rate or the maximum heat evolution\textsuperscript{9}. The autocatalytic kinetic equations [2-6] and [2-7] have been successfully used to describe the curing reactions of both epoxy resins and unsaturated polyesters.

The kinetic parameters have been determined by fitting the experimental rate data to a kinetic model using linear or non-linear least square fitting techniques, or alternatively, by combining the variables so as to produce a linear relationship from which the kinetic parameters could be estimated.\textsuperscript{10,15} There is another method that relies on characteristic features of the exotherm such as the rate at the peak and the \( \alpha \) at the peak\textsuperscript{10,15,20}. For example, the maximum curing rate occurs at the point \( \alpha_{\text{max}} \) which can be solved from equation \( d^2\alpha/dt^2 = 0 \).
When equation [2-6] is used,
\[ \frac{d^2\alpha}{dt^2} = k\alpha^{n-1} - k\alpha^n(1-\alpha)^{m-1} = 0 \] [2-8]
\[ \alpha_{\text{max}} = \frac{m}{m+n} \] [2-9]

Substituting equation[2-9] into equation [2-6] and rearranging the equation, the following relation is obtained:
\[ (d\alpha/dt)_{\text{max}} = k^*m^nn^*/(m+n)^{m+n} \] [2-10]

The parameters of \( m, n \) can be estimated from experimental values of \((d\alpha/dt)_{\text{max}}\) and \( \alpha_{\text{max}} \).

It is well known that the crosslinking reaction can be controlled by different processes\(^{21,22,23}\).

(1) Chemical kinetic control process

The reactivities of functional groups are independent of the size and topology of the macromolecules to which they are bound. Their reactivity may depend, however, on the state of the groups in the monomer units. The chemical kinetics for the reaction can be adequately represented by an Arrhenius type overall rate constant with a single overall activation energy. (The reaction rate constant is temperature dependent and obeys the Arrhenius law.)
\[ k = Ae^{-E/RT} \] [2-11]

(2) Diffusion control

The reaction rate is controlled by segmental mobility. In such a case, at
constant reaction temperature, the reacting system passes through the main transition region. Segmental motions are slowed down. The mobility of the reacting groups is hindered, and the chemical reaction is controlled by these motions rather than by chemical factors. If Tg becomes sufficiently higher than the reaction temperature, the curing ceases due to diffusion control before all functional groups have reacted. Various approaches have been performed in the literature to describe this phenomenon mathematically. According to the generally accepted view of relaxation processes controlled by diffusion of molecular chain segments in the glass transition region of amorphous polymers, the extent of segmental motion can be related to the difference between the reaction temperature and Tg using the theory of glass transition and the Williams-Landel-Ferry (WLF) equation (more details about the WLF equation will be discussed in chapter V). For example, if the reaction is controlled fully by segmental mobility in the glass transition region, the rate constant kd should be equal to

\[
\log k_d - \log k_{dTg} = c1(Tc-Tg)/(c2+Tc-Tg) \tag{2-12}
\]

where \( k_{dTg} \) is the value of \( k_d \) at \( Tc=Tg \).

Gillham et al\textsuperscript{23} used a modified form that includes the absolute value of \( |T-Tg| \) in the denominator which allows for application of this relationship after vitrification (\( Tc<Tg \)) in the following form:

\[
\log k_d - \log k_{dTg} = c1(Tc-Tg)/(c2+|Tc-Tg|) \tag{2-13}
\]

They assumed that \( k_{dTg} \) is constant and \( c2=51.6 \).

22
Martin, et al.\textsuperscript{24,25} modeled the cure-dependent diffusion of epoxy amine resins by the Huguenin and Klein equation based on the free volume theory as follows:

\[ k_d = k_0 \cdot D_0 \exp\left\{ b_D \left[ 1 - 1/(f_g + B_f(T-T_g)) \right] \right\} \] \hspace{1cm} \text{(2-14)}

where \( k_0, D_0, \) and \( b_D \) are constants, \( f_g \) is the fractional free volume at \( T_g \) and \( B_f \) is the thermal expansion coefficient of the free volume. In their work \( f_g \) was taken as \( .025 \), and \( B_f \) was taken as \( 4.8 \times 10^{-4} \text{K}^{-1} \) for \( T_g < T < T_g + 100 \) and \( 4.8 \times 10^{-5} \text{K}^{-1} \) for \( T < T_g \).

Simon and Gillham\textsuperscript{26} applied the Doolittle equation and expressed \( k_d \) as a function of free volume fraction \( f \):

\[ k_d = A \exp(-b_d/f) \] \hspace{1cm} \text{(2-15)}

where \( A \) and \( b_d \) are taken as adjustable parameters and \( f \) is assumed to be the universal value found for various polymers from the WLF equation:

\[ f = (T_c - T_g)(4.8 \times 10^{-4}) + 0.025 \] \hspace{1cm} \text{(2-16)}

Cole, et al.\textsuperscript{15} adapted Chern and Poehlein’s simple semiempirical approach to describe \( k_d \) in the following equation:

\[ k_d = k_c \exp(-c(\alpha - \alpha_c)) \] \hspace{1cm} \text{(2-17)}

where \( k_c \) is the rate constant for chemical controlled kinetic rate constant, \( \alpha_c \) is a critical value of degree of cure beyond which the diffusion control takes over, and \( c \) is a constant. This equation corresponds to a rather abrupt onset of diffusion control at \( \alpha = \alpha_c \).

These different approaches all give satisfactory fitting results for the
system each author investigated. There are not enough experimental data to decide which is the best. The WLF equation is probably preferable to the empirical equations.

In the curing process of thermoset resins, the onset of diffusion is gradual and there is a region where both chemical and diffusion control are significant. For the range of mixed chemical control and diffusion control process, the rate constant can be calculated using the Rabinowich model as suggested by Dusek, etc. as follows:

\[
\frac{1}{k_{r(a,T)}} = \frac{1}{k_{c(T)}} + \frac{1}{k_{d(a,T)}}
\]

This equation simply and clearly expressed that the time scale of the reaction equals the time scale of diffusion plus the time scale of the chemical reaction. The total reaction rate constant \( k_{r(a,T)} \) is governed by the temperature and the extent of reaction.

Thermal characterization of Pr500 and My720 systems by DSC

The extent of curing was determined by using a Perkin Elmer DSC-7 differential scanning calorimetry. A baseline was established by means of two empty sample pans. The DSC was calibrated using high purity Indium (99.999%). About 10 mg of sample was sealed in an aluminum sample pan. A hole was punched on the top lip to allow the release of any volatiles. The sealed sample was then introduced to the sample holder. Observed weight losses were
negligible in our study. Initially, a temperature ramp of uncured resin was conducted to determine the onset cure temperature and peak maximum temperature of the reaction by heating a sample in a DSC cell at a rate of 5°C/min. Fig 2.3a & Fig 2.3b represent the temperature scans of unreacted Pr500 and My720 respectively. The temperatures for the isothermal kinetic studies were then selected from an interval defined about the onset temperature of the reaction and a point midway to the peak maximum temperature from the thermal curves. In this work, isothermal experiments were conducted at 150, 160, 170, 180 and 190°C for Pr500 system, and at 160, 177, and 190°C for My720 system in order to obtain both the cure rate and extent of cure as a function of time (Fig 2.4a to Fig 2.11a). The residual heat of the isothermal runs was determined from the post cure after each isothermal run (Fig 2.4b to Fig 2.11b). In the post curing process, the sample was ramped from 30°C to 340°C at 5°C/min. All the DSC measurements were carried out under a dry nitrogen atmosphere.

Fig 2.8a shows the DSC output for an isothermal cure of Pr500 at 190°C for two hours. A line is drawn back from where the curve begins to flatten out. This indicates that either the reaction has come to completion or it is very slight and not detectable with the present equipment by the isothermal method at 190°C. The area under the line is the isothermal reaction heat.

A post cure was conducted right after the isothermal run and the output is shown in Fig 2.8b. It is observed that the residual exotherm for a partially
cured sample, which is due to the presence of remaining monomers, begins to appear just beyond the temperature of isothermal cure. The endotherm peak is the annealing peak which appears around the glass transition region due to the higher degree of order in the glassy state for the annealed sample\textsuperscript{17}. Samples that have been vitrified after being cured for long times at a given temperature underwent physical annealing (physical aging). The physical aging refers to the process in which the glass spontaneously densifies to approach equilibrium. When the sample is scanned in the DSC, the effect of aging appears due to enthalpy relaxation. The presence of the annealing peak complicates the assignment of $T_g$. If an aged sample is heated above $T_g$ and then quenched to room temperature, and a second scan of the same sample is conducted, the endothermic peak will disappear. However, some reaction will take place in this procedure. Therefore, another thermal analysis method, thermal mechanical measurement of softening, was used to measure the glass transition temperature of partially cured samples instead of DSC in our investigation (see chapter III, TMA measurements).

The degree of advancement at a particular time is determined by the following equation [2-19]:

$$\alpha(t) = \frac{H(t)}{H_{iso} + H_r}$$  \hspace{1cm} [2-19]

where $H(t)$ is the amount of heat released up to time $t$ determined by using the rate of heat generations measured by the isothermal scanning experiments as follows:

$$H(t) = \int_0^t (dH/dt) \cdot dt$$  \hspace{1cm} [2-20]
$H_{iso}$ is the heat generated by the isothermal cure, and $H_r$ is the residue heat from the post cure. The isothermal and ramp data were converted to ASCII files and input into a Quick Basic integration program called "plotheal". This program then transforms the raw data such as heat flow, time and temperature into the heat of reaction ($H(t)$), degree of cure, $\alpha$, and $d\alpha/dt$. The resulting $\alpha$ versus time for each isothermal temperature is illustrated in Fig 2.12a for Pr500 system and Fig 2.12b for My720 system. The extent of conversion increases with either increasing the curing time or the curing temperature.

The experimental cure rates corresponding to each curing temperature are presented in Fig 2.13a and 2.13b for Pr500 and My720. The cure rate goes through a maximum then decreases as the degree of cure is increased. The time to reach the maximum cure rate ($t_{max}$) and alpha value at the maximum cure rate ($\alpha_{max}$) at each isothermal temperature are summarized in Table 2.1.

<table>
<thead>
<tr>
<th>Resin</th>
<th>Cure Temp(°C)</th>
<th>$t_{max}$ (min)</th>
<th>$\alpha_{max}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr500</td>
<td>150</td>
<td>48.3</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>160</td>
<td>31.5</td>
<td>0.38</td>
</tr>
<tr>
<td></td>
<td>170</td>
<td>22.5</td>
<td>0.38</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>15.0</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td>190</td>
<td>10.2</td>
<td>0.34</td>
</tr>
<tr>
<td>My720 &amp; DDS</td>
<td>160</td>
<td>34.0</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td>177</td>
<td>17.1</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>190</td>
<td>9.6</td>
<td>0.19</td>
</tr>
</tbody>
</table>

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The data show that $\alpha_{\text{max}}$ decreases slightly with increasing cure temperature and is in the range of 34%-39% for Pr500 systems and 19%-23% for My720 systems.

**Reaction Kinetic Models for Pr500 and My720 during Cure**

Kinetic models were developed to predict the reaction conversions for each DSC isothermal run. Since the effect of diffusion on the cure kinetics is insignificant in the pregel stage, the pregel data were then employed to evaluate the Arrhenius type kinetic controlled rate constant. SYSTAT, a statistic analysis software program was employed to fit the experimental data into the autocatalytic equation [2-6]:

$$\frac{d\alpha}{dt} = k^*\alpha^m(1-\alpha)^n$$

The values of the parameters $k$, $m$ and $n$ were generated by a non-linear least square fit method for each isotherm. The values of $m$ and $n$ were then averaged to obtained simplified temperature independent reaction orders and substituted back to equation [2-6] to obtain $k$ values for each temperature. The resultant $k$ values are listed in Table 2.2a and Table 2.2b for Pr500 and My720.

| Table 2.2a Pr500 $m=0.39$, $n=1.01$ |
|-----------------|---|---|---|---|---|
| Cure Temp (C)   | 150 | 160 | 170 | 180 | 190 |
| $k$ (1/min)     | 0.0212 | 0.0320 | 0.0452 | 0.0595 | 0.0838 |

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Table 2.2b My720 & DDS $m=0.25$, $n=1.15$

<table>
<thead>
<tr>
<th>Cure temp (°C)</th>
<th>160</th>
<th>177</th>
<th>190</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k$ (1/min)</td>
<td>0.0142</td>
<td>0.0264</td>
<td>0.0413</td>
</tr>
</tbody>
</table>

$k$ was then related to the activation energy and temperature according to equation [2-11], which is

$$k = A \exp(-E/RT) \text{ (before gel)}$$

where $A$ is the Arrhenius pre-exponential factor, $R$ is the ideal gas constant equal to 1.987 cal/K.mol, and $T$ is the temperature in Kelvin.

Fig 2.14a and Fig 2.14b show the natural log of the isothermal rate constants $\ln k$ before gel versus inverse temperature for Pr500 and My720 systems. The parameters for the kinetic rate expression were determined from the slope and intercept of the linear least square fit of the data (solid line). These parameters were then substituted back in the kinetic equation to produce the Arrhenius type kinetic models before gel as follows:

$$\frac{da}{dt} = e^{11.79}e^\left(-54.95\text{kJ/mol}/RT\right)\alpha^{0.39}(1-\alpha)^{1.01} \text{ (Pr500)} \tag{2-21}$$

$$\frac{da}{dt} = e^{11.46}e^\left(-58.99\text{kJ/mol}/RT\right)\alpha^{0.25}(1-\alpha)^{1.15} \text{ (My720&DDS)} \tag{2-22}$$

Values for $\alpha$ could then be back calculated using the equations provided above. This was achieved by employing a Quick Basic program, "Backcal.Bas", which numerically integrates the rate equation. The back calculated $\alpha$ was then plotted against time in comparison with the experimental data in Fig 2.15a and Fig 2.15b. The solid curve represents $\alpha$ from calculation. It is apparent the
chemical kinetics before gel for the reactions of these two epoxy-amine systems can be represented by the simple autocatalyzed kinetics through the region before gelation.

Now we can evaluate the maximum cure rate. According to equation [2-9] the degree of cure at the maximum cure rate is $\alpha_{\text{max}} = m/(m+n)$. Based on our simplified approach, $m$ and $n$ are independent of cure temperature. The average was taken in the kinetic modeling. Substituting the $m$ and $n$ from equation [2-21] and [2-22] to the expression of $\alpha_{\text{max}}$, the $\alpha_{\text{max}}$ can be calculated. The results are as follows:

For Pr500, $\alpha_{\text{max}} = 0.28$;

For My720 & DDS, $\alpha_{\text{max}} = 0.19$.

Our experimental results indicate that $\alpha_{\text{max}}$ decreases slightly with increasing cure temperature and is in the range of 34%-39% for Pr500 systems, and 19%-23% for My720 systems. The discrepancies are probably brought from the unequal reactivity or functionality of the epoxy or diamine at different cure temperatures. However, the simplified models still provide a good estimation of cure advancement before gel as seen in Fig 15a and Fig 15b.

Diffusion control becomes important for the reaction after vitrification when the mobility of polymer segments are hindered in the glassy state. The diffusion control mechanism was incorporated into the reaction model by using the Rabinowitch equation [2-18] similar to other studies of diffusion controlled kinetics of thermosetting resins.
\[
\frac{1}{k_{\alpha(T,\alpha)}} = \frac{1}{k_{c(T)}} + \frac{1}{k_{d(T,\alpha)}}
\]

It was necessary to establish the correlations between the glass transition temperature and cure time at each isothermal temperature prior to this study. The glass transition temperature was measured with a thermal mechanical analyzer (TMA). The details concerning the TMA method and the one to one relation between \( \alpha \) and \( T_g \) are in chapter III.

The experimental \( \alpha \) and \( \frac{d\alpha}{dt} \) values in the later stage of cure after vitrification were then used to determine diffusion controlled kinetic constants after vitrification.

\[
k_{d(\alpha,T)} = \frac{d\alpha/dt}{\alpha^m(1-\alpha)^n} \quad (T_g \geq T_c)
\]

[2-23]

The time to reach vitrification \( (T_g = T_c) \) at each isotherm was determined from the \( T_g \) versus time curve in chapter III. The kinetic constant at vitrification was then achieved from \( k_{d(T_g=T_c)} = k_{d(\alpha_{T_g=T_c},T)} \) for each isotherm. The results are summarized in Table 2.3a and Table 2.3b.

**Table 2.3a Pr500 m=0.39, n=1.01**

<table>
<thead>
<tr>
<th>Cure Temp (C)</th>
<th>150</th>
<th>160</th>
<th>170</th>
<th>180</th>
<th>190</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_{d(T_c=T_g)} ) (1/min)</td>
<td>0.0174</td>
<td>0.0229</td>
<td>0.0339</td>
<td>0.0354</td>
<td>0.0457</td>
</tr>
</tbody>
</table>

**Table 2.3b My720 & DDS m=0.25, n=1.15**

<table>
<thead>
<tr>
<th>Cure temp (°C)</th>
<th>160</th>
<th>177</th>
<th>190</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_{d(T_c=T_g)} ) (1/min)</td>
<td>0.00123</td>
<td>0.0106</td>
<td>0.0390</td>
</tr>
</tbody>
</table>
It is observed that there is a linear relationship between \( \log k_{d(T_c=T_g)} \) and cure temperatures for both systems (see Fig 2.16a and Fig 2.16b).

For Pr500 system, \( \log k_{d(T_c=T_g)} = -6.097 + 0.0103 \times T_c \) \[2-24\]

\( k_d(a,T) \) and the corresponding time \( t \), curing temperature \( T \), \( \alpha(t,T) \) and \( T_g(t,T) \) were then used to establish the modified WLF equation. The parameter \( c_2 \) was taken as the universal value of 51.6°C.

