Auto-adaptive multistage curing epoxy coatings

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8·13·09
Date
DEDICATION

This thesis is dedicated to my love and future wife, Astrid, who supported and motivated me during this two years spent in the US. Thanks also to my parents Nicole and Pierre, my brothers and my closest friends.
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LIST OF ABBREVIATIONS

AIBN: Azobisisobutyronitrile

ATR: Attenuated Total Reflectance

BPO: Benzoyl peroxide

CPMG: Carr-Purcell-Meiboom-Gill

DGEBA: Diglycidyl ether of bisphenol A

DMA: Dynamic Mechanical Analyzer

DMPT: N,N dimethyl para toluidine

DSC: Differential Scanning Calorimetry

FID: Free Induction Decay

FTIR: Fourier Transform Infrared Spectroscopy

GMA: Glycidyl methacrylate

ONR: Office of Naval Research

TEPA: Tetraethylenepentamine

\( T_g \): Glass transition temperature

TGA: ThermoGravimetric Analyzer

VOC: Volatile organic compound
Corrosion is an expensive issue for the Navy. Epoxy based protective coatings are used by the Navy to minimize corrosion. The goal of this work is to reduce the cost of corrosion by improving the reliability of the coating application. A better application process decreases defects and reduces early failures. A novel hybrid epoxy coating system composed of two layers has been developed. A first layer with two curing stages (an epoxy/amine polycondensation combined with a vinyl free radical polymerization) and a standard second layer were created and tested. A room temperature free radical initiator system was selected to perform the free radical polymerization. Diffusion predictions were carried out in order to determine the viability of the initiator diffusion. Kinetics measurements and theoretical modeling were performed in order to characterize the curing behavior. A novel formulation was developed and showed a potential for practical application.
CHAPTER I

INTRODUCTION

Everything made of steel needs to be protected against corrosion. The application of polymeric coatings to steel surfaces is a solution widely used. Corrosion protection by polymeric coating is a very active field of research because many everyday life items are made of steel. Scientists try to improve the lifetime of the paint and the resistance to corrosion in harsh environments like high temperature, acidic or salted conditions.

Corrosion protection of ship tanks and ballasts is a fundamental problem in the preservation of both military and civil fleets. For the US Navy alone, the annual maintenance cost of tanks amounted to $384,000,000 in 2003. In order to decrease the annual expense, the Office of Naval Research (ONR) funds research project to improve protective coatings.

The project called Innovative multifunctional anticorrosion coating encompasses reducing maintenance requirements by extending the coating lifetime, detecting early corrosion to allow remediation before failure, and reducing technical constraints during application by shipyards.

One of these approaches is entitled “auto-adaptive multistage curing epoxy coatings” and aims to improve the application side of the coating. This topic is the focus of the study.

1.1 Goal

As the environmental requirements for coatings become more stringent, application becomes substantially more challenging. Previous generations of solvent based coatings only required pail mixing prior application. Application could be done at any pace, with roller or
sprayers. Overcoating (a second layer of paint) also could be done anytime. However, critical issues with these coatings have required their ban (volatile organic carbon VOC release). The newest generation of coatings have no solvent, very fast curing, are more challenging to remove (blast or grind), and are less tolerant to overcoating. These current coatings are two component systems that can be either mixed before spraying with limited time for application, or are mixed as they are being applied (plural systems). Applicators are faced with the challenges of meeting these stringent application requirements with personnel having limited knowledge of coating chemistry.

The project “auto-adaptive multistage curing epoxy coatings” aims to improve the process of coating application on steel. The type of paint selected is epoxy based because these coatings have great barrier properties (which confer excellent anticorrosion properties) and are widely used by the Navy. The projected innovation would provide improved reliability of the coating and save money. Bringing ships into dry dock for maintenance is very costly, with “time in dry dock” the major cost component. Consequently, shipyards race against the clock to return the vessels to sea. Repainting involves a time-consuming process, such as sand blasting and allowing sufficient time for each coat of paint to dry and harden. The whole process has to be repeated whenever there is a mistake. While easy to overlook, new coatings that are easier and faster to apply correctly have the potential to both save money and return ships to sea sooner.

In order to reduce these application problems, the project proposed to develop an epoxy coating that has a first layer which cures in two stages to allow an almost unlimited overcoat window which provides time for use of chemical strippers to correct base layer application errors and in the meantime reduces adhesion problems between the two coats.
The current process is briefly described in order to understand the issues which are encountered nowadays. Next, the approach that has been developed during this project is outlined.

1.2 Description of the current process

A typical paint employed in the Navy shipyards is an epoxy based resin called MIL-DTL-24441. This paint is a two component system. The process of painting involves several steps. The first step is the surface cleaning. Sand blasting is usually the method used, it allows to remove the old paint and in the meantime to prepare a clean surface free of rust. Next, the first layer of paint is applied. And finally the second layer is applied. The thickness of each layer is approximately 250 μm (Figure 1.1). The required coating thickness to provide efficient protection is unreachable in only one layer. Two layer of paint have to be applied.

![Figure 1.1: scheme of the paint on steel surface](image)

During standard coating application, the second layer has to be applied during a time window defined by a cure of at least about 40% in order to have a coating tack and sag free and no later than about 80% cure for the first layer. Beyond this value, the coating is too hard and
unreactive for interlayer crosslinking to provide an efficient adhesion between layers. The time window is easy to overlook and the quality of the coating can be greatly affected.

Figure 1.2 represents the conceptual curing kinetics of the two independent layers. The blue line corresponds to the cure of the first layer whereas the red one is related to the second layer. The second layer must be applied during the time window (the red box) to allow good adhesion between the two layers. It can be a short time, as little as 15 minutes depending on the system (for MIL-DTL-24441 is it a couple of hours).

![Figure 1.2: kinetics of the current process](image)

The objective of this project is the expansion of the time window to an almost infinite time. For this, modifications in the composition of the paint are necessary. The strategy is described in the following section.

1.3 **Description of the novel process**

The critical point to increase the overcoating application window is the control of the first layer cure. The approach used to resolve the problem is to stop the cure of the first layer at a certain point and to resume it only when the second layer is applied.
In the novel coating proposed, the first layer curing is limited to 50% in order to allow a much longer period of time to apply the second layer (blue line) (Figure 1.3). The first layer will resume its curing to its fully extent upon the application of the second layer (Figure 1.3). With such a product, the second layer can be applied at any time.

![Conceptual kinetics of the novel curing process](image)

**Figure 1.3: Conceptual kinetics of the novel curing process**

1.4 **Approach**

In order to perform the two steps of the first layer cure, different chemistries are required for each of the steps. For the first step of curing in the first layer, a classic reaction of epoxy ring opening with an amine takes place.

\[
\text{R} = \text{H or alkyl OH} \quad \text{V} + \text{NH}_2 \quad \text{R} \quad \text{H or alkyl}
\]

The second curing step in the first layer is performed by a free radical polymerization of vinyl compound with a free radical initiator. R1 an
The first curing step forms a network. The second step of curing has to continue to increase the crosslinking density of the network formed during the first step. Then in order to achieve this target, vinyl bonds need to be attached to the network at the end of the first curing step. A new molecule with both a reactive side to be linked to the network during the first curing stage and a vinyl bond is required.

The free radical polymerization within the first layer has to be performed by a room temperature free radical initiator (application of the coating at room temperature) and triggered by the second layer application. The option of a molecule diffusing from the second to the first layer has been taken. Figure 1.4 is a scheme of the different step of the paint application with its curing.

*Figure 1.4: concept scheme of the novel coating curing step*
This thesis has been divided into five chapters. Chapter II provides a review of the different techniques available to follow the curing kinetics of epoxy resin. The third chapter is dedicated to kinetic experiments and modeling of epoxy resin curing. The fourth chapter describes the incorporation of a free radical polymerization for the second curing stage of the first layer. In the last chapter, systems for room temperature initiation of the free radical polymerization, a model for the diffusion and an experiment simulation the full process are presented.
CHAPTER II

BIBLIOGRAPHY REVIEW: METHODS FOR THE MONITORING OF EPOXY RESIN CURING

2.1 Introduction

Epoxy resins are used in many applications such as in anticorrosion coatings, insulating layers in electronics and high-strength glue. The curing reaction mechanism has been extensively studied. A better understanding of the molecular network gives better control over the final mechanical and chemical properties of the materials. That is the reason why several techniques have been developed to study epoxy resins curing and more particularly in academy laboratories for fundamental characterizations as well as understanding of the curing process. Industries using epoxy resins have developed several in-situ techniques for fundamental characterization of the curing process and to increase the quality and process control of their products.