For the Pr500 system,

\[
\log k_d = \log k_{d(T_c=T_g)} + c_1 \frac{(T_c-T_g)}{(c_2 + |T_c-T_g|)}
\]

\[2-25\]

where \( T_g \) was measured by TMA (see Chapter III for details), and \( c_1 = c + d \times T_c \) (\( c_1 \) is linearly dependent on \( T_c \)). The \( c \) and \( d \) were fitting parameters. This method is similar to Gillham\(^23\). But he had both \( c_1 \) and \( c_2 \) fixed. A non-linear least square estimate method in SYSTAT was used to estimate the values of \( c \) and \( d \). From the results, the linear expression for \( c_1 \) was obtained,

\( c_1 = 11.2 - 0.0237 \times T_c \) \[2-26\]

The above parameters and kinetic equation was incorporated into Rabinowitch model to determine the overall rate constant for the chemical and diffusion controlled region. For a given isothermal cure temperature, \( k_c \) does not change with time and \( T_g \). However, the value of \( k_d \) depends on the difference between \( T_g \) and \( T_{\text{cure}} \). The expression for \( k_T \) is substituted in the autocatalytic rate expression, equation [2-21]. The resulting differential equation has the form

\( \frac{d\alpha}{dt} = f(\alpha, T_g, T) \) which can be integrated numerically at each temperature to

32
obtain the conversion as a function of time.

The degree of cure estimated from the kinetic and diffusion controlled reaction kinetics for Pr500 system is shown in Fig 2.17a with the conversion data determined from the experiments for the Pr500 system. The discrepancy between experimental data and the calculated data is less than 5%.

For the My720 and DDS system,

\[ \log k_d(T_c = T_g) = -24.67 + 0.0503 \times T_c \]  \hspace{1cm} [2-27]

\[ \log k_d = \log k_d(T_c = T_g) + c_1(T_c - T_g)/(c_2 + |T_c - T_g|) \]

\[ = -24.7 + 0.0503 \times T_c + (c + d \times T_c)(T_c - T_g)/(51.6 + |T_c - T_g|) \]  \hspace{1cm} [2-28]

When \( c_2 = 51.6 \) was used, \( c_1 = 20.36 - 0.0428 \times T_c \) \hspace{1cm} [2-29]

The degree of conversion estimated from the kinetic and diffusion controlled reaction kinetics for the My720 & DDS system is shown in Fig 2.17b. The model fits are satisfactory.

The values of \( \log k_d(T_c = T_g) \) and \( c_1 \) used in the modified WLF equations are summarized in Table 2.4a and Table 2.4b for Pr500 and My720 respectively. The diffusion reaction rate constant estimated from this method increases as temperature increases. \( c_1 \) decreases as temperature increases.

The agreement between calculation and the experimental data is good. Therefore the parameters, kinetic and diffusion controlled equations can be used to predict the degree of conversion for any temperature through the entire curing process.

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Table 2.4a Pr500 Resin

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>log K(\text{T}_c=T_c)</th>
<th>c1</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>-1.74</td>
<td>1.17</td>
</tr>
<tr>
<td>160</td>
<td>-1.64</td>
<td>0.934</td>
</tr>
<tr>
<td>170</td>
<td>-1.54</td>
<td>0.697</td>
</tr>
<tr>
<td>180</td>
<td>-1.43</td>
<td>0.460</td>
</tr>
<tr>
<td>190</td>
<td>-1.33</td>
<td>0.223</td>
</tr>
</tbody>
</table>

Table 2.4b My720 & DDS Resins

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>log K(\text{T}_c=T_c)</th>
<th>c1</th>
</tr>
</thead>
<tbody>
<tr>
<td>160</td>
<td>-2.91</td>
<td>1.82</td>
</tr>
<tr>
<td>177</td>
<td>-2.06</td>
<td>1.09</td>
</tr>
<tr>
<td>190</td>
<td>-1.40</td>
<td>0.537</td>
</tr>
</tbody>
</table>

Conclusions:

The effects of curing temperature and glass transition temperature on the reaction kinetics for two epoxy-amine systems were discussed. The Arrhenius-type temperature dependencies of the chemical controlled rate constants were expressed in the pregel stage, and the resulting activation energies were given. The diffusion controlled reaction rate constants were modeled by a modified WLF equation, and the effect of diffusion control was incorporated by modifying the overall rate constant according to the Rabinovitch model. The degree of conversion predicted by the kinetic models generally agrees with experimental data.
References to Chapter II


Fig 2.3a DSC temperature scan of pt500 from 50 to 340°C at 5°C/min

Fig 2.3b DSC temperature scan of My720&DDS from 50 to 340°C at 5°C/min
Fig 2.4a DSC isothermal cure of Pr500 at 150°C

Fig 2.4b DSC temperature ramp after a 150°C isothermal cure of Pr500
Fig 2.5a DSC isothermal cure of Pr500 at 160°C

Fig 2.5b DSC temperature ramp after a 160°C isothermal cure of Pr500
Fig 2.6a  DSC isothermal cure of Pr500 at 170°C

Fig 2.6b  DSC temperature ramp after a 170°C isothermal cure of Pr500

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Fig 2.7a DSC isothermal cure of Pr500 at 180°C

Fig 2.7b DSC temperature ramp after a 180°C isothermal cure of Pr500
Fig 2.8a DSC isothermal cure of Pr500 at 190°C

Fig 2.8b DSC temperature ramp after a 190°C isothermal cure of Pr500

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Fig 2.9a DSC isothermal cure of MY720 & DDS at 160°C

Fig 2.9b DSC temperature ramp after a 160°C isothermal cure of MY720 & DDS
Fig 2.10a  DSC isothermal cure of MY720 & DDS at 177°C

Fig 2.10b  DSC temperature ramp after a 177°C isothermal cure of MY720 & DDS
Fig 2.11a DSC isothermal cure of MY720 & DDS at 190°C

Fig 2.11b DSC temperature ramp after a 190°C isothermal cure of MY720 & DDS
Pr500 at 150, 160, 170, 180 and 190°C

Fig 2.12a Degree of cure(α) versus cure time at 150, 160, 170, 180 and 190°C for Pr500.

My720 and DDS at 160, 177, and 190°C

Fig 2.12b Degree of cure(α) versus cure time at 160, 177, and 190°C for My720 & DDS.
Pr500 at 150, 160, 170, 180 and 190°C

Fig 2.13a Reaction rate da/dt vs cure time of Pr500 system

My720 and DDS at 160, 177 and 190°C

Fig 2.13b Reaction rate da/dt vs cure time of My720 & DDS system

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
Pr500 at 150, 160, 170, 180 and 190°C

My720 and DDS at 160, 177 and 190°C

Fig 2.14a Kinetic controlled rate constant vs 1/Temp for Pr500

Fig 2.14b Kinetic controlled rate constant vs 1/Temp for My720 & DDS

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Pr500 at 150, 160, 170, 180 and 190°C

Fig 2.15a α calculated by kc(T) before gel and experimental data for Pr500

My720 and DDS at 160, 177 and 190°C

Fig 2.15b α calculated by kc(T) before gel and experimental data for My720 & DDS.
Pr500 at 150, 160, 170, 180 and 190°C

Fig 2.16a Diffusion controlled rate constant at vitrification vs cure temp for Pr500

My720 and DDS at 160, 177 and 190°C

Fig 2.16b Diffusion controlled rate constant at vitrification vs cure temp for My720 & DDS
Fig 2.17a Degree of cure vs time for Pr500. Solid curve represents the calculated \( \alpha \).

Fig 2.17b Degree of cure vs time for My720 & DDS. Solid curve represents the calculated \( \alpha \).
Chapter III

Mechanical Measurements

Thermal and dynamic mechanical experiments have been conducted on the Pr500 and My720 systems. The occurrence of gel, build up in the glass transition temperatures and the viscosities as a function of time and temperature during cure were studied. The one to one relationship between glass transition temperature and degree of cure was established.

TMA Measurements

Principle

A Thermal Mechanical Analyzer (TMA) can be used to study the effects of a polymeric material undergoing a mechanical deformation under compressive or tensile load at various temperatures. The TMA technique employs a vertical sample probe resting on the sample. The linear displacement of the probe by a change in sample dimension is detected and translated into an electrical signal by the displacement of the core of a linear variable differential transformer (LVDT) and recorded as a function of temperature or time. The signal can be read as the actual displacement in micrometers, or as a percentage of the known initial length.
or thickness of the sample. The TMA can be operated in various modes with changeable probes to measure penetration, expansion, and elongation. A schematic of it is given in Fig 3.1. The coefficient of linear thermal expansion, glass transition temperature, and melting temperature can be determined by TMA.

**Measurement of Tg for Pr500 and My720 Systems by TMA**

Understanding the glass transition temperature of thermosetting polymers is very important for various reasons. The most obvious is that Tg determines an upper bound for the use temperature of the polymer. Other reasons include the intimate relationship between Tg and degree of conversion, the influence of Tg on the rheology of a thermoset, etc.

In this study, a Shimadzu TMA-50 thermomechanical analyzer was used in the penetration mode. In this mode, changes such as softening and glass transition were measured as a function of temperature of the sample material. Resin samples cured at the same isothermal temperature Tc corresponding to the DSC experiments for each scheduled time were removed from the oven and quenched to the room temperature. The Tg of these partially cured samples was measured by scanning them from room temperature to the curing temp at 5°C/min with a constant load of 30 gram. Tg was picked at the point where the derivative of penetration reached the maximum.
Fig. 3.2 represents the TMA output for a Pr500 sample which had been cured at 160°C for 50 minutes. Tg is indicated on the plot.

**Time and Temperature Dependent Tg**

The glass transition temperature, Tg, of the epoxy systems was determined as a function of cure time and cure temperature as a means of monitoring the relative degree of cross-linking in the system.

Fig 3.3a and Fig 3.3b plot Tg versus the natural log of the cure time for the Pr500 and My720 systems. At a given cure temperature, Tg increases with an increase in the cure time. At a given cure time, Tg increases with an increase in the cure temperature. The shape of each curve at each isothermal temperature is similar.

The shift in the glass transition temperature is composed of two effects. Before gel, as the extent of reaction increases, the average molecular weight of the polymer chains increases, therefore Tg is also expected to increase. Beyond the gel point, an additional factor that leads to an increase in Tg is the introduction of increasing numbers of cross-links within the system. At high degrees of conversion, Tg is sensitive to relatively small changes in the number average molecular weight.

By choosing 160°C as the reference temperature, and shifting the remaining curing curves along the x axis, a master curve at 160°C was generated.
based on Fig 3.3a and Fig 3.3b respectively. It is observed that the data points started to diverge from the master curve approximately after vitrification (Tc=Tg) where the reaction became diffusion controlled (Fig 3.4a and Fig 3.4b). This was also observed by Gillham\textsuperscript{3} and others.\textsuperscript{6,7} The shift factors, 
\[ aT = \ln(t_{\text{Temp}}) - \ln(t_{\text{ref}}) \], are listed in Table 3.1a and Table 3.1b.

<table>
<thead>
<tr>
<th>Table 3.1a Shift factors used for Pr500.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr500</td>
</tr>
<tr>
<td>-------</td>
</tr>
<tr>
<td>aT</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 3.1b Shift factors for My720 system.</th>
</tr>
</thead>
<tbody>
<tr>
<td>My720&amp;DDS</td>
</tr>
<tr>
<td>-----------</td>
</tr>
<tr>
<td>aT</td>
</tr>
</tbody>
</table>

The reaction rate is decreased due to the effect of diffusion control which causes the Tg data to rise only slowly and appear to level off to lower values for lower cure temperatures.

Glass Transition vs Degree of Cure

It is well known that the glass transition temperature may increase over 100 °C during cure accompanying the changes in chemical conversion. At high conversions especially near the completion, the reaction rate is very low, and the DSC measurement is not sensitive enough to record the heat flux as mentioned.
in chapter II. However, Tg can be measured accurately and easily throughout the entire range of cure. This suggests that Tg can be a more sensitive and practical parameter for following the cure process of reactive thermosetting systems. It has been observed that there is a one to one relationship between Tg and conversion which is independent of cure temperature for both epoxy and polyester curing systems. The one to one relationship between Tg and conversion implies that either the molecular structure of the materials cured at different temperatures is the same or that the difference in molecular structure for materials cured at different temperatures does not have a significant effect on the glass transition temperature.

Several equations have been derived and utilized to correlate the glass transition temperature of cross-linked polymers to the extent of conversion. DiBenedetto related the shift in the glass-transition temperature to the degree of cross-linking as follows:

\[
\frac{T_g - T_{go}}{T_{go}} = \frac{(Ex/Em-Fx/Fm)\alpha}{1-(1-Fx/Fm)\alpha} \tag{3-1}
\]

where Tgo is the glass transition of the unreacted material, Ex/Em is the ratio of lattice energies for crosslinked and uncrosslinked polymer and Fx/Fm is the corresponding ratio of segmental mobilities. Fx/Fm is a function of the distance between crosslinks. It decreases as the cross-linking density increases, and it is reflected by the increase in \(T_{g_{\infty}}\) as the network builds up (\(T_{g_{\infty}}\) is the glass transition temperature of the network).
transitional temperature of the fully cured network).

Based on the Couchman's approach and assumption that a crosslinked polymer can be treated as a blend of monomer and completely crosslinked polymer, Pascault and Williams have derived the following equation:

$$\frac{(T_g - T_{go})}{(T_{go} - T_{go})} = \lambda \alpha / [1 - (1 - \lambda) \alpha]$$  \[3-2\]

where $\lambda = \Delta C_p / \Delta C_p$; $\Delta C_p$ represents the change in the specific heat at $T_g$. The subscript $\infty$ indicates the fully cured network with $\alpha = 1$, and the subscript $o$ represents the unreacted system. They further extend equation [3-2] for systems that do not attain complete conversion. The modified equation becomes:

$$\frac{(T_g - T_{go})}{(T_{gm} - T_{go})} = \lambda' \alpha' / [1 - (1 - \lambda') \alpha']$$  \[3-3\]

where $T_{gm}$ is the glass transition temperature for the network reacted to the maximum possible conversion $\alpha_m$, $\lambda' = \Delta C_p m / \Delta C_p$, and $\alpha' = \alpha / \alpha_m$.

Venditti and Gillham also modified Couchman's approach to be able to apply to a DGEBA/TMAB crosslinking system and a polyamic acid ester/polyimide reaction system:

$$\ln(T_g) = (1 - \alpha) \ln(T_{go}) + \lambda \alpha \ln(T_{go}) \quad \frac{(1 - \alpha) + \lambda \alpha}{\alpha_m}$$  \[3-4\]

It was assumed the system behaves as a random mixture of reacted and unreacted ends. The parameters have the same meaning as in equation [3-2].

Hale et al. published an equation that relates $T_g$ to the conversion and cross-link density of the material. This equation was later adapted by Simon and Gillham for both epoxy rich and amine rich DGEBA/TMAB crosslinking
reaction systems.

\[
T_g(\alpha) = \frac{1}{(1 - k\alpha)(1 - KX)} \frac{1}{(1 - \Psi X^2)}
\]  

[3-5]

where the variable \( X \) is taken as the effective cross-link density, the parameters \( k, K \) and \( \Psi \) reflect the effects on \( T_g \) of chain ends, cross-links, and the non-Gaussian nature of the segments between crosslinks respectively.

There are not enough good experimental data available to decide with any degree of confidence which equation is the best. However, the DiBenedetto equation [3-1] has been used by many authors with a moderate degree of success\(^{15,16,17}\). Therefore, we selected this equation to describe the correlation between \( T_g \) and degree of cure for both the Pr500 and My720 systems.

In our study, \( T_{go} \) was determined by dielectric measurements in an acetone bath since the TMA-50 can not measure \( T_g \) below room temperature. For Pr500, \( T_{go} = -13^\circ C \); for My720 & DDS \( T_{go} = 1^\circ C \). The experimental \( T_{go} \), \( T_g \) and conversion data were used in equation [3-1] to determine the value of \( Ex/Em \) and \( Fx/Fm \) by a least square fitting program in the SYSTAT software.

Fig. 3.5a and Fig. 3.5b show \( T_g \) versus degree of cure at different isothermal temperatures for the Pr500 and My720 systems respectively. The symbols are the experimental data. It is apparent for these two epoxy/amine systems that there is a one to one relationship between \( T_g \) and \( \alpha \), independent of
cure temperature. The solid curve represents the DiBenedetto equation fit. The predicted data from this model agrees well with the experimental results. The fitting parameters are listed as follows:

Pr500 system, \( \frac{Ex}{Em} = 1.42, \frac{Fx}{Fm} = 0.78 \).

My720 and DDS system, \( \frac{Ex}{Em} = 0.84, \frac{Fx}{Fm} = 0.43 \).

These values for both systems are either in or close to the value range for other epoxy-amine systems studied by Gillham\(^{15}\) and Martin\(^{17}\). Their results show \( \frac{Ex}{Em} \) ranging from 0.34 to 1.61; \( \frac{Fx}{Fm} \) varying from 0.19 to 0.74 for several epoxy-amine systems. The values for the Pr500 system are higher than those of the My720 system. This may be due to the functionality of the epoxy resin. The My720 has four epoxide groups in one molecule. After being fully cured, the crosslink density is expected to be higher than the Pr500 which has only two epoxide groups. So the chain mobility between crosslinks is less than that of Pr500. \( \frac{Fx}{Fm} \) is the ratio of segmental mobilities of crosslinked and uncrosslinked resins. It decreases as the cross-linking density increases. Therefore, \( \frac{Fx}{Fm} \) is expected to be smaller for the My720 system.
Rheological Analysis of Epoxy Resins

Theory and Instrumentation

A Rheometric Dynamic Analyzer (RDA) is a dynamic mechanical testing system which is used to measure rheological behavior of materials.\(^{18}\)

The simplest type of rheological behavior of a sample is a Newtonian fluid described by the relationship

\[ S = \eta \gamma \]  \hspace{1cm} \text{[3-6]}

where \( S \) is the shear stress, \( \eta \) is a property of the material known as viscosity and \( \gamma \) is a rate of shear. The viscosity is independent of shear rate and strain history.