The objective of this chapter is to give an overview of the different techniques used to monitor the curing of epoxy resins. First, the chemistry occurring and the resulting critical transformation of the physical properties are described. Then, the different characterization methods are listed with some details on the parameters involved in the monitoring of the curing. Finally, the monitoring techniques have been summarized in a table (Table 2.4).

Cured epoxy resins are thermoset polymers which are obtained by the reaction between two components. The first component is the epoxy resin strictly speaking (epoxide function). The most common epoxy resins are based on diglycidyl ether of bisphenol A (DGEBA). The
second component is the hardener which can be any molecule having a functional group that can react with the epoxy function; such as an anhydride acid, amide or amine. Amine based hardeners are the most commonly used and most studied, therefore the epoxy / amine system will be taken as an example for this review. Systems with other hardeners exist and can be easily adapted.

The epoxy ring opening mechanism depends on the pH of the mixture\(^1\). If the pH is acidic, the addition of the nucleophilic moiety (here the amine group) occurs on the most substituted carbon while in alkaline solution the addition occurs on the less substituted carbon. Because of the presence of the amine (pKa ~9-10), the pH of the reaction mixture (epoxy resin + hardener) is high, therefore the addition of the nucleophilic moiety will occur on the less substituted carbon of the epoxy ring.

During the curing of the epoxy resin with an amine as hardener, there are three different types of reaction taking place\(^2,3\):

The first reaction occurs between an epoxy group and a primary amine.

-Epoxy-primary amine

\[
\text{R1—NH}_2 + \text{R2—O} \rightarrow \text{R1—N—R2} + \text{OH}
\]

The second one is the reaction of an epoxy group with a secondary amine created by the first reaction (Reaction 1 and 2 are often considered to occur at the same rate\(^4\), thus reaction 2 can happen before the total consumption of the primary amine).
The third reaction is the reaction of an alcohol with the epoxy ring. This later reaction is possible but is not always considered.

Note: the mechanism of curing reactions will be further described in the next chapters.

It is important to understand the changes that happen in the molecular structures during the curing; it helps to comprehend the range of chemical and physical parameters. Due to the bi-functionality and more often multi-functionality of the reactive molecules, the length (molecular weight) of the molecules increases with the extent of reaction. The curing of the epoxy resin can be separated into three different parts (Figure 2.1):
The first part is defined between the start up to the gel point.

Gelation corresponds to the formation of an infinite length network. At this point there are still small molecules remaining but the system’s matrix behaves as an infinite network. Monomers are all connected by at least one side to the network. Different theories have been developed to model the extent of reaction at the gelation point (1940’s Flory and Stockmayer, percolation 1970’s,...).

The second part starts after the gel point and up to the vitrification point.

Vitrification is the phenomenon which occurs when the $T_g$ of the materials become greater than the temperature of curing (Latin: Vitrum meaning glass).

The last part is the finalization of the curing after the vitrification point.

The gelation and the vitrification points are important parameters in term of change of physical properties and that is why the monitoring of these points is critical to the process.
The temperature of curing is an important parameter. The higher the temperature the faster (and more complete) the curing is. Arrhenius’s law (equation 2.1) shows the relation between the kinetics constant $k$ and the temperature $T$.

$$k = Ae^{\frac{E_a}{RT}}$$  \hspace{1cm} (2.1)

The curing temperature depends on the system and its application. Some curing temperatures are around room temperature for coating application and some are at higher temperature to have easier casting or better properties. It is the chemistry of the epoxy/hardener which defines the temperature of curing. Aliphatic amines are usually more reactive than aromatic amines. This is due to the delocalization of the electron pair of the nitrogen which reduces the nucleophilic property and leads to a decrease in reactivity. The temperature of cure is higher for resins using aromatic amine (N-methylaniline reacts at 110°C).

The monitoring of the curing of epoxy resins can be performed with different analytical techniques. These techniques are split in two groups; direct and indirect methods.

- The direct analytical techniques allow to follow the consumption or the production of one or more chemical groups in the resin composition with time. These techniques are for example FTIR or NMR.
- In contrast with direct methods; indirect methods follow the variation of mechanical, thermal and electrical properties which are indirectly related to the degree of curing with time (DSC, ultrasound...).
2.2 Direct techniques

The direct techniques are essential to study the mechanism of the reaction because it is possible to directly follow the chemical moieties. These techniques are used as reference for the indirect methods to relate the variation of the parameter measured by the indirect method with the extent of reaction by the intermediate of the reaction time.

2.2.1 InfraRed Spectroscopic techniques

Infrared spectroscopic techniques are able to quantify the concentration of a moiety in a system. According to the infrared spectroscopy theory, each moiety has a specific vibrational frequency.

According to the Beer-Lambert's law (Figure 2.2), the absorbance is proportional to the concentration in the sample, equation 2.3.

\[ A = \log \left( \frac{I_0}{I} \right) \]  \hspace{1cm} (2.2)

\[ A = \varepsilon(\lambda) \times l \times c \]  \hspace{1cm} (2.3)

Where \( I_0 \) and \( I \) are the initial intensity and intensity of the beam respectively

\( \varepsilon(\lambda) \) is the molar absorptivity at a specific wave length

\( l \) is the length of the beam path through the sample
c is the concentration of the moiety in the sample

The Infrared technique is used to determine the degree of conversion from which kinetics parameters\(^3\) can be obtained. In order to be able to obtain the conversion as a function of time, it is required to collect spectrum at different times during the curing of the epoxy resin. Therefore the conversion versus time is calculated according to the equation 2.4

\[
\alpha = 1 - \frac{C(t)}{C(t = 0)}
\]  

(2.4)

Then using the Beer-Lambert’s Law and an internal standard (a moiety of the system which is not consumed during the curing). The extent of conversion is obtained according to equation 2.5.

\[
\alpha = 1 - \frac{\bar{A}_t}{\bar{A}_0}
\]  

(2.5)

With \(\bar{A}_t = \frac{A_x(t)}{A_{ref}(t)}\)

Where: \(A_x(t)\) and \(A_{ref}(t)\) are the peak absorbance of the reactive group and the reference band at time \(t\), respectively.

Using this approach, it is possible to use different spectroscopic techniques: Fourier Transform InfraRed (FTIR) spectroscopy in Middle InfraRed (MIR) or Near InfraRed (NIR) or even Raman spectroscopy.

2.2.1.1 Fourier Transform InfraRed Spectroscopy in Middle Infrared

The FTIR MIR is widely used to study the kinetics of curing\(^3,4\). Mijovic et al. used it to study specifically the mechanism of reaction. The MIR frequency range goes from 400 cm\(^{-1}\) to 4000 cm\(^{-1}\). Depending on the rate of curing and the temperature of curing several methods can be used to acquire the different spectra with time.
If the curing needs to be performed at temperature above room temperature, it is not easy to place the sample in the FTIR at this temperature. The resin is cured in an oven and samples are collected periodically for IR analysis. The spectrum can be obtained from traditional pellet of salt (NaCl, KBr, CaF2 or CsI) or using an Attenuated Total Reflection (ATR) setup.

If the curing of the resin occurs at room temperature, a direct recording of the spectrum can be performed. The resin is placed between two salt pellets or directly on the ATR crystal.

In order to monitor the extent of reaction as a function of time, characteristic bands from the spectrum should be selected. The band at approximately 915 cm\(^{-1}\) is generally used to follow the consumption of epoxy during the curing. Musto et al. showed that the peak is decreasing with time during curing (Figure 2.3).

![MIR spectra collect at different times for a curing process carried out at 140°C with a tetrafunctional epoxy resin / diamine system](image)

The spectrum with time shows variation because of the change of state (from liquid to solid). To account for this, it is required to select a peak as internal standard in order to obtain
The selection of the bonds used to interpret the curing reaction is function of the epoxy resin/hardener system. Below is a table summarizing the characteristic absorption peaks present in the mixture (Table 2.1). Sometime there is overlapping of peaks which complicates the determination of the relative absorbance and in some cases a deconvolution of the peaks is required.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Range of absorption of wave numbers (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Terminal epoxy ring stretch</td>
<td>916-906</td>
</tr>
<tr>
<td>Aromatic C-H out of plane band</td>
<td>835-806</td>
</tr>
<tr>
<td>Aromatic C=C stretch</td>
<td>1517-1507</td>
</tr>
<tr>
<td></td>
<td>1609-1605</td>
</tr>
<tr>
<td>Primary amine N-H in plane bend</td>
<td>1632-1614</td>
</tr>
<tr>
<td>Primary aliphatic amine N-H stretch</td>
<td>3344-3324</td>
</tr>
<tr>
<td></td>
<td>3475-3375</td>
</tr>
<tr>
<td>Primary aromatic amine N-H stretch</td>
<td>3211-3456</td>
</tr>
<tr>
<td></td>
<td>3460-3509</td>
</tr>
<tr>
<td>Secondary