If the material is a linear elastic solid,

\[ S = G \gamma \]  \hspace{1cm} \text{[3-7]}

The proportionality, \( G \), is a property of the material called the shear modulus. \( \gamma \) is the shear strain.

These two classical models, however, are not adequate to describe certain nonlinear and time dependent deformation behavior that is usually observed in polymer molecules. Many polymers show behavior intermediate between elastic solids and viscous liquids. Such materials are classified as viscoelastic materials.\(^{19,20,21}\) The rheometric dynamic analyzer (RDA) can be used to measure the ability of these viscoelastic materials to store and dissipate mechanical energy on deformation under sinusoidal load.
RDA consists of several functional elements as shown in Fig 3.6. These include a test station and a control center which includes a control computer, system control unit and a test control analysis station. The control center controls the strain, frequency and temperature of the measurement and performs the data acquisition numerical analysis. The test station is comprised of a dynamic motor which is used to apply a sinusoidal oscillating strain to the sample; a torque transducer which measures the resultant stress in the sample and sends the signal back to the control center; and an environmental system which controls the sample temperature.

If the material measured is an ideal fluid, the resulting stress will alternate sinusoidally but out of phase with the strain. In the case of an elastic solid, stress and strain are in phase. For a viscoelastic material, the oscillatory stress lags the stain by a phase angle $\delta$. Fig 3.7 represents the stress-strain-time relationships for these three different materials individually.

In the case of viscoelastic materials,

$$S = S_0 \sin(\omega t + \delta)$$

$$= S_0 \cos \delta \sin \omega t + S_0 \sin \delta \cos \omega t$$

$$\gamma = \gamma_0 (G' \sin \omega t + G^* \cos \omega t) \tag{3-8}$$

$$\gamma = \gamma_0 \sin \omega t \tag{3-9}$$

where $S_0$ is the maximum amplitude of the stress and $\gamma_0$ is the maximum amplitude of the strain.

The modulus is given by $G^* = G' + iG^*$. Both $G'$ and $G^*$ depend on the frequency
of oscillation \( f \). This is due to the ability of a flexible chain to undergo a large number of configurational relaxations. The moduli are then expressed as follows,

\[
G' = \frac{S_0}{\gamma_0} \cos \delta; \quad [3-10]
\]

\[
G'' = \frac{S_0}{\gamma_0} \sin \delta; \quad [3-11]
\]

\[
\frac{G''}{G'} = \tan \delta. \quad [3-12]
\]

The elastic modulus, \( G' \), is a measure of the amount of energy stored and recovered per cycle of sinusoidal deformation. The loss modulus \( G'' \) is a measure of energy dissipated as heat per cycle. \( \tan \delta \) is a measure of the energy dissipation (damping) determined by measuring the driving force required to maintain a constant amplitude of vibration at the resonance frequency. It is usually convenient to express the sinusoidally varying stress as a complex quantity.

Another quality determined by this method is the dynamic viscosity, which is defined as the magnitude of the complex viscosity,

\[
| \eta^* | = | \eta^* - i \eta'' | = (|\eta|^2 + |\eta''|^2)^{1/2} = (G'^2 + G''^2)^{1/2} / \omega. \quad [3-13]
\]

The real part \( \eta' \) is the ratio of stress in phase with rate of strain divided by the rate of strain.

In sinusoidal deformations, if the strain is

\[
\gamma(t) = \gamma_0 e^{i \omega t} \quad [3-14]
\]

the rate of strain \( \gamma'(t) \) is \( i \omega \gamma_0 e^{i \omega t} = i \omega \gamma(t) \quad [3-15] \)

Hence \( \eta^* = G'' / i \omega \quad [3-16] \)

\( \eta' = G'' / \omega \quad [3-17] \)
\[ \eta'' = \frac{G'}{\omega}. \]  

[3-18]

For simplicity, \( \eta' \) is often called the dynamic viscosity. \( \eta' \) approaches the ordinary steady flow viscosity at low frequencies. For a newtonian fluid, \( \eta'' = 0 \).

RDA is an attractive technique to characterize the cure behavior of thermosetting resins\(^{22,23}\). The wide dynamic range of the RDA’s transducer (three decades) permits the cure process of epoxy resins to be monitored on a macroscopic level by measuring the elastic modulus \( G' \), loss modulus \( G'' \) and complex viscosity as the resin changes from liquid to rubber and eventually to glass. Specimen preparation is fast, and only a few grams of material are needed for optimizing processing conditions.

Since the RDA studies the behavior of materials, it is used to provide quality control information on incoming materials that affect the producer’s outgoing products. The viscosity-time-temperature curve provides a time-temperature window in which flow processes may proceed. It is very useful for optimizing composite fabrications.

**Rheological Behavior of Pr500 and My720 during Cure**

A Rheometries Dynamic Analyzer (RDA-700) was used in this study. The elastic modulus \( G' \), loss modulus \( G'' \) and complex viscosity were measured as a function of time by sinusoidal shearing between two parallel plates (19.5 mm in diameter) at constant frequency (40 rad/s). The initial strain value was set at
10%. Auto-Strain mode was selected in order to compensate for material hardening during cure. Therefore, measurements can be made without exceeding the limits of the transducer. Isothermal measurements were performed at 150, 160, 170, 180 and 190°C for Pr500 and 160, 177 and 190°C for My720 corresponding to the isothermal DSC experiments. The plates were preheated in the rheometer environmental chamber for approximately 5-10 minutes at the curing temperature. The gap between the plates was zeroed at this temperature. The plates were then separated and the sample was loaded on the plate as quickly as possible to minimize the heat loss. The gap between the two parallel plates was set around 0.65mm. The measurement was started when the indicator on the RDA-700 panel reached the isothermal curing temperature.

Fig 3.8-Fig 3.15 represent the RDA output: G', G'' and η vs time for the Pr500 and My720 & DDS systems at each isothermal temperature. In the later data analysis, an adjusted time t(0) was designed at the point which the viscosity reached a minimum value for all RDA output. This time correlation factor, usually 3-4 minutes, allows the time needed for the resin and the rheometer oven to achieve thermal equilibrium.

Fig. 3.16a and Fig. 3.16b represent the measured dynamic viscosity as a function of time for Pr500 and My720 systems individually. The initial viscosity levels of these two systems appear to be the same. As curing proceeds, the magnitude of viscosity increases more than 3 decades. The higher the curing temperature, the faster the viscosity increases.
Gelation Point and Gel Conversion

Gelation is one of the most important factors influencing the processing of thermosetting resins. Gel point is responsible for the transformation from a liquid to a rubbery state. On a molecular level, gelation can be approximated as the point at which the resin begins to be insoluble. In the rheological point of view, the gel point has been determined in several different ways in the literature\textsuperscript{24,25}. It is often defined as the point at which viscosity increases very rapidly (inflection point of viscosity). Alternatively, a value of 1000 Pa*S (10000 poise) for the dynamic viscosity is arbitrarily identified as the gel point\textsuperscript{25}. The classical theory\textsuperscript{26} indicates that the steady shear viscosity $\eta$ approaches infinity at the gel point and becomes meaningless in the post gel region. Therefore, gel can be determined from the steady shear viscosity data by plotting $1/\eta$ against conversion and extrapolating to zero. In the modulus point of view, the crossover point between the real and imaginary components of the complex modulus ($\tan\delta = G''/G' = 1$) has been suggested as a convenient measure of the instant of gelation of a network\textsuperscript{27,28}. In a small amplitude oscillatory shear experiment at constant angular frequency $\omega$, the gel point is reached when $G'$ and $G''$ cross each other. As seen in Fig 3.8, in early stages of cure, the viscous properties are dominant in the liquid state, i.e., $G'' > G'$. While after the gel point, the elastic ones predominate in the solid state, where $G' > G''$. This is a simple and accurate method and has been widely used. However, some
authors\textsuperscript{29} suggested it is not appropriate to use this method since it is frequency dependent. Multifrequency experiments have been designed to determine a frequency independent loss tangent ($\tan \delta = G'/G''$). There are other suggestions such as determining the gel point from the slowing down of the rate of increase of the loss modulus $G''$ during cure\textsuperscript{30}.

In our studies, the crossover point of $G'$ and $G''$ was used to detect gel with a time adjustment as mentioned early in this chapter. This criterion was selected because of its clear rheological meanings. However, the occurrence of an inflection point of viscosity, and the point at which the dynamic viscosity reaches $10^3$ Pa*S were also reported for comparison.

The adjusted time to achieve the crossover point ($G',G''$) $t_{gel}$, to reach the inflection point of viscosity ($t_{c}$) and the time for the viscosity to reach $10^3$ Pa*S and the corresponding reaction conversion are listed in Table 3.2.

The gel conversion ($\alpha_{gel}$), according to a statistical treatment by Flory\textsuperscript{26}, depends on the reactants functionalities. Infinite network structure or gelation does not occur until the polymerization has progressed to a critical value which is determined by

\[
b_c = 1/(f-1)
\]  

[3-19]

where $b_c$ is the critical value of the branching coefficient which is defined as the probability that a given functional group of a cross-linking agent will lead along a chain to another cross-linking unit. $f$ is the functionality of the branch unit. It is fixed as long as the reaction mechanism is not a function of temperature.
Table 3.2.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>at G' = G&quot; inflection point of η</th>
<th>η reaches $10^3$ Pa*S</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$t_{gel}$ (min)</td>
<td>$t_\alpha$ (min)</td>
</tr>
<tr>
<td>Pr500</td>
<td></td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>99.5 0.75</td>
<td>87.5 0.69</td>
</tr>
<tr>
<td>160</td>
<td>66.2 0.75</td>
<td>58.0 0.68</td>
</tr>
<tr>
<td>170</td>
<td>47.2 0.75</td>
<td>40.5 0.68</td>
</tr>
<tr>
<td>180</td>
<td>32.7 0.70</td>
<td>27.5 0.63</td>
</tr>
<tr>
<td>190</td>
<td>24.0 0.72</td>
<td>20.0 0.64</td>
</tr>
<tr>
<td>My720 &amp; DDS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>160</td>
<td>58.2 0.39</td>
<td>58.4 0.39</td>
</tr>
<tr>
<td>177</td>
<td>26.7 0.34</td>
<td>26.9 0.34</td>
</tr>
<tr>
<td>190</td>
<td>15.3 0.31</td>
<td>15.2 0.31</td>
</tr>
</tbody>
</table>

However, temperature might modify reactivities of functional groups or introduce substitution effects or intramolecular reactions, changing in consequence the $\alpha_{gel}$. Several assumptions are needed to simplify the statistical approach to a manageable degree. First, it is assumed that all functional groups are equally reactive. Second, it is assumed that all condensation steps take place between different molecules and that internal condensation such as homopolymerization and etherification do not occur. With these assumptions, the critical extent of reaction at the gel point is obtained

$$bc = r\alpha_{gel}^2p/(1-r\alpha_{gel}^2(1-p))$$  \[3-20\]
where \( r \) is the ratio of epoxide to amine hydrogen, \( p \) is the fraction of amine hydrogen that is part of a multifunctional reactant \((f>2)\). If there are no bifunctional amine groups present, equation [3-20] can be simplified and rearranged:

\[
\alpha_{gel} = \frac{1}{(r(f-1))^{1/2}} \tag{3-21}
\]

For Pr500, the ratio of epoxide to amine is approximately 1:1 based on the information provided by the manufacturer. 

\[ r = 1, \quad p = 1, \quad f = 4. \]

\[
\alpha_{gel} = \frac{1}{[(1*(4-1))]^{1/2}} = 0.58
\]

The experimental gel conversion \( \alpha_{gel} \) corresponding to \( G' \) and \( G'' \) crossover at five different isothermal temperatures range from 0.72 to 0.75 which are much higher than the predicted values. In the case of My720 & DDS system, the weight ratio is 100:28, \( r = 2.1, \quad p = 1, \) and \( f = 4. \)

\[
\alpha_{gel} = \frac{1}{[2.1*(4-1)]^{1/2}} = 0.40
\]

The \( \alpha_{gel}(G' = G'') \) at 160°C is 0.39 which is relatively close. However, as the curing temperature increases, \( \alpha_{gel} \) decreases. At 190°C, the variation is over 25%. The discrepancy between the experimental and theoretical values for \( \alpha_{gel} \) at higher temperatures may be attributed to the unequal reactivity of the primary and secondary amines and intramolecular reactions which usually occur at higher curing temperatures.

Comparing the gel time and conversion determined by different methods listed in Table 3.2, it is observed that both the inflection point of viscosity and
the point where \( \eta \) reaches 1000 Pa*S occur slightly prior to the gel point determined by the crossover of \( G' \) and \( G'' \) for Pr500. The difference in degree of cure at these three points is not significant with

\[
(\alpha_{tgel(G'=G'')} - \alpha_{(\text{inflection point of } \eta)}) \leq 0.07
\]

and \( (\alpha_{tgel(G'=G'')} - \alpha_{1000\text{Pa}*s}) \leq 0.08 \) for each isothermal temperature.

For the My720 & DDS systems, the inflection point of \( \eta \) occurs approximately simultaneously with the \( G' \) and \( G'' \) crossover point.

\[
\alpha_{tgel(G'=G'')} \approx \alpha_{(\text{inflection point of } \eta)}
\]

However, the point at which \( \eta \) reaches 10^3 Pa*S occurs slightly later than the gel point \( (G'=G'') \) and the inflection point of \( \eta \). The difference in degree of cure is not significant,

\[
\alpha_{1000\text{Pa}*s} - \alpha_{tgel(G'=G'')} \leq 0.05 \text{ for isothermal cure at 160, 177 and 190°C.}
\]

The Influence of Frequency on Gel Measurements

In order to examine the frequency dependence of \( t_{gel} \) determined by \( G' \) and \( G'' \) crossover, isothermal measurements were conducted at 0.4, 4, 40 and 400 radian/s for Pr500 at 170°C. The testing results are shown in Fig 3.17 to Fig 3.20. The time to reach the crossover point of \( G' \) and \( G'' \) at each frequency after time-0 adjustment as mention previously is listed in Table 3.3. It is observed that there is a slight frequency dependence. As the frequency of the RDA increases a decade, the value of \( t_{gel} \) decreases by approximately two minutes. However,
around the conventional measurement range 10 to 50 Hz, the frequency
dependence should be negligible. This agrees with Bidstrup and Macosko’s
observation on DGEBA and DDS at the stoichiometric ratio\textsuperscript{16}. They reported that
the conversion at the $G'$ and $G''$ crossover point is approximately identical at
three frequencies (10 rad/s, 50 rad/s and 100 rad/s).

<table>
<thead>
<tr>
<th>Frequency of measurement (rad/s)</th>
<th>0.4</th>
<th>4</th>
<th>40</th>
<th>400</th>
</tr>
</thead>
<tbody>
<tr>
<td>$tg_{el}$ ($G'=G''$) min</td>
<td>52*</td>
<td>50*</td>
<td>48.5</td>
<td>46</td>
</tr>
</tbody>
</table>

* The run automatically stopped right before $G'$ reaches $G''$. The value listed is
an extrapolated value.

The test results also confirmed that 40 rad/s is an appropriate frequency
to measure the curing of a thermoset among those four frequencies. The initial
viscosity at the curing temperature is very low for the epoxy-amine systems
tested. When the frequency of testing was too low (0.4 or 4 rad/s), the torque
signal is very weak in the early stage of cure. Therefore data are scattered for
a period of time (Fig 3.17 and Fig 3.18). When the frequency of measurements
is too high, it does not allow equilibrium to occur which also affect the accuracy
of measurements. At 40 rad/s, $G'$, $G''$ and $\eta'$ can be measured through gel to
nearly full cure smoothly (Fig 3.19). The reproducibility is acceptable.
Conclusions

A study of the glass transition temperature, viscosity and gel fraction of Pr500 and My720 systems has been carried out as a function of cure times and temperatures. The results show that both Tg and viscosity increase with an increase in cure time at a given temperature. At a given cure time, Tg and viscosity increase with increasing cure temperature.

A Tg versus ln(time) master curve at 160°C can be made by applying a shift factor along the x axis. The point started to diverge from the master curve after vitrification due to the diffusion controlled mechanism.

The relationship between Tg and $\alpha$ (degree of cure) during cure was found to be independent of the curing temperature. The Tg was related to the degree of cure by the DiBenedetto equation. The experimental data were in agreement with the data predicted by the models.

The condition for gel formation was analyzed in terms of gel time and gel fraction. For the Pr500 system, the experimental gel conversion is much higher than the value predicted by Flory’s classical theory. In the case of the My720 & DDS system, the $\alpha_{gel}$ (experimental) is very close to the calculated value at 160°C. However, the experimental conversion diverged from the calculated value at higher curing temperatures. This confirmed that temperature does affect reaction functionalities of the epoxide and the reactivity of hydrogens on the amine group.
The gel conversion determined from the inflection point of $\eta$ and the point where $\eta$ reaches 1000 Pa*S do not always coincide with the $G'$, $G''$ crossover point. However, the differences are not significant.

The frequency dependence of the crossover point of $G'$ and $G''$ is negligible in the conventional frequency range (10 to 50 rad/s).
References to Chapter III


2. Shimadzu Menu, Shimadzu Corporation.


18. Rheometrics Dynamic Analyzer menu, Rheometric Inc.


Fig 3.1 Schematic diagram of a thermomechanical analyzer (TMA)
Fig 3.2 TMA output of a Pr500 sample cured at 160°C for 50 minutes
Fig 3.3a The evolution of Tg vs ln(time) for Pr500 at 150, 160, 170, 180 and 190°C

Fig 3.3b The evolution of Tg vs ln(time) for MY720 & DDS at 160, 177 and 190°C
Fig 3.4a A superposition of the Tg vs ln(time) to form a master curve at 160°C by shifting each curve in Fig 3.3a by a constant factor (at=ln(_w)-ln(_a)) along the ln(time) axis for Pr500, My720 and DDS at 160, 177 and 190°C.

Fig 3.4b A master curve at 160°C for My720, DDS system based on Fig 3.3b.
Pr500 at 150, 160, 170, 180 and 190°C

My720 and DDS at 160, 177 and 190°C

Fig3.5a Tg vs α for isothermal cure of Pr500 at 150, 160, 170, 180 and 190°C. The solid curve represents the DiBenedetto equation fit.

Fig3.5b Tg vs α for isothermal cure of My720 & DDS at 160, 177, 190°C. The solid curve represents the DiBenedetto equation fit.
Fig 3.6 Schematic of RDA50 test station

Fig 3.7 Material response to a sinusoidal deformation
Fig 3.8 $G', G''$ and $\eta^*$ versus time for isothermal cure of Pr500 at 150°C

Fig 3.9 $G', G''$ and $\eta^*$ versus time for isothermal cure of Pr500 at 160°C
Fig 3.10 $G', G^*$ and $\eta^*$ versus time for isothermal cure of Pr500 at 170°C

Fig 3.11 $G', G^*$ and $\eta^*$ versus time for isothermal cure of Pr500 at 180°C
Fig 3.12 $G', G''$ and $\eta^*$ versus time for isothermal cure of Pr500 at 190°C

Fig 3.13 $G', G''$ and $\eta^*$ versus time for isothermal cure of MY720 & DDS at 160°C

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Fig 3.14 $G', G''$ and $\eta^*$ versus time for isothermal cure of MY720 & DDS at 177°C

Fig 3.15 $G', G''$ and $\eta^*$ versus time for isothermal cure of MY720 & DDS at 190°C
Pr500 at 150, 160, 170, 180 and 190°C

Fig 3.16a  η vs time for isothermal cure of Pr500 at 150, 160, 170, 180 and 190°C

My720 and DDS at 160, 177 and 190°C

Fig 3.16b  η vs time for isothermal cure of MY720, DDS at 160, 177 and 190°C

85
Pr500 log#4b1r
0.4 rad/s, 10% strain

Fig 3.17 RDA isothermal cure of Pr500 at 170°C measured at 0.4 rad/s

Pr500 log#4b1r
4 rad/s, 10% strain

Fig 3.18 RDA isothermal cure of Pr500 at 170°C measured at 4 rad/s

86
Fig 3.19  RDA isothermal cure of Pr500 at 170°C measured at 40 rad/s

Fig 3.20  RDA isothermal cure of Pr500 at 170°C measured at 400 rad/s

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Chapter IV
FDEMS Measurements

Frequency dependent dielectric measurements, often called frequency dependent electromagnetic sensing (FDEMS), provide a sensitive, convenient automated means for characterizing the molecular behavior of polymer materials. Through the measurement of impedance over Hz to MHz frequency range, this technique is able to monitor chemical and physical changes throughout the entire cure process of epoxy resins in the laboratory and in situ in the fabrication tool during manufacturing\textsuperscript{1,2}.

In this study, the isothermal cure behavior of two epoxy systems has been monitored by FDEMS. The changes in ionic conductivity and dipolar relaxation time have been studied as a function of curing time at several isothermal temperatures. The ability of these parameters to detect the occurrence of gel, as well as to predict viscosity and degree of conversion is explored in this chapter.

Dielectric Theory

All dielectric studies involve the determination of the electrical polarization
and conduction properties of a sample subjected to a time-varying electric field.
The static and complex permittivities can be related to the dipole moments of
chain segments, to the angular correlations between dipoles and to the
orientational motions of the chain segments.

There are two major bulk effects in the dielectric studies:3,4,5,6,7

(1) Ionic conductivity

Fig 4.1 illustrates the ionic conduction effects under an applied electric
field. The distribution of ions is random initially. In the presence of an applied
electric field, the positive ions move toward the negative electrode and the
negative ions toward the positive electrode. They finally accumulate at the
electrodes, producing charged layers at both electrodes (electrode polarization).

Fig 4.1  Schematic illustration of ion conduction under an applied electric
field8.

The ionic conductivity in epoxy resin has been generally believed to be

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caused by impurities such as sodium and chloride ions (Na⁺ and Cl⁻) from fragments of polymerization catalysts, as well as degradation and dissociation products of the polymer itself from manufacturing process. Even after treatment to remove NaCl, there are residual ions present in commercial resins at concentrations typically on the order of tens of ppm⁸. These impurities have been used as a probe of the resin system. The ion mobility in a resin depends primarily on the mobilities of the polymer segments. The basic equation to describe the conduction process is
\[ \sigma = qn\mu \]  

where the conductivity is determined by three factors: the charge q, concentration n and drift mobility \( \mu \). Drift mobility characterizes the ease with which the charged species will move under the influence of the applied electric field and is usually expressed as a velocity per unit field (m²V⁻¹s⁻¹). The ionic conduction strongly affects the dielectric permittivity of the medium.

(2) Polarization

There are basically three categories of polarization in homogeneous dielectric materials:

(a) Dipole polarization or orientation polarization \( P_d \)

When a molecule having a permanent dipole moment is placed in an electric field, the positive end will tend to move in the direction of the field and
the negative end in the opposite direction. Therefore the molecules tend to rotate. If there is no net charge on the molecule, then it will experience no translational force. Fig 4.2 illustrates the dipole orientation process in an applied electric field.

Fig. 4.2 Dipole orientation in an applied electric field

(b) Electronic polarization $P_e$

In this case, the electric field induces a shift of electron cloud with respect to the nucleus of the atom. So the center of negative charge and the center of the positive charge are separated. This type of polarization exists in all atoms and molecules of both polar and nonpolar dielectrics, regardless of the possibility of the appearance of other types of polarization. Electronic polarization usually occurs at very high frequency, of the order of $10^{14}$-$10^{16}$ Hz, which is comparable with the period of luminous vibrations.
(c) Atomic polarization $P_a$

It results from a shift of relative position between atomic nuclei in a molecule. This is observed in the IR region and the magnitude of this type of polarization is only about one tenth of that of the electronic polarization.

The total polarization of the molecule is therefore equal to the sum of all these three types of polarization.

$$P_T = P_e + P_a + P_d$$  \[4-2\]

The dipolar rotation, ionic mobility and polarization are the most commonly concerned dielectric properties in polymer studies.

### Dielectric Permittivity

Consider a parallel plate capacitor with plate area $A$ and plate separation $d$. If the space between the electrodes is a vacuum, the capacitance $C_0$ of the capacitor is given by

$$C_0 = A \varepsilon_0 / d \text{ (in farads)}$$  \[4-3\]

where $\varepsilon_0$ is the permittivity of free space and has the value of $8.85 \times 10^{-14}$ Farads/cm. If the capacitor is filled with a dielectric material, dielectric permittivity in static fields $\varepsilon$ can be expressed as the ratio of the capacitance filled with a dielectric $C$ to the capacitance in vacuum $C_0$:

$$\varepsilon = C / C_0$$  \[4-4\]

Another quantity, electric displacement, is introduced to describe the
electric field in dielectrics

\[ D = E \varepsilon \]  \hspace{1cm} [4-5]

The difference between \( D \) and \( E \) depends on the degree of polarizability of the dielectric in an electric field.

When an alternating electronic field \( E(t) = E_0 \cos \omega t \) is applied to a dielectric material, it will produce polarization which alternates in direction. For electronic and atomic polarizations, the processes are instantaneous. In the case of dipole-orientation polarization, since reorientation of the molecules or molecular segments is involved, the process interferes with the surrounding molecules. Therefore, the polarization process is delayed and an equilibrium state is reached in a relatively longer time. When the field is removed, it takes a long time for polarization to disappear (this phenomenon is called the dielectric relaxation). If the frequency of the applied field is high enough to reach a certain point above which the polarization of the system is no longer able to follow the more rapid changes of the electric field, the electric displacement will lag behind the applied field by a phase angle \( \phi \):

\[ D = D_0 \cos(\omega t - \phi) \]  \hspace{1cm} [4-6]

which can be rearranged as

\[ D = (D_0 \cos \phi) \cos \omega t + (D_0 \sin \phi) \sin \omega t \]  \hspace{1cm} [4-7]

A complex dielectric constant or permittivity is then defined as \( \varepsilon^* = \varepsilon' - i \varepsilon'' \) \[8\]

where \( \varepsilon' = (D_0 \cos \phi)/(\varepsilon_0 E_0) \); \( \varepsilon'' = (D_0 \sin \phi)/(\varepsilon_0 E_0) \)

\( \varepsilon' \) is the relative permittivity, also referred to as the dielectric constant of the
medium. $\varepsilon''$ is the dielectric loss factor which arises from energy loss associated with the time-dependent polarization and bulk conduction process.

Both $\varepsilon'$ and $\varepsilon''$ can be determined by experimental measurements. Considering a capacitor filled with a material which has the relative permittivity $\varepsilon^*$ under an alternating electric field $V = V_0 e^{i\omega t}$, the current flowing in the external circuit can be calculated as follows:

$$I = \frac{dQ}{dt} = \varepsilon^* C_0 \frac{dV}{dt} = i\omega \varepsilon^* C_0 V = \omega C_0 (\varepsilon'' + i\varepsilon') V \quad [4-9]$$

The capacitive component of the current which is out of phase with the voltage is

$$I_c = i\omega C_0 \varepsilon' V \quad [4-10]$$

Whereas, the resistive component which is in phase with the voltage is

$$I_R = \omega C_0 \varepsilon'' V \quad [4-11]$$

The energy is dissipated by the dielectric, and the energy loss per cycle is proportional to the loss factor.

In the frequency range $10^{-4}$ to $10^8$ Hz, a polymer sample can be regarded as being electrically equivalent to a capacitor, $C_x$, in parallel with a resistor, $R_x$, at a particular frequency$^{4,9}$(Fig 4.3).
The total impedance $Z$ will then be given by

$$Z^{-1} = \frac{1}{R_x} + i\omega C_x = G + i\omega C_x \quad [4-12]$$

Application of an alternating voltage $V = V_0 e^{i\omega t}$ will produce a capacitive current which is out of phase with the voltage:

$$I_c = \text{Imaginary part of } (V/Z) = i\omega C_x V \quad [4-13]$$

and an in-phase or resistive current

$$I_R = \text{Real part of } (V/Z) = V/R_x \quad [4-14]$$

Comparing equations [4-10], [4-11], [4-13] and [4-14], the permittivity and loss factor can be expressed as follows:

$$\varepsilon' = \frac{C_x}{C_0} = \frac{C(\omega)}{C_0} \text{ material/C}_0 \quad [4-15]$$

$$\varepsilon'' = \frac{1}{(R_x C_0 \omega)} = \frac{G(\omega)}{C_0 \omega} \quad [4-16]$$

where $\omega = 2\pi f$, $f$ is the frequency, and $C_0$ denotes the vacuum filled capacitance. $\varepsilon'$ and $\varepsilon''$ are experimentally observable quantities which can be used to characterize the dielectric dispersion over a range of frequencies.

The simplest model for hindered dipole orientation was derived by...
Debye\textsuperscript{10,11,12} based on the assumption that the time dependent dielectric relaxation function (the process of establishing equilibrium) is a single exponential decay which is independent of the frequency or the temperature for all molecular species.

$$\varepsilon' = \varepsilon_{\infty} - \frac{(\varepsilon_0 - \varepsilon_{\infty})}{(1 + i\omega \tau)} \quad [4-17]$$

$$\varepsilon'' = \frac{(\varepsilon_0 - \varepsilon_{\infty})}{(1 + \omega^2 \tau^2)} \quad [4-18]$$

$$\varepsilon^* = (\varepsilon_0 - \varepsilon_{\infty}) \omega \tau / (1 + \omega^2 \tau^2) \quad [4-19]$$

where $\varepsilon_{\infty}$ is the instantaneous dielectric constant, which is measured immediately after the field is applied, allowing no time for dipole orientation to occur. It is the limiting high frequency permittivity. If sufficient time is allowed after the application of an electric field, the dielectric will finally reach maximum polarization, corresponding to the highest observable dielectric constant $\varepsilon_0$, the limiting low frequency permittivity. Then the tangent of the angle of dielectric loss is obtained:

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} = \frac{(\varepsilon_0 - \varepsilon_{\infty}) \omega \tau / (\varepsilon_0 + \varepsilon_{\infty} \omega^2 \tau^2)} {\varepsilon_{\infty}} \quad [4-20]$$

This single relaxation condition is satisfied by dilute solutions or polar liquids. However, polymers and many other nonpolymers exhibit a broad distribution of relaxation times. Various empirical modifications of the Debye equation [4-17] have been proposed. Among them, the Cole-Cole\textsuperscript{13} and Cole-Davidson\textsuperscript{14} equations have been used extensively for polymer relaxation:

Cole-Cole \quad $\varepsilon^* = \varepsilon_{\infty} - \frac{(\varepsilon_0 - \varepsilon_{\infty})}{(1 + (i\omega \tau)^{\alpha})} \quad [4-21]$  

Cole-Davidson \quad $\varepsilon^* = \frac{(\varepsilon_0 - \varepsilon_{\infty})}{(1 + i\omega \tau)^{\alpha}} \quad [4-22]$
where $\beta$ is a parameter that measures the distribution in relaxation times ($0 < \beta \leq 1$).

The loss curves from Cole-Cole equation are broadened symmetrically with respect to the frequency of maximum loss. It corresponds to a superposition of a group of Debye-like relaxation processes with a range of relaxation times that are symmetrically distributed about $\tau$, the most probable relaxation time which corresponds to the frequency at which $\varepsilon'' = \varepsilon''_{\text{max}}$. At $\beta = 1$, the Cole-Cole equation becomes the Debye equation. Davidson and Cole improved the fit with a slightly different semi-empirical form. The loss curves from the Cole-Davidson equation, are broadened asymmetrically on the high frequency side. A further modification of the relaxation function has been proposed by Williams and Watts\textsuperscript{15,16} based on an empirical form introduced by Kohlrausch in 1854.

$$\Phi(t) = \exp[-(t/\tau)^\beta]$$

where $\beta$ is a parameter that measures the distribution in relaxation times. This empirical representation is commonly known as the Kohlrausch-Williams-Watts (KWW) function which has been widely applied to relaxation data for glass-forming systems. Fig 4.4 compares the Debye single relaxation, the Cole-Cole expression with $\beta = 0.5$ and KWW expression with $\beta = 0.5$. The Davidson-Cole function is very similar the KWW function.
Both the real and imaginary elements of the complex permittivity consist of an ionic term as well as a dipolar term due to the presence of mobile ions, as described in equation [4-23] and [4-24]:
\[
\epsilon' = \epsilon'_d + \epsilon'_i \tag{4-24}
\]
\[
\epsilon'' = \epsilon''_d + \epsilon''_i \tag{4-25}
\]

The dipolar component arises from diffusion of a bound charge of molecular dipole moments. It generally dominates the impedance signal at high frequencies and in highly viscous media. The ionic component is due to the DC conduction of the material. It often dominates at low frequencies, low viscosities, and/or high temperature.

In general, contributions to the overall dielectric polarization come from the particles or chain segments whose relaxation times are faster than the time scale of the applied signal. This characteristic enables one to distinguish between various dielectric polarization mechanisms on the basis of their different
frequency dependencies. The dipolar contribution to \( \varepsilon^* \) is generally observed at frequencies in the kilohertz and megahertz range. In the hertz to megahertz range, usually both ionic mobility, \( \sigma \), and the rotational mobility of the dipole, \( \tau \), can be measured. The magnitude of these two parameters depend on the extent of the reaction and the physical state of the material.

Conductivity effects on the frequency dependence in \( \varepsilon' \) and \( \varepsilon'' \) were derived empirically by Johnson and Cole as shown below

\[
\varepsilon' = C_0 Z_0 \sin(n\pi/2) \omega^{(\sigma^{n+1})} (\sigma/\varepsilon_0)^2 \quad [4-26]
\]

\[
\varepsilon'' = \sigma/(\varepsilon_0^* \omega) C_0 Z_0 \cos(n\pi/2) \omega^{(\sigma^{n+1})} (\sigma/\varepsilon_0)^2 \quad [4-27]
\]

Where \( Z^* = Z_0 (i\omega)^n \) is the electrode impedance induced by the ions and \( n \) is an empirical parameter between 0 and 1. \( \sigma \) is the conductivity (\( \Omega^{-1} \text{cm}^{-1} \)), an experimentally determined intensive parameter that measures the translational mobility of the ions. The first term in equation [4-27] is due to the conductance of ions translating through the medium. The second term is due to electrode polarization as described previously. The electrode polarization is insignificant at frequencies above 10 Hz. Therefore equation [4-27] can be simplified as

\[
\varepsilon'' = \varepsilon''_d + \sigma/(\omega \varepsilon_0) \quad [4-28]
\]

In the early stages of cure, the dielectric loss is mainly caused by ionic conduction. So equation [4-28] becomes

\[
\sigma = \omega \varepsilon_0 \varepsilon''_d \quad (\Omega^{-1} \text{m}^{-1}) \quad [4-29]
\]

where \( \varepsilon_0 \) is the permittivity of free space (\( \varepsilon_0 = 8.85 \text{pF/m} \)), and \( \omega \) is the angular frequency.
Curing Studies by FEDMS

The FEDMS technique in curing studies consists of three major steps: (1) measurement of complex impedance and permittivity of a resin, (2) converting the measured signal to the actual value of the dielectric property such as conductivity and dipolar mobility, and (3) conversion of the experimentally determined dielectric properties to Tg, viscosity, time to reach gel and degree of conversion of the material using calibration-correlation models. The procedures by which these tasks are achieved are shown below in Fig 4.5.

![Diagram of FDEMS measurement](image)

Fig 4.5 Diagram of FDEMS measurement

The most direct and accurate method for measuring the complex permittivity of a material is to use parallel plates of known geometry and measure the impedance using a commercial impedance bridge. However, if the material's dimensions are...
changing with time or temperature during measurements such as the curing of thermostet resins, the measurements will be very difficult. The geometry independent microsensor was developed in recent years. In this study, planar geometry-independent sensors patented by Kranbuehl\textsuperscript{1} were used. This type of sensor consists of a fine array of interdigitated comb electrodes constructed from a noble metal and a substrate made from high temperature ceramics as illustrated in Fig 4.6

![Diagram of a comb electrodes sensor]

Fig 4.6 Diagram of a comb electrodes sensor

In this study, the impedance measurements were made using a Hewlett-Packard 4192 LF Impedance Analyzer and/or a Schlumberger 1260 Impedance/gain Phase Analyzer controlled by a micro-computer. The interdigitated planer electrode permits measurement of the relaxation and diffusion parameters insitu in almost any environment during the cure of thermosets automatically. Impedance measurements were taken at regular time intervals at frequencies of .005, .50, .125, .25, .5, 5, 50, 250, 500, 100 kHZ continuously throughout the polymerization process and converted to the complex permittivity. A kapton

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sensor, which has a functional surface area of 1/2 inch$^2$ and a thickness about 0.06mm, can be put on the bottom plate of the rheometer. In this method, the dielectric test and rheological measurement can be done simultaneously. The parallel plates with the sensor were preheated to the temperature of measurement before the resin was applied. In this way, the dielectric properties can be correlated to viscosities directly.

The FDEMS experiments were also carried out in an air circulated oven. In this case, a glass sensor and a thermocouple were placed in an aluminum sample pan and covered by a small amount of sample and then transferred to a constant-temperature (Tc) oven with forced air circulation for curing. The measurement was started when the reading of the thermocouple in the sample reached Tc-4°C. $\epsilon'$ and $\epsilon''$ were measured continuously throughout the cure.

In this investigation, FDEMS measurements were conducted at 150, 160, 170, 180 and 190 °C for the Pr500 system and at 160, 177, 190 °C for the My720 system corresponding to the isothermal DSC and RDA measurements. Fig 4.7 to Fig 4.14 represent the typical sensor outputs of these measurements. The frequencies multiplied by the imaginary component of the complex permittivity, $\epsilon''*\omega$, along with the temperature of the material during cure were plotted against time for each measurement. Each line represents a single frequency as indicated on Fig 4.8. The onset of reaction is marked by a sudden drop in $d\epsilon''/dt$. In the early stage of cure, a few curves overlap, which indicates that ionic translational diffusion is the dominant factor in the loss term while the
viscosity is low. After a certain period of time the curves start to separate. The peaks in the $\varepsilon'' \omega$ curves for the individual frequencies indicate that the dipolar relaxation process dominates the physical process.

As the liquid resin converts first to a gel and ultimately to a glassy solid, the translational and rotational diffusion of individual molecules in the thermoset become more sterically hindered. In the dielectric aspect of curing, the changes that occur as a result of the crosslinking reaction which determine the dielectric properties are as follows: (1) decreases in the mobility of the impurity ions; (2) decreases in the net dipole moment per unit volume as well as the ionic population which contributes to dielectric permittivity as a result of increased chain length; (3) a general decrease of dipole reorientation rate caused by an increased steric hindrance, and (4) an increase in the distribution of relaxation time.

The frequency dependence of the complex permittivity is used to determine $\sigma$ and $\tau$, the ionic and dipolar mobility parameters as mentioned early in this chapter.

**Ionic Conductivity**

The general agreement in most studies on epoxy resin is that the cure itself does not generate ions, the ions are primarily due to impurities. Hence the ion concentration does not change during cure$^8$. According to equation [4-1], the
Ionic conductivity of one type of ion is expressed as \( \sigma = q n \mu \), where \( q \) is the charge, \( n \) is the concentration and \( \mu \) is the drift mobility (m^2 V^{-1} s^{-1}). The ionic concentration factor is slightly dependent on temperature and reflects the ability of the polymer to solvate a salt into mobile ions\(^{17}\). For an isothermal cure without generation of ions, the ionic conductivity is proportional to the mobility of ions. The ionic mobility factor is strongly temperature dependent and is a function of the size of the ion and the mobility of the polymer chain segments.

The relation between the mobility of the ion and the properties of the resin can be qualitatively examined with the aid of Stoke's law for the drift of a spherical object in a viscous medium and the Einstein relationship exists between the mobility of ions and the ionic diffusion coefficient\(^{18}\):

\[
\mu = \frac{q D}{(k_B T)} \tag{4-30}
\]
\[
\mu = \frac{q}{(6 \pi \eta r)} \tag{4-31}
\]

where \( q \) is the charge carried by an ion, \( D \) is the diffusion coefficient of ions, \( k_B \) is the Boltzmann's constant, \( T \) is the temperature and \( r \) is the radius of a spherical particle. This Stokes-Einstein approach (eq[4-31]) which suggests \( \mu \eta = \text{constant} \) has been successfully correlated with experimental data in many cases. However, this oversimplified model fails when the resin approaches gel. The ionic mobility depends primarily on the mobilities of the polymer segments (since polymer chain segment motion is necessary for ion motion).

If we neglect the electrode polarization effect which is usually very small at frequencies above 10Hz, the ionic conductivity can be determined from the
early portion of the dielectric loss curve by multiplying the loss by the field frequency and the permittivity of free space ($\sigma = \omega \varepsilon_0 e^\omega$). The lowest frequency in the overlapping portion which was smooth was selected to calculate $\sigma$. For the Pr500 system, 125 Hz was used. For My720, 500 and 5000 Hz were selected. Prior to any experimental data processing, a time adjustment factor was introduced. Time 0 was selected as the point where $\varepsilon^\omega$ reached the maximum (the onset of reaction). This correction from the raw experimental data was required for the FDEMS to compensate the time delay incurred in the resin heating up and reaching the programmed temperature in the oven.

Fig 4.15a presents the ionic conductivity at 125Hz as a function of time for the isothermal cure of Pr500 at 150, 160, 170, 180 and 190°C. The ionic conductivity at 160, 177 and 190°C as a function of time for My720 and DDS is given in Fig 4.15b. During cure, $\sigma$ decreases slowly at first, then more rapidly. As the cure proceeds, an inflection point is observed in which the $d\sigma/dt$ reaches a maximum magnitude. The shapes of the curves at different cure temperatures are similar, but accelerated in time at higher cure temperatures.

**Dipolar Relaxation Time**

The dipoles in a curing resin are embedded in a viscous medium and are hindered by attachment to a growing network. The orientation process has a characteristic time, called the dipolar relaxation time. Because of the hindering
mechanism, there is energy loss associated with the orientation process. The
dipolar relaxation time can be determined from dielectric loss data. The local
maximum in $\varepsilon''$ at a given frequency ($f$) corresponds to the mean relaxation rate
$1/\tau$ of the dipolar rotational movement. The mean relaxation time $\tau$ is then given
by $1/(2\pi f)$. By observing the dielectric loss at several different frequencies
during cure, the evolution of $\tau$ can be characterized by observing the time at
which the loss reaches a local maximum at each frequency. Fig 4.16a represents
a plot of dipolar relaxation time versus cure time for the isothermal cure of
Pr500. Fig 4.16b represents the My720 system. In the early stages of cure, $\tau$
is short. As the cure progresses, the dipolar relaxation time increases over
several orders of magnitude. The evolution of relaxation time is a reflection of
the differences in the molecular size, shape and charge distribution in different
types of molecules and of the consequent differences in their crosslinking reaction
kinetics.

Ionic Conductivity vs Viscosity

Viscosity is a macroscopic polymer property that characterizes polymer
chain segment mobility. It is the measured response of polymer chain segments
to an applied stress, while ionic conductivity measures the mobility of ions in
response to an applied electric potential. Several studies have reported that there
is an inverse relationship between experimental ionic conductivity and viscosity

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well prior to gel. This can be interpreted quantitatively by the Stoke’s law (Equation [4-31] $\mu = q/(6\pi \eta r)$ as mentioned early in this chapter). Based on the assumption that ion concentration does not change during cure, the resistivity $\rho$, which is the quantity $1/\sigma$, is proportional to viscosity as seen by equation [4-1] and [4-31]:

$$1/\sigma \propto \eta$$

The correlations of experimental ionic conductivity and viscosity for the Pr500 and My720 & DDS systems are presented in Fig 4.17a & Fig 4.17b individually. It is observed that well before gel there is a linear one to one relationship between log$\sigma$ and log$\eta$ which is independent of cure temperature. The slope of log$\sigma$ vs log$\eta$ is approximately -1 before the viscosity reaches 1 Pa*S. This indicates that well before gel the resistivity ($1/\sigma$) and viscosity have similar dependencies on polymer segment mobility. As the cure progresses, the inverse relationship breaks down, and the change in viscosity is more rapid than that of the ionic conductivity. This is due to the fact that viscoelastic properties of the resin involve the cooperative motions of many chains while the conduction of ions continues to involve motions over much smaller molecular dimensions. Sanford and McCullough\textsuperscript{22} applied a power law $\eta = \sigma^{1.3}$ to describe the faster change in viscosity than that of ionic conductivity during the isothermal polymerization of DGEBA with bis-p-aminocyclohexyl methane(PACM 20). However, the power law can not explain the temperature dependency observed in the gel and post gel regions in our experimental results. In Chapter V, a free
volume based WLF equation will be utilized to discuss the quantitative correlation between $\sigma$ and $\eta$.

**Ionic mobility and Degree of Cure**

The establishment of the relation between ionic conductivity and the conversion of epoxy groups would be essential for the application of FDEMS as an on-line cure monitor. Fig 4.18 is a plot of $\log \sigma$ versus $\alpha$ by correlating the experimental data for Pr500 based on plots of $\alpha$ vs time and $\sigma$ vs time. Several attempts to relate the ionic conductivity and the degree of cure directly have been made in the literature.\textsuperscript{24,25,26} In recent years, Mijovic's group\textsuperscript{25,26} has proposed that the resistivity which represents the dissipative contribution to the dielectric polarization from all migrating charges can be used to monitor the process of reaction.

$$\alpha = \frac{\log \rho - \log \rho_0}{\alpha_m \log \rho_m - \log \rho_o}$$  \hspace{1cm} [4-32]

where $\rho$ is the resistivity which equals $1/\sigma$, $\alpha_m$ is the maximum value of extent of reaction attainable under given cure conditions, $\rho_m$ is the corresponding resistivity, and the subscript "o" denotes initial conditions.

Fig 4.19a and Fig 4.19b show the comparison of $\alpha$ calculated from Mijovic's model with the $\alpha$ determined from DSC measurements for the Pr500 and My720 systems respectively. The fits are not satisfactory.
Another attempt was made to correlate $y = \frac{\varepsilon'(i) - \varepsilon'(0)}{\varepsilon'(0) - \varepsilon'(i)}$ with $\alpha$. 

$\varepsilon'$ measured at 25,000Hz was used in this study. $\varepsilon'(0)$ is the initial $\varepsilon'$ value, and $\varepsilon'(i)$ is the value at the end of the run. Fig 4.20 shows $y$ vs $\alpha$ at five isothermal temperatures for the Pr500 system. It is evident that this model does not agree well with data determined by DSC either.

As we have already known from chapter III, $T_g$ can be used as an index of degree of cure since there is a one to one relationship between $T_g$ and $\alpha$ for both Pr500 and My720 systems. In the next chapter, we describe the correlation between $\sigma$ and $\alpha$ through the change in $T_g$ during cure by the free volume based WLF equation. The recognition of this WLF dependence on $T_g$ has been widely used in epoxy-amine cure study in recent years. (See chapter V for details)

**Ionic Conductivity and Gelation**

The decrease in ionic conductivity during the isothermal curing of a thermoset has been described in terms of a critical phenomenon in which the irreversible sol-gel conversion occurs by a negative feedback process between molecular diffusion and chemical reactions. As the curing proceeds, the viscosity of the system increases, and the molecular diffusion rate decreases. At a time when sufficient crosslinking has occurred to form an infinitely connected network, gelation occurs. It has been suggested that the inflection point of ionic
conductivity (the point that dlog\(\sigma/dt\) reaches a maximum magnitude) is an indication of gel.\textsuperscript{26}

Table 4.1 reports the time at which the rate of change in \(\sigma\) goes through an inflection point, the corresponding degree of conversion as well as the \(t_{gel}\) determined by dynamic mechanical criteria \(G' = G''\) and the inflection point of viscosity.

<table>
<thead>
<tr>
<th>Technique used</th>
<th>RDA at (G' = G'')</th>
<th>inflection point of (\eta)</th>
<th>inflection point of (\sigma)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(t_{gel})</td>
<td>(\alpha_{gel})</td>
<td>(t_e)</td>
</tr>
<tr>
<td>Pr500</td>
<td>99.5</td>
<td>0.75</td>
<td>87.5</td>
</tr>
<tr>
<td>150</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>160</td>
<td>66.2</td>
<td>0.75</td>
<td>58.0</td>
</tr>
<tr>
<td>170</td>
<td>47.2</td>
<td>0.75</td>
<td>40.5</td>
</tr>
<tr>
<td>180</td>
<td>32.7</td>
<td>0.70</td>
<td>27.5</td>
</tr>
<tr>
<td>190</td>
<td>24.0</td>
<td>0.72</td>
<td>20.0</td>
</tr>
<tr>
<td>My720 &amp; DDS</td>
<td>58.2</td>
<td>0.39</td>
<td>58.4</td>
</tr>
<tr>
<td>160</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>177</td>
<td>26.7</td>
<td>0.34</td>
<td>26.9</td>
</tr>
<tr>
<td>190</td>
<td>15.3</td>
<td>0.31</td>
<td>15.2</td>
</tr>
</tbody>
</table>

It is evident that for both the Pr500 and My720 systems, the time to reach the inflection point of \(\sigma\) (\(t_{e}\)) is shorter than \(t_{gel}\) (\(G' = G''\)) at all the isothermal cure
temperatures. The degree of conversion at the inflection point varies about 10%. The results suggest that the inflection point in $\sigma$ can be used as a means of detecting the buildup of a particular network structure which occurs near the gel point. However it is not a fundamental means for determining the gel point.

To further study the ability of the inflection point of $\sigma$ to detect the occurrence of gel, a non-crosslinking linear epoxy-amine system was investigated. 4-biphenylamine which has one amine group was purchased from Aldrich Chemical. The diglycidyl ether of bisphenol-A (DGEBA), containing two epoxide groups was donated by Dow Chemicals under the trade name D.E.R 332. Both components were liquified before use. Accurately weighed stoichiometric amounts of the components were mixed thoroughly in a glass container.

The DSC, rheology and dielectric measurements were conducted on this material at 70°C, 90°C and 110°C. Fig 4.21 represents the degree of conversion based on DSC results versus the time of reaction at 90 and 110°C. It is observed that the reaction approaches completion in 5 hrs at 110°C and in 8 hrs at 90°C. The reaction at 70°C, however, is too slow to be measured accurately by the DSC. Plots of the product of frequency($\omega$) multiplied by the imaginary component of the complex permittivity($\varepsilon''$) against time at 70, 90, and 110°C are illustrated in Fig 4.22 to Fig 4.24. The overlapping values of $\omega \varepsilon''$ determine the ionic conductivity $\sigma$ ($\sigma = \varepsilon_0 \omega \varepsilon''$) as mentioned early in this chapter. It is observed that there is an inflection point present for all three temperatures. Theoretically, both DGEBA and 4-biphenylamine have a reaction functionality of two.
Therefore, they should form a linear polymer product instead of going through a gel point to form a crosslinked network. To test this point, we performed solubility tests on totally reacted samples. It is well known that a highly crosslinked sample is insoluble in any solvent. However, a piece of the DGBEA & 4-biphenylamine sample which had been cured at 110°C for 20 hours dissolved in chloroform completely in a couple of hours (the glass transition temperature of this cured sample is 130.6°C measured by the TMA). This confirms that an non-crosslinked polymer was formed for this system. The overall experimental results indicate that an inflection point is present as the material approaches a glassy state in this non-gelled polymer system. This further questions the veracity of using the inflection point to detect gel.

Figures 4.25 to 4.27 show the log\(\sigma\) versus log\(\eta\) at 70, 90 and 110°C respectively for this DGEBA & 4-biphenylamine system. The linear relationships are observed for all three temperatures with a slope around 0.85 for a long time and high degree of cure (up to \(\alpha=0.92\) at 90°C and 110°C). This further supports the concept that the changing value of the ionic mobility as measured by \(\sigma\) can be used to quantitatively monitor the viscosity of the resin during a non-gelled polymerization reaction.

It is seen from Table 4.1 that there is a difference in the reaction time at which the inflection point of viscosity vs time curve the inflection point of log\(\sigma\) vs time curve occurred during the polymerization. These differences may be related to the relative proportions of free volume necessary for segment and ion

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Johari and his coworkers suggested that the ionic mobility can be used to determine the time to reach gel during the curing reaction of DGEBA with different diamines based on the scaling equation:

\[
\sigma_0(t) = \sigma_0(t \rightarrow 0) \left[ \left( \frac{t_{	ext{gel}} - t}{t_{	ext{gel}}} \right) \right]^x \quad [4-33]
\]

or

\[
\log \sigma_0(t) = \log \sigma_0(t \rightarrow 0) + x \log \left[ \left( \frac{t_{	ext{gel}} - t}{t_{	ext{gel}}} \right) \right] \quad [4-34]
\]

where \( \sigma_0(t \rightarrow 0) \) is the ionic conductivity of the unreacted thermoset liquid at \( t_{\text{cure}} \rightarrow 0 \), and \( t_{\text{gel}} \) is the time required to form the gelled network structure. In their studies, the conductivity data were fitted to equation [4-33] using an iterative procedure until a value chosen for \( t_{\text{gel}} \) gave minimum mean-square deviations of the data from those calculated. The fit was satisfactory. However, they did not provide any \( \eta, G' \) and \( G'' \) data from dynamic mechanical measurement for comparison.

In our study, the validity and applicability of the scaling equation to determine the gel point was investigated. Several methods have been tried for both the Pr500 and My720 systems.

First, the log \( \sigma \) were plotted against \( \log \left( \frac{t_{\text{gel}} - t}{t_{\text{gel}}} \right) \) individually for every system at each isothermal temperature. The dynamic mechanical \( t_{\text{gel}} \) (the time when \( G' = G'' \)) has been used in the equation. The results are shown in Fig 4.28a and Fig 4.28b for the two systems individually. The fit is not linear and becomes worse as the gel point is approached.

Second, let \( t_{\text{gel}} = t_i \) (time to reach the inflection point in log \( \sigma \)) and plot log \( \sigma \)
vs log((t-t)/t) for both systems (Fig 4.29a and Fig 4.29b). The curves are similar to Fig 4.28a and 4.28b.

Another approach was to let \( t_{gel} \) be a fitting parameter as well as \( \log\sigma_0 \) and \( x \) with the restriction \( t_{gel} > \text{time} \). An iterative procedure in SYSTAT software was used until a value chosen for \( \sigma_0(t \to 0) \), \( t_{gel} \) and \( x \) gave minimum mean-square deviations of the data from those calculated. The conductivity data \( \log\sigma_{max} \) which corresponds to adjusted time 0 and \( t_{gel} \) determined by experiments along with the fitting parameter of \( t_{gel} \), \( \sigma_0 \) and \( x \) are listed in Table 4.2. Fig 4.30a and Fig 4.30b show the curve fit for Pr500 and My720 using the parameters listed in Table 4.2. Linear fits are observed. However, the values of \( t_{gel} \) become much greater than the dynamic mechanical determined gel points.

Table 4.2

<table>
<thead>
<tr>
<th>Resin</th>
<th>temp (°C)</th>
<th>log(\sigma_{max}) (\mu)S/m</th>
<th>log(\sigma_0(t \to 0)) (fit)</th>
<th>(x) (fit)</th>
<th>(t_{gel}) (fit) min</th>
<th>(t_{gel}) G' = G'' min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr500</td>
<td>150</td>
<td>-6.90</td>
<td>-6.75</td>
<td>9.84</td>
<td>160.8</td>
<td>99.5</td>
</tr>
<tr>
<td></td>
<td>160</td>
<td>-6.86</td>
<td>-6.70</td>
<td>9.98</td>
<td>112.7</td>
<td>66.2</td>
</tr>
<tr>
<td></td>
<td>170</td>
<td>-6.81</td>
<td>-6.67</td>
<td>9.60</td>
<td>83.9</td>
<td>47.2</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>-6.76</td>
<td>-6.64</td>
<td>10.41</td>
<td>65.1</td>
<td>32.7</td>
</tr>
<tr>
<td></td>
<td>190</td>
<td>-6.69</td>
<td>-6.58</td>
<td>10.82</td>
<td>48.4</td>
<td>24.0</td>
</tr>
<tr>
<td>My720, DDS</td>
<td>160</td>
<td>-5.63</td>
<td>-5.68</td>
<td>113.4</td>
<td>1440.3</td>
<td>58.2</td>
</tr>
<tr>
<td></td>
<td>177</td>
<td>-5.48</td>
<td>-5.46</td>
<td>14.4</td>
<td>108.0</td>
<td>26.7</td>
</tr>
<tr>
<td></td>
<td>190</td>
<td>-5.44</td>
<td>-5.39</td>
<td>6.04</td>
<td>32.9</td>
<td>15.3</td>
</tr>
</tbody>
</table>
It is observed that the fitting parameters of $\log \sigma_0(t \to 0)$ are very close to the measured $\log \sigma_{\max}$ for the My720 & DDS system. However, there is little discrepancy between these two values for the Pr500 system. Another approach was made for the Pr500 system as follows, let $\sigma_0(t \to 0) = \sigma_{\max}$, the point where time zero is set, and only let $t_{gel}$ and $x$ be the fitting parameters. The results are listed in Table 4.3.

<table>
<thead>
<tr>
<th>Resin</th>
<th>temp (C)</th>
<th>$\log \sigma_{\max}$ (fit)</th>
<th>$x$ (fit)</th>
<th>$t_{gel}(fit)$ (min)</th>
<th>$t_{gel}(exp)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr500</td>
<td>150</td>
<td>-6.90</td>
<td>7.66</td>
<td>142.0</td>
<td>99.5</td>
</tr>
<tr>
<td></td>
<td>160</td>
<td>-6.86</td>
<td>7.50</td>
<td>97.2</td>
<td>66.2</td>
</tr>
<tr>
<td></td>
<td>170</td>
<td>-6.81</td>
<td>6.98</td>
<td>70.4</td>
<td>47.2</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>-6.76</td>
<td>7.30</td>
<td>54.0</td>
<td>32.7</td>
</tr>
<tr>
<td></td>
<td>190</td>
<td>-6.69</td>
<td>7.42</td>
<td>38.2</td>
<td>24.0</td>
</tr>
</tbody>
</table>

The $\log \sigma$ versus $\log [(t_{gel}-t)/t_{gel}]$ using this approach are shown in Fig 4.31. A linear fit is observed. The fitting values of $t_{gel}$ are closer to the measured $t_{gel}$ compared to $t_{gel}(fit)$ listed in Table 4.2. However, they are still greater than $t_{gel}(G' = G'')$ by about 50%.

The validity of the scaling relation $[(t_{gel}-t)/t_{gel}]^x$ which was used to predict the gel point is seriously questioned by these results.

It has been suggested in the literature that the degree of cure should be used in the scaling equation instead of cure time$^{31}$. Then equation [4-33] becomes

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\[ \sigma_0(t) = \sigma_0(t=0)[(\alpha_{\text{gel}}-\alpha)/\alpha_{\text{gel}}]^x \]  

Experimental data of Pr500 at 150 and 170°C were used to test the validity of this equation. The resulting parameters \( \sigma_0, \alpha_{\text{gel}}, x \) and \( \alpha_{\text{gel}}(G' = G'') \) are listed in Table 4.4.

<table>
<thead>
<tr>
<th>Resin</th>
<th>temp (C)</th>
<th>( \log \sigma_{\text{max}} ) ( \mu\text{S/m} )</th>
<th>( \log \sigma_0 ) ( \mu\text{S/m} ) ( \text{(fit)} )</th>
<th>( x ) ( \text{fit} )</th>
<th>( \alpha_{\text{gel}} ) ( t ) ( \text{fit} ) ( \text{min} )</th>
<th>( \alpha_{\text{gel}}(G' = G'') ) ( t_{\text{gel}} ) ( \text{min} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>pr500</td>
<td>150</td>
<td>-6.90</td>
<td>-6.96</td>
<td>5.36</td>
<td>0.90</td>
<td>164</td>
</tr>
<tr>
<td></td>
<td>170</td>
<td>-6.81</td>
<td>-6.79</td>
<td>6.98</td>
<td>0.85</td>
<td>63</td>
</tr>
</tbody>
</table>

The linear correlations between \( \log \sigma \) and \( \log((\alpha_{\text{gel}}-\alpha)/\alpha_{\text{gel}}) \) were observed at these two temperatures (Fig 4.32a and Fig 4.32b). However, the values of \( \alpha_{\text{gel}} \) determined by this method are higher than the value determined dynamically.

Conclusions

The dielectric properties of Pr500 and My720 during isothermal cure have been analyzed. The evolution of the complex dielectric permittivity was used to calculate the ionic conductivity and dipolar relaxation time. The curing time dependent ionic mobility goes through an inflection point, which can be used to detect the time to reach a certain network structure prior to and close to the dynamic mechanically determined gel point. The scaling relation \( [(t_{\text{gel}}-t)/t_{\text{gel}}]^x \)

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when used to predict the time of occurrence of gelation does not agree with the dynamically determined gel time.

Well before gel there is a linear relationship between ionic conductivity and viscosity which is independent of isothermal temperature for both the Pr500 and My720 systems. When gel is approached, the linear relationship breaks down. The change in viscosity is much faster than that of ionic conductivity.

The dielectric sensing technique can not predict the degree of cure directly. However, after the reaction rate and conversion of a resin have been established by other methods, the dielectric parameter $\sigma$ can be employed to predict the advancement of the degree of cure during part fabrication. This will be discussed in the next chapter.
References to Chapter IV


Fig 4.7 \( \log e^{\omega} \) versus time for isothermal cure of Pr500 at 150°C

Fig 4.8 \( \log e^{\omega} \) versus time for isothermal cure of Pr500 at 160°C
Fig 4.9 $\log_e \omega$ versus time for isothermal cure of Pr500 at 170°C

Fig 4.10 $\log_e \omega$ versus time for isothermal cure of Pr500 at 180°C
Fig 4.11 \( \log e^* \omega \) versus time for isothermal cure of Pr500 at 190°C

Fig 4.12 \( \log e^* \omega \) versus time for isothermal cure of My720 & DDS at 160°C
Fig 4.13 loge$^\omega$ versus time for isothermal cure of My720 & DDS at 177°C

Fig 4.14 loge$^\omega$ versus time for isothermal cure of My720 & DDS at 190°C
Fig 4.15a Ionic conductivity ($\sigma$) versus cure time for isothermal cure of Pr500 at 150, 160, 170, 180 and 190°C

Fig 4.15b Ionic conductivity ($\sigma$) versus cure time for isothermal cure of MY720 & DDS at 160, 177 and 190°C
Pr500 at 150, 160, 170, 180 and 190°C

Fig 4.16a Dipolar relaxation time(τ) vs cure time for isothermal cure of Pr500

My720 and DDS at 160, 177 and 190°C

Fig 4.16b Dipolar relaxation(τ) vs cure time for isothermal cure of My720 & DDS
Pr500 at 150, 160, 170, 180 and 190°C

Fig 4.17a log(σ) versus log(η) for isothermal cure of Pr500

My720 and DDS at 160, 177 and 190°C

Fig 4.17b log(σ) versus log(η) for isothermal cure of My720 & DDS

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DGEBA, 4-biphenylamine
1:1 mole ratio

Fig 4.21 Experimental $\alpha$ versus time for DGEBA and 4-biphenylamine system
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Fig 4.23 $\log e^\omega$ versus time for isothermal cure of DGEBA and 4-biphenylamine system at 90°C

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Fig 4.24 loge^\omega versus time for isothermal cure of DGEBA and 4-biphenylamine system at 110°C

DGEBA and 4-biphenylamine cure at 70°C

Fig 4.25 Ionic conductivity(\sigma) versus viscosity(\eta) for isothermal cure of DGEBA and 4-biphenylamine system at 70°C

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DGEBA and 4-biphenylamine
cure at 90°C

![Graph showing the relationship between log conductivity (S/m) and log viscosity (poise) for isothermal cure of DGEBA and 4-biphenylamine system at 90°C.]

Fig 4.26 Ionic conductivity ($\sigma$) versus viscosity ($\eta$) for isothermal cure of DGEBA and 4-biphenylamine system at 90°C

DGEBA and 4-biphenylamine
cure at 110°C

![Graph showing the relationship between log conductivity (S/m) and log viscosity (poise) for isothermal cure of DGEBA and 4-biphenylamine system at 110°C.]

Fig 4.27 Ionic conductivity ($\sigma$) versus viscosity ($\eta$) for isothermal cure of DGEBA and 4-biphenylamine system at 110°C
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my720, DDS(100:28 by wt)
isootherm at 160, 177 and 190C

Fig 4.28b logσ vs log[(t_{gel}-t)/t_{gel}], where t_{gel} is determined by G' and G" crossover for My720 and DDS
Pr500 at 150, 160, 170, 180 and 190°C

Fig 4.29a logσ vs log[(ts-t)/ts], where ts is the inflection point of σ for Pr500

My720 and DDS at 160, 177 and 190°C

Fig 4.29b logσ vs log[(ts-t)/ts], where ts is the inflection point of σ for My720 and DDS

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Fig 4.30a \( \log \sigma \) vs \( \log((t_{gel(t)} - t)/t_{gel(t)}) \), where \( t_{gel} \), \( x \), and \( \log \sigma_0 \) are fitting parameters for Pr500.

Fig 4.30b \( \log \sigma \) vs \( \log((t_{gel(t)} - t)/t_{gel(t)}) \), where \( t_{gel} \), \( x \), and \( \log \sigma_0 \) are fitting parameters for My720 and DDS.
Pr500 at 150, 160, 170, 180 and 190°C

Fig 4.31 $\log\sigma$ vs $\log\left(\frac{t_{gel(fit)}-t}{t_{gel(fit)}}\right)$, where and x are fitting parameters for Pr500

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Pr500 at 150°C

Fig 4.32a logσ vs log([(αpel-t)/αpel]), where αpel and x and logσo are fitting parameters for Pr500 at 150°C

Pr500 at 170°C

Fig 4.32b logσ vs log([(αpel-t)/αpel]), where αpel and x and logσo are fitting parameters for Pr500 at 170°C
Chapter V

A Free Volume Based WLF Approach to Model Epoxy Cure Behavior

The application of the WLF model to epoxy resins during cure will be explored. The glass transition temperature, viscosity, ionic conductivity and dipole relaxation time during cure will be shown to be connected by the WLF equations.

Free Volume Concepts in Polymer Chemistry

Free volume is a semiquantitative concept. It is defined as holes on the order of molecular (monomeric) dimensions or smaller voids associated with packing irregularities which present in polymeric or non-polymeric material. The total macroscopic volume per gram, \( v_m \), of a material can be pictured as the sum of free volume, \( v_f \), and an "occupied volume", \( v_o \), which includes not only the volume of the molecules as represented by their van der Waals radii but also the volume associated with vibrational motions. The occupied volume increases with temperature but its magnitude and thermal expansion coefficient remain a matter of conjecture and can not be estimated directly\(^1\).
\[ v_{vp} = v_0 + v_f \]  

Amorphous or semicrystal polymers generally have free volume resulting from geometrical mismatch among neighboring molecular chains/segments. The sizes and concentrations of these free volume cells depend on the polymer molecular architecture and affect many properties. In particular, the thermal expansion coefficient of liquids (whether polymeric or not) represents primarily the creation of additional free volume with rising temperature, whereas the much smaller magnitudes characteristic of crystalline solids and glasses arise from anharmonicity in the dependence of potential energy on interatomic or intermolecular distances. Viscosity, diffusion, and gas permeation of polymers are known to be strongly influenced by free volume. Fig 5.1 illustrates the dependence of specific volume on temperature.

Fig 5.1 The volume-temperature relationship for a typical amorphous polymer.
Free volume concept and the WLF Equation

Historically, the free volume concept was developed to explain the dependence of the fluidity or viscosity of liquids on temperature. As first proposed by Eyring and others, molecular motion in the bulk state depends on the presence of holes or places where there are vacancies or voids. When a molecule moves into a hole, the hole exchanges places with the molecule. A similar model can be constructed for the motion of a polymer chain. For a polymeric segment to move from its present position to an adjacent site, a critical void volume (free volume) must first exist before the segment can jump. The classical liquid theory is based on an Arrhenius type of flow. The temperature dependence of viscosity is determined by an energy barrier for hole formation. This leads to a viscosity proportional to $e^{\Delta H/RT}$ where $\Delta H$ is the activation energy. For polymeric systems, this type of temperature dependence is applicable at temperatures very far above $T_g$ when the polymer is liquid like and there is a relatively large amount of free volume present in the system.

Non-Arrhenius type behavior is observed in viscous polymer and viscous non-polymer liquids. Doolittle introduced the concept that the mobility at any temperature depends primarily on the free volume remaining. This principle led to an empirical equation which was found to represent viscosities of ordinary viscous liquids:

$$\ln \eta = \ln A + B \frac{v_0}{v_f} = \ln A + \frac{B}{f}$$ \[5-2\]
where \( v_0 \) is the actual molecular volume of the liquid molecules, the occupied volume, \( v_f \) is the proportion of holes or voids, the free volume, \( f \) is the fraction of free volume, and \( A \) and \( B \) are empirical constants.

Equation [5-2] implies that free volume is the sole parameter in determining the rate of molecular rearrangements and transport phenomena. Another well known formulation of this free volume theory is the William-Landel-Ferry (WLF)\(^2\) equation.

The WLF equation was first introduced as an empirical equation to describe the time-temperature superposition principle in viscoelastic properties of polymers above the glass transition. The simplest superposition principle suggests that the viscoelastic behavior (spectrum of relaxation) at one temperature can be related to that at another temperature by a shift in the time scale only. Consider the creep compliance curves of an idealized polymer at two temperatures (Fig 5.2\(^{b}\)), these two curves can be superimposed exactly by a horizontal displacement \( \log a_T \). \( a_T \) is known as the temperature shift factor.

![Figure 5.2](image_url)

**Fig 5.2**

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\[ \log(a_T) = \log(t_{T_1}) - \log(t_{T_2}) \]  

where \( t_{T_1} \) is the time required to reach a particular response at temperature \( T_1 \), and \( t_{T_2} \) is the time required to reach the same response at the reference temperature \( T_2 \). Generally, for temperatures above the reference temperature, it takes less time to reach a particular response. Therefore \( a_T \) is less than 1, and vice versa.

Ferry's superposition principle implies that at temperatures above \( T_g \), all properties governed by the segmental relaxation rate (e.g. viscous flow, mechanical and dielectric relaxation, etc.) will vary with temperature in essentially the same way. One can use the time-temperature superposition principle to trace out the viscoelastic properties measured by experiments which are usually covering perhaps two or three decades of logarithmic time scale or frequency scale over a much larger effective range. In dynamic mechanical analysis, this is achieved by measuring the properties at different frequencies over a wide temperature range. An isothermal master curve may then be constructed by choosing the temperature of interest as the reference temperature and shifting the segments of curves at other temperatures along a horizontal logarithmic time scale (frequency) by a shift factor, \( \log a_T \), until they all superimpose smoothly. In this way a relaxation spectrum versus a wide range of frequency can be established at the temperature of interest.

For viscosity, the shift factor can be written as

\[ a_T = \frac{(\eta T_0 \rho_0)}{(\eta_0 T \rho)} \]  

where \( T_0 \) is the reference temperature, \( \rho_0 \) and \( \rho \) are the densities at the reference temperature and temperature of interest, respectively.
or \( \log a_T = \log(\eta/\eta_0) + \log(T_0 \rho_0/T \rho) \) \[5-5\]

where \( \eta \) and \( \rho \) are the viscosity and density at temperature \( T \), and \( \eta_0 \) and \( \rho_0 \) are the viscosity and density at the reference temperature \( T_0 \). The term \( T_0 \rho_0/T \rho \) is small and is often ignored in the reduction of the viscosity data. Williams, Landel and Ferry found that the shift factor can be described empirically by the equation

\[
\log a_T = -c_1(T - T_0)/(c_2 + T - T_0) \quad (T_g < T < T_g + 100) \tag{5-6}
\]

where \( c_1 \) and \( c_2 \) are constants which depend on the reference temperature \( T_0 \) and on the material.

Important contributions to the physical interpretation of the WLF equation were made by Doolittle, Fox and Flory, and Cohen based on the free volume theory\textsuperscript{3,4,5,6}.

It is argued that the free volume increases linearly with temperature

\[
f = f_0 + \alpha_f(T - T_0) \tag{5-7}
\]

where \( f_0 \) is the fractional free volume at \( T_0 \), and \( \alpha_f \) is the thermal expansion coefficient of free volume. Combining Doolittle’s equation [5-2] with equation [5-7], the shift factor of viscosity can be written as

\[
\log a_T = \log \eta - \log \eta_0 \\
= B/2.303(1/f - 1/f_0) \\
= -b/2.303f_0(T - T_0) \\
\frac{f_0/\alpha_f + T - T_0}{f_0/\alpha_f + T_g - T_0} \tag{5-8}
\]

Equation[5-8] and [5-6] are equivalent. Therefore, the WLF parameters can be.
interpreted from the free volume theory with

\[ cl = \frac{b}{2.303f_0} \]  \[ c2 = \frac{f_0}{\alpha_f}. \]

When \( T_g \) is chosen as the reference temperature, the WLF constants can be rewritten as:

\[ cl = \frac{B}{(f_g \times 2.303)} \]
\[ c2 = \frac{f_g}{\alpha_f} \]

where \( f_g \) is the free volume fraction of the glass, \( \alpha_f \) is the free volume thermal expansion coefficients. William, Landel and Ferry found the average value of 17.44 for \( cl \) and 51.6 for \( c2 \) have fit for a large number of polymers when \( T_g \) was chosen as the reference temperature. These "universal" values imply that at \( T_g, f_0 = 0.025B \) and \( \alpha_f = 4.8 \times 10^{-4}B/K \).

Fox and Flory\(^7\) proposed that \( T_g \) is an iso-free volume state (\( f_g = \text{constant} \)) and evidence showed that \( f_g = 0.025 \pm 0.003 \) for most amorphous polymers. The thermal coefficient of expression of free volume, \( \alpha_f \), is a more variable quantity, but has the physically reasonable "universal" average value of \( 4.8 \times 10^{-4}K^{-1} \). So the parameter \( B \) is approximately equal to 1.

In terms of the Cohen and Turnbull\(^8\) free volume theory, the free volume can be redistributed without a change in energy. The Doolittle parameter \( B \) is expressed as \( \gamma f^* \), where \( \gamma \) is a factor to account for the overlap of free volume, and \( f^* \) is the critical free volume fraction for a certain chain movement. The WLF constants can be rewritten as

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\[ c_1 = \gamma f'(2.303f_j) \]  
\[ c_2 = f_j/a_f \]

Since rheological properties such as viscosity at \( T_g \) are difficult to measure accurately, it is suggested that a reference temperature, \( T_s \), which is usually about 50°C above \( T_g \), is chosen. It has been observed that the following equation could be applied to a wide variety of polymers, polymer solutions and other glass forming liquids over a temperature range of \( T_s \pm 50^\circ \).

\[ \log a_f = -8.86(T-T_s)/(101.6+T-T_s) \]

It is evident that the actual variation from one polymer to another. These "universal" values are expected to apply in the absence of other specific data.

The WLF equation has been applied to a wide variety of thermoplastic polymers over the range of \( T_g \) to \( T_g+100 \) where the free volume is the sole parameter in determining the rate of molecular rearrangements and transport phenomena. When the temperature is below \( T_g \) the configurations of polymer chain backbones are largely immobilized and don't show tremendous changes with changing frequency. Above \( T_g+100 \) the free volume is no longer the flow limitation factor, so the temperature of viscosity is determined by the Arrhenius type equation.

**Applying the WLF correlation to thermoset material**

The free volume based William-Landel-Ferry (WLF) models have been
widely and successfully used to describe the temperature dependence of mobility related material properties in the glass transition region for thermoplastic polymers and other glass forming liquids. In those systems, the chemical composition does not change with temperature. Curing of thermosetting materials involves the transformation of low molecular weight liquids to high molecular weight amorphous solids by chemical reactions. During cure, crosslinks are formed and $T_g$ rises with curing time and temperature. The chemical composition and structure change as curing proceeds. The segmental relaxation rate which governs most rate processes in polymers (mechanical or dielectric relaxation, viscous flow etc.) depends on the chemical structure of the polymer, but these structural effects are negligible if the polymers are compared in corresponding states. Therefore, the WLF equation may be applied in this case.

The WLF equation has been applied to model the temperature dependence of the mean dipole relaxation time and ionic conductivity in totally cured thermoset resins or precured resin systems in which the $T_g$ remained constant. S. Wu employed the WLF equation in uncured polymer blends of high molecular weight. Other researchers applied the WLF equation in the totally cured epoxy systems using equation [5-12] with $c_1=8.86$, $c_2=101.6$ and letting $T_s$ be the fitting parameter. In those cases, the glass transition temperature remained constant, while the properties were monitored with varying temperatures.

Recently, the relation between viscosity or dielectric properties, curing
temperature and the glass transition temperature has been studied for the curing system of thermosets by different authors. These approaches are preferred because they conveniently yield a model which describes the desired viscoelasticity of the polymeric materials and offer potential to generate fundamental relationships between the structure and the properties of thermosetting resin systems during cure.

Tajima and Crozier applied the WLF equation to describe the temperature dependence of the viscosity of an amine cured epoxy resin exhibiting second-order kinetic behavior. In their approach, the reference temperature and the viscosity at the reference temperature of the WLF equation were found to be simple functions of the resin advancement as follows:

\[
\log \eta(T) = \log \eta(T_s) - c_1(T - T_s)/(c_2 + T - T_s) \quad [5-13]
\]

where \( \log \eta(T_s) = A \alpha + B \); \( T_s = 307.53 \alpha^2 + C \)

\( c_1 = 15.46 \); \( c_2 = 54.40 \)

where \( c_1 \) and \( c_2 \) are the model constants and \( T_s \) is the reference temperature which was chosen by them so the viscosity data could be described by a single curve. The physical meaning of each parameter was not discussed in their paper.

Sheppard and Senturia found that the temperature dependent conductivities of a homologous series of DEGBA epoxy resins (without hardener) of varying molecular weights obey WLF relations. Analysis of this neat resin data revealed that while the WLF constant \( c_1 \) is relatively independent of the molecular weight of the resin, the \( c_2 \) constant and the reference conductivity,
log\(\sigma(T_g)\) can be represented by a simple linear dependence on \(T_g\) of the material. Therefore the WLF equation can be rewritten:

\[
\log\sigma(T) = c_5 + c_6*T_g + c_1(T-T_g)/(c_3 + c_4*T_g + (T-T_g)) \tag{5-14}
\]

where \(\log\sigma(T_g) = c_5 + c_6*T_g\). Then the similar behavior of \(c_2\) and \(\log\sigma(T_g)\) was used by their group to model ionic conductivity changes during the cure of a DGEBA with a tetra-functional amine and My720 with a tetra-functional amine\(^{17}\). Their results showed the behavior of \(\sigma\) with a changing \(T_g\) during the isothermal cure is consistent with the WLF behavior of the homologous resins. However, in equation \([5-14]\) the ionic conductivity increases with increasing \(T_g\). This result is contrary to what has been observed by many authors that at a fixed temperature as the glass transition temperature increases, the ionic conductivity decreases as the viscosity increases\(^{16,22,23,24}\).

Martin, et al.\(^{24}\) analyzed the isothermal viscosity data by the equation

\[
\log\eta(T) = c_5 + c_6*T_g + c_1(T-T_g)/(c_2 + T-T_g) \tag{5-15}
\]

They also found that at low conversions of their epoxy system, \(\log\eta(T_g)\) can be approximated as linear functions of the conversion, \(\alpha\). Equation \([5-15]\) can be rewritten as

\[
\log\eta(T) = c_5 + c_6*\alpha + c_1[T-(c_3+c_4\alpha)/(c_2+T-(c_3+c_4\alpha))] \tag{5-16}
\]

The model predictions from these two equations and the experimental data are in agreement. There is, however, an apparent contradiction between the parameters from these two models. From equation \([5-15]\), both \(c_5\) and \(c_6\) are positive. So \(\log\eta(T_g)\) increases as \(T_g\) increases. From equation \([5-16]\), \(c_5\) is positive while
is negative, so the log\(\eta\) at the reference temperature \(T_g\) decreases as \(\alpha\) increases. Fuller, et al\(^{25}\) observed that there is a one to one correlation between \(T_g\) and \(\alpha\) for the same system and \(T_g\) increases as \(\alpha\) increases. These contradictions occur because the physical meaning of each parameter, such as the reference viscosity at a reference temperature, is not clearly defined in their work.

In our studies, the relation between ionic conductivity, dipolar relaxation time and viscosity and glass transition temperature for Pr500 and My720 during isothermal cure is explored by using the WLF equation. Several methods have been tried.

First, we ignored the physical meanings of each parameter in the WLF equation and tried to modify the equation in different mathematical models including those proposed by others such as equation \([5-14]\) and equation \([5-15]\). The reference quantity \(\log X_{\text{ref}}\) such as viscosity \(\log \eta_{\text{ref}}\), ionic mobility \(\log \sigma_{\text{ref}}\) or dipolar relaxation \(\log \tau_{\text{ref}}\) and \(c_1, c_2\) were determined by nonlinear least-squares parameter estimations using SYSTAT software. It was observed that these three quantities during cure can be fit to several different types of modified WLF models. Here are some examples:

\[
\log X = \log X_{\text{ref}} - c_1(T_c-T_g)/(c_2+T_c-T_g) \quad \text{when } X \text{ represents } \eta \text{ and } \tau.
\]

\[
\log X = \log X_{\text{ref}} + c_1(T_c-T_g)/(c_2+T_c-T_g) \quad \text{when } X \text{ represents } \sigma.
\]

(1) Let \(\log X_{\text{ref}} = a + b*T_c\), and either \(c_1\) or \(c_2\) equals \(c+d*T_c\).

(2) Let \(\log X_{\text{ref}} = a + b*T_g\), and either \(c_1\) or \(c_2\) equals \(c=d*T_g\).
(3) Let $\log X_{\text{ref}} = a + b \cdot T_g$, $c_1$ and $c_2$ are constant.

(4) Let $\log X_{\text{ref}} = a + b \cdot T_c$, $c_1$ and $c_2$ are constant.

In these cases, the modified WLF equation agrees with the experimental data to different degrees of accuracy, but they are totally empirical. There is no physical meaning for each parameter.

Thus, a good fit of experimental results cannot be a sufficient criteria for validating a given theory. In order to use the free volume based theory to examine the physical meaning of the WLF equation, certain criteria should be used. In the case of curing studies, $T_c$ is constant, $T_g$ builds up during cure and reaches $T_c$ at vitrification ($T_c = T_{gv}$). Regarding $T_g$ as reference temperature, the quantity $\log X$ ($\log \eta$, $\log \tau$, or $\log \sigma$) at $T_g$ as the reference is not appropriate, since $T_g$ varies with curing time and temperature. Only the onset of vitrification ($T_c = T_g$) has clear physical and experimental meaning. Therefore, the vitrification point should be chosen as the reference point in the free volume based WLF equations.

$$\log X_{T_c} = \log X_{T_c=T_g} = \frac{B}{(2.303 f_g) (T_{gv} - T_g) / ((f_g / \alpha_f + (T_{gv} - T_g))} \quad (X = \eta \text{ or } \tau) \quad [5-17]$$

$$\log X_{T_c} = \log X_{T_c=T_g} + \frac{B}{(2.303 f_g) (T_{gv} - T_g) / ((f_g / \alpha_f + (T_{gv} - T_g))} \quad (X = \sigma) \quad [5-18]$$

We assumed that $\log X_{T_c=T_g}$ changes linearly with the glass transition temperature at vitrification ($T_{gv}$) as in equation [5-19],

$$\log X_{T_c=T_g} = a + b \cdot T_{gv} = a + b \cdot T_c, \quad [5-19]$$

and adopted Fox and Flory’s iso-free volume at glass transition theory, $f = 0.025$, $a_f = 4.8 \times 10^{-3}$, so $c_2 = 51.6$. 

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When we let \( \log X_{Tc=Tg} = a + b \cdot Tc \); \( c1 = c + d \cdot Tc \) and \( c2 = 51.6 \), we got a better fit (smaller loss value) than with \( c1 \) constant. Our modified WLF correlation of Pr500 and My720 & DDS then become

\[
\log \sigma = \log \sigma_{Tc=Tg} + c1 \cdot (Tc-Tg)/(c2 + Tc-Tg) \tag{5-20}
\]
\[
\log \eta = \log \eta_{Tc=Tg} - c1 \cdot (Tc-Tg)/(c2 + Tc-Tg) \tag{5-21}
\]
\[
\log \tau = \log \tau_{Tc=Tg} - c1 \cdot (Tc-Tg)/(c2 + Tc-Tg) \tag{5-22}
\]

where, \( c2 = c2 = c2 = 51.6 \)

\[
\log X_{Tc=Tg} = a + b \cdot Tc
\]

\[
c1_{Tc=Tg} = c + d \cdot Tc
\]

The parameters from this type of fit are listed in Table 5.1a and 5.1b. It is observed that at a given isotherm cure temperature, \( \log X_{Tc=Tg} \), \( c1 \) and \( c2 \) are all constant.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>( c1_r )</th>
<th>( \log \tau_{Tc=Tg} )</th>
<th>( c1_\sigma )</th>
<th>( \log \sigma_{Tc=Tg} )</th>
<th>( c1_\eta )</th>
<th>( \log \eta_{Tc=Tg} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>9.111</td>
<td>-1.892</td>
<td>8.926</td>
<td>-13.84</td>
<td>12.26</td>
<td>7.718</td>
</tr>
<tr>
<td>170</td>
<td>11.27</td>
<td>0.05059</td>
<td>10.19</td>
<td>-14.82</td>
<td>16.24</td>
<td>10.90</td>
</tr>
<tr>
<td>190</td>
<td>13.43</td>
<td>1.993</td>
<td>11.46</td>
<td>-15.81</td>
<td>20.22</td>
<td>14.09</td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>$c_1^r$</th>
<th>$\log\tau_{\text{tr}=T_g}$</th>
<th>$c_1^\sigma$</th>
<th>$\log\sigma_{\text{tr}=T_g}$</th>
<th>$c_1^\eta$</th>
<th>$\log\eta_{\text{tr}=T_g}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>160</td>
<td>45.27</td>
<td>23.87</td>
<td>23.21</td>
<td>-23.25</td>
<td>35.89</td>
<td>25.14</td>
</tr>
<tr>
<td>177</td>
<td>40.61</td>
<td>21.78</td>
<td>26.07</td>
<td>-25.59</td>
<td>38.85</td>
<td>27.92</td>
</tr>
<tr>
<td>190</td>
<td>37.05</td>
<td>20.18</td>
<td>28.27</td>
<td>-27.38</td>
<td>41.12</td>
<td>30.04</td>
</tr>
</tbody>
</table>

Log$\tau$, log$\sigma$ and log$\eta$ vs $T_g$ are shown in Fig 5.3a, 5.3b, 5.4a, 5.4b, 5.5a and 5.5b for the Pr500 and My720 & DDS systems. The solid curve represents the WLF fit.

### Interpretation of $c_1$ and $c_2$

As mentioned before, $c_2 = f_\pi / a_r$. Applying Fox and Flory’s iso-free volume as glass transition, $c_2$ should be constant and generally has the value of 51.6.

According to Cohen and Turnbull’s theory,

$$c_1 = \gamma f^*/(2.303 f)$$

where $f^*$ is the fraction of critical volume large enough to permit certain movements, $f$ is proportional to the critical volume $v^*$

$$f = v^*/v_0$$

where $v_0$ is the occupied volume.

When this concept is applied to viscosity, the $v^*$ has been interpreted as the volume necessary for the transport of the polymer chain segment. As for
dielectric relaxation of polymers, the $v^*$ has been interpreted as the volume required for the polar segment to relax. In the case of ionic mobility of polymers, $v^*$ has been interpreted as the volume required for ion transport. Therefore, in a given material at a given isothermal temperature, the WLF parameters $c_{1\sigma}$, $c_1$, and $c_{1\tau}$ should differ, since the critical volume for mobility of ionic impurities, dipole reorientation, and viscoelastic transport of polymer chain segments differ due to the different nature of the movement and the size of the moving unit. The critical volume required for ionic motion should be smaller than that for segmental motion (either viscous transport or dipole rotation) due to the small size of ions. Therefore $c_{1\sigma} < c_1$, and $c_{1\sigma} < c_{1\tau}$ are expected. As seen from Table 5.1a and 5.1b, at an given isothermal temperature, $c_{1\sigma} < c_1$, and $c_{1\sigma} < c_{1\tau}$ are true for both the Pr500 and My720 systems. The results agree with the results of Koike et al\textsuperscript{10} on the epoxied prepolymer systems with $c_{2\sigma} = c_{2\tau}$, and $c_{1\sigma} < c_{1\tau}$. They did not have data on $c_{1\tau}$.

For a given resin system, it is observed that $c_{1\sigma}$ increases as isothermal cure temperature or $T_{gv}$ increases. The reason for this is that the transport of ions not only depends on its size and concentration but also depends on ion mobility which is strongly affected by polymer molecular chain movements. For example, there are interactions between the cations and Lewis base sites on the polymer (such as the lone pair electrons on oxygen atoms). The association and dissociation of cations with polymer chain sites are responsible for cation transport in polymer systems\textsuperscript{26}. It is generally believed that the temperature
dependence of the ionic conductivity results from the mobility of ionic impurities, \( \text{Na}^+ \) and \( \text{Cl}^- \) due to the manufacturing process. The curing processes do not generate ions. Therefore the ion impurity concentration and size are approximately identical during cure. However, the polymer segmental movements depend on the crosslink density. Furthermore, the structure of the oxygen lone pairs changes as epoxide goes to hydroxide or ether. In our study, we pick the vitrification point \( (T_g=T_c) \) as the reference temperature. Thus \( c_1 \) is not only material dependent but also determined by the size of the moving unit which is expressed by the critical volume \( v^*(T_c=T_g) \) at vitrification. As the isothermal curing temperature increases, the degree of cure at vitrification increases since \( T_g \) at vitrification increases \( (T_g=T_c) \). Increasing the extent of cure of the thermoset system will increase molecular weight and crosslinking, which removes free ends and restrains thermal motions. Thus the critical volume needed for ionic movement increases due to the larger chain segments which are involved in ion diffusion at higher crosslink density. Therefore \( c_{1_r} \) is expected to increase with cure temperature or \( T_{gv} (T_c=T_{gv}) \). We also expect that \( c_{1_r} \) and \( c_{1_l} \) increase with isothermal temperature since the transport mobility of the polymer chain and dipolar relaxation of the polymer chain are also strongly dependent on the degree of crosslinking. Our results listed in Table 5.1a for Pr500 are consistent with the theory in which all three \( c_1 \) values increase as \( T_{gv} \) increases. For the My720 system, it is observed that \( c_{1_r} \) and \( c_{1_l} \) rise as \( T_{gv} \) rise. However, \( c_{1_l} \) decreases as \( T_g \) increases (Table 5.1b). We can not explain this
based on the free volume theory. However, if the dipolar group and the volume it sweeps out becomes smaller as $\alpha$ increases, $c_1$ would decrease. We speculate that the OH has a smaller relaxing volume than the epoxide.

The $\log \sigma_{T_c=T_g}$, $\log \tau_{T_c=T_g}$ and $\log \eta_{T_c=T_g}$ terms are also listed in Table 5.1. These values are predicted by the models we used. For the Pr500 system, $\log \tau_{T_c=T_g}$ and $\log \eta_{T_c=T_g}$ increase as $T_{gv}$ or $T_c$ increases; $\log \sigma_{T_c=T_g}$ decreases as $T_{gv}$ increases. The results are reasonable since these quantities are also linked to the size of the chain segments involved in various processes. The higher the degree of crosslinking, the more difficult for chain segments to move to a new equilibrium state. The relaxation time increases and ionic mobility decreases as the degree of crosslink increases. It is also observed that $c_1$ is less affected by curing temperature due to the small volume of ionic impurities. For the My720 & DDS system, $\log \tau_{T_c=T_g}$ decreases as $T_{gv}$ or $T_c$ increases, which is consistent with the anomalous trend in $c_1$, discussed above.

In future work, it would be valuable to conduct experiments to measure these quantities at vitrification directly.

Quantitative Correlation of $\sigma$ and $\eta$

The correlation of $\sigma$ and $\eta$ from experimental data has been established in Chap IV. The theoretical correlation models are explored in our study based on the WLF equations where $c_1$ changes with degree of cure and $c_2$ is constant.
Combining Equation [5-20] and [5-21] and rearranging them, the following equation which relates \( \log \sigma \) and \( \log \eta \) is obtained. The correlation depends on both \( T_g \) and \( T_c \).

\[
\log \sigma = \log \eta + \left( \log \sigma_{T_c=T_g} + \log \eta_{T_c=T_g} \right) + \frac{(c_1 - c_2)(T_c - T_g)}{c_2 + T_c - T_g}
\]

where \( \log \sigma = \log \sigma_{T_c=T_g} + c_1 \sigma (T_c - T_g)/(c_2 \sigma + T_c - T_g) \);

\[
\log \eta = \log \eta_{T_c=T_g} - c_1 \eta (T_c - T_g)/(c_2 \eta + T_c - T_g); \quad \text{and} \quad c_2 \eta = c_2 \sigma = 51.6
\]

It is obvious that there is an inverse relation between \( \log \sigma \) and \( \log \eta \) only when \( (c_1 - c_2)(T_c - T_g) \) is approximately constant. This occurs when \( T_g < < T_c \), that is in the earlier stages of cure.

By substituting the WLF parameters listed in Table 5.1 into this equation, a quantitative correlation is obtained. Fig 5.6 illustrates the WLF correlation between \( \log \sigma \) and \( \log \eta \) in comparison with the experimental data for the Pr500 system. The solid curves represent the predicted correlation. In general, the calculated values agree with experimental data.

**Analysis of a relationship of \( \sigma \) to degree of cure**

The DiBenedetto equation was used to model the relationship between \( \sigma \) and \( T_g \) in Chapter III. DiBenedetto related the shift in the glass-transition temperature to the degree of cross-linking as follows:

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\[
\frac{T_g - T_{go}}{T_{go}} = \frac{(Ex/Em-Fx/Fm)\alpha}{1-(1-Fx/Fm)\alpha}
\]

[3-1]

where \(T_{go}\) is the glass transition of the unreacted material, \(Ex/Em\) is the ratio of lattice energies for crosslinked and uncrosslinked polymer and \(Fx/Fm\) is the corresponding ratio of segmental mobilities.

Rearranging equation [3-1], an expression for \(T_g\) as a function of \(\alpha\) is:

\[
T_g = \frac{(Ex/Em-Fx/Fm)T_{go}^*\alpha + T_{go}}{1-(1-Fx/Fm)\alpha}
\]

[5-24]

It is observed that only when \((1-Fx/Fm)\alpha < < 1\), \(T_g\) can be expressed linearly as

\[
T_g = (Ex/Em-Fx/Fm)T_{go}^*\alpha + T_{go} = A + B*\alpha
\]

[5-25]

where \(A = T_{go}\) and \(B = (Ex/Em-Fx/Fm)T_{go}\).

From the plots of \(T_g\) versus \(\alpha\) for both the Pr500 system (Fig 3.5a) and the My720 system (Fig3.5b), it is observed that the linear relationship is approximately valid before \(\alpha\) reaches 0.5 for both systems.

In chapter IV, we examined the Mijovic relationship [4-31] in which he proposes to relate the resistivity to the reaction conversion.

\[
\alpha = \frac{\log\rho - \log\rho_m}{\alpha_m \log\rho_m - \log\rho_o}
\]

[4-31]

where \(\rho\) is the resistivity which equals to \(1/\sigma\), \(\alpha_m\) is the maximum value of extent of reaction attainable under given cure conditions, \(\rho_m\) is the corresponding resistivity, and the subscript "o" denotes initial conditions. The Pr500 and My720 experimental data do not agree well with values predicted by their relationship as seen in Fig4.19a.
and Fig4.19b.

If we assume that $T_g$ increases linearly with $\alpha$, the Mijovic relation can be derived from the WLF equation based on certain conditions.

Substituting the equation $T_g = A + B\alpha$ into the WLF equation, one obtains

$$\log \sigma = \log \sigma_{T_g=T_c} + \frac{c1(T-A-B\alpha)}{(c2+T-A-B\alpha)} \quad [5-26]$$

Rearranging this equation, we get

$$\log \sigma = \log \sigma_{T_g=T_c} + \frac{(A'(T)-c1\alpha)}{(B'(T)-\alpha)} \quad [5-27]$$

where $A'(T)=c1(T-A)/B$ \hspace{1cm} [5-28]

$$B'(T)=(c2+T-A)/B \quad [5-29]$$

For a given isotherm, both $A'$ and $B'$ are constant.

Based on equation [5-27], the following expressions can be derived,

$$\log \sigma_0 - \log \sigma_i = \frac{(A'/B')-(A'-c1\alpha)}{(B'-\alpha)} \quad [5-30]$$

Similarly, $\log \sigma_0 - \log \sigma_m = \frac{(A'/B')-(A'-c1\alpha_m)}{(B'-\alpha_m)} \quad [5-31]$

where $\alpha_m$ and $\sigma_m$ are the value of $\alpha$ and $\sigma$ at a late final reference stage of cure.

Combining equations [5-30] and [5-31],

$$\frac{\log \rho - \log \rho_m}{\log \rho_m - \log \rho_o} = \frac{\alpha(B'-\alpha_m)}{\alpha_m(B'-\alpha)} \quad [5-32]$$

It is observed that when $B'-\alpha \approx B'-\alpha_m$, the Mijovic relationship can be obtained.

Thus, this relation is approximately valid if $\alpha$ and $\alpha_m$ are much smaller than $B'$. The values of $B'$ can be determined by combining equation [5-29] with values of $A$ and
B from a linear fit of Tg versus \( \alpha \) using equation [5-25] as follows

\[
B' = \frac{(c_2 + T - T_{go})}{((E_x/E_m - F_x/F_m)T_{go})}.
\]  

[5-33]

where \( c_2 \) is 51.6 as discussed in an earlier section. For the Pr500 system, \( T_{go} = -13^\circ C \), \( E_x/E_m = 1.42 \) and \( F_x/F_m = 0.78 \). In the case of My720, \( T_{go} = 1^\circ C \), \( E_x/E_m = 0.84 \) and \( F_x/F_m = 0.43 \) (Chapter III). Thereby, the temperature dependent \( B' \) can be calculated using equation [5-33]. The values are listed in Table 5.2a and 5.2b for Pr500 and My720 individually.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>150</th>
<th>160</th>
<th>170</th>
<th>180</th>
<th>190</th>
</tr>
</thead>
<tbody>
<tr>
<td>B'</td>
<td>1.29</td>
<td>1.35</td>
<td>1.41</td>
<td>1.47</td>
<td>1.53</td>
</tr>
</tbody>
</table>

**Table 5.2a** Pr500 system

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>160</th>
<th>177</th>
<th>190</th>
</tr>
</thead>
<tbody>
<tr>
<td>B'</td>
<td>1.87</td>
<td>2.02</td>
<td>2.14</td>
</tr>
</tbody>
</table>

**Table 5.2b** My720 and DDS system

It is observed that the values of \( B' \) for the Pr500 system are not big enough to ignore the factor of \( \alpha \) or \( \alpha_m \) (around 0.8) except when \( \alpha \) approaches \( \alpha_m \). For the My720 system, the values of \( B' \) are greater than those of the Pr500. In addition to that, \( \alpha_m \) (around 0.4) is smaller. Therefore, the expression

\[
B' - \alpha = B' - \alpha_m
\]

is a better approximation for My720 than for the Pr500 system. This explains why the plots of the Mijovic relation fit better for My720 (Fig 4.19b) than for Pr500 (Fig. 19a).

Another approach can be made for Pr500 by using data where we set \( \alpha_m \) equal
to 0.45. Figure 5.7 illustrates the resulting Mijovic relation fit. It is better than the fit shown in Fig 4.19a.

Based on our study, the application of the Mijovic relationship is limited to the conditions of a linear Tg versus $\alpha$ relationship and to $B'-\alpha \approx B'-\alpha_m$, ie $B' > \alpha_m$.

Conclusions

The dielectric response (ionic conductivity and dipolar relaxation time) and viscosity were characterized by the free volume based modified WLF equation. A free volume fraction of 0.025 and a thermal expansion coefficient of $4.8 \times 10^{-3}$ were used to achieve $c_2 = 51.6$ for $\sigma, \tau$ and $\eta$. A modified WLF equation, which under the assumption that the qualities at reference temperature and the values of $c_1$ change linearly with temperature $T_c = T_{gC}$, describes the experimental data well. The results of this work support the use of the free volume based WLF equation for analyzing the dielectric and viscosity changes during cure of the epoxy system. Based on the modified WLF equations, the glass transition temperature, degree of cure and viscosity can be predicted on-line during a composite fabrication process by FDEMS sensing techniques. The Mijovic relationship of the ionic conductivity to degree of cure has limited application. The degree of cure can be determined better on-line using the dielectric technique through a one to one relationship with the glass transition temperature and measurement of the dipolar relaxation time ($\tau$).
References to Chapter V


Pr500 at 150, 160, 170, 180 and 190°C

![Graph showing log(α) vs Tg for Pr500 at different temperatures]

Fig 5.3a log(α) vs Tg for Pr500 (solid curve represents the WLF fit)

My720 and DDS at 160, 177 and 190°C

![Graph showing log(α) vs (T - Tg) for My720 and DDS system at different temperatures]

Fig 5.3b log(α) vs Tg for My720 and DDS system (solid curve represents the WLF fit)
Pr500 at 150, 160, 170, 180 and 190°C

Fig 5.4a log(σ) vs Tg for Pr500 (solid curve represents the WLF fit)

My720 and DDS at 160, 177 and 190°C

Fig 5.4b log(σ) vs Tg for My720 and DDS system (solid curve represents the WLF fit)
Pr500 at 150, 160, 170, 180 and 190°C

Fig 5.5a logη vs Tg for Pr500 (solid curve represents the WLF fit)

My720 and DDS at 160, 177 and 190°C

Fig 5.5b logη vs Tg for My720 and DDS system (solid curve represents the WLF fit)
Fig 5.6 Ionic conductivity versus viscosity for Pr500 (solid curve represents the WLF fit)

Fig 5.7 $\alpha$ calculated from Mijovic model in comparison with $\alpha$(exp) for Pr500 ($\alpha_m=0.45$)

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Conclusions

The Frequency Dependent Electromagnetic Sensing (FDEMS) technique combined with DSC and rheometry measurements can be used to characterize the cure of an epoxy resin. Once correlated with degree of conversion, glass transition temperature and viscosity, the values of ionic and dipolar mobilities as measured by FDEMS can be used to quantitatively determine the degree of reaction, glass transition temperature and the corresponding viscosity insitu during composite fabrication.

In this investigation, the reaction kinetics for epoxy-amine systems were satisfactorily described by an autocatalyzed reaction mechanism. The Arrhenius-type temperature dependent rate constants were determined in the pregel stage, whereas the diffusion controlled reaction rate constants were modeled and determined using a modified WLF equation. The relationship between glass transition temperature (Tg) and degree of cure (α) during cure was observed to be independent of the curing temperature.

The condition for gel formation was analyzed in terms of gel time and gel fraction. For the Pr500 system, the experimental gel conversion is much higher than the value predicted by Flory's classical theory. In the case of the My720...
& DDS system, the $\alpha_{gel}$ (experimental) is very close to the calculated value at 160°C. However, the experimental conversion diverged from the calculated value at higher curing temperatures. This suggests that temperature does affect reaction functionalities of the epoxide and the reactivity of hydrogens on the amine group.

The evolution of the complex dielectric permittivity was used to calculate the ionic conductivity and dipolar relaxation time. The curing time dependent ionic mobility goes through an inflection point for both crosslinked and non-crosslinked epoxy-amine systems. This questions the veracity of using the inflection point to detect gel. When the scaling relation $[(tgel-i)/tgel]^x$ was used to predict the time of occurrence of gelation from dielectric data it did not agree with the mechanically determined gel time.

Well before gel there is a linear relationship between ionic conductivity and viscosity which is independent of isothermal temperature for both the Pr500 and My720 systems. When gel is approached the linear relationship breaks down. The change in viscosity is much faster than that of ionic conductivity. However, for the non-crosslinked DGEBA and 4-biphenyl system the linear relationship holds for a long time and to a high degree of cure ($\alpha=0.92$).

The dielectric response (ionic conductivity and dipolar relaxation time) and viscosity were characterized by the free volume based modified WLF equation. A free volume fraction of 0.025 and a thermal expansion coefficient of $4.8 \times 10^{-3}$ were used to achieve $c_2=51.6$ for $\sigma, \tau$ and $\eta$. A WLF equation, which has the value of $\sigma, \tau$ and $\eta$ at the reference temperature and the value of C1 changing
linearly with temperature, describes the experimental data well. The results of this work support the use of the free volume based WLF equation for analyzing the dielectric and viscosity changes during cure of the epoxy system. Based on the modified WLF equations, the glass transition temperature, degree of cure and viscosity can be predicted on-line using FDEMS sensing techniques during resin cure or the composite fabrication process.

The empirical relationship proposed by Mijovic which relates the ionic conductivity to degree of cure was derived using the WLF and DiBenedetto equations and shown to have limited application. It can only be applied when $\alpha$ is small. The degree of cure can be determined better on-line using the dielectric technique through a one to one relationship with the glass transition temperature and measurement of the dipolar relaxation time ($\tau$).
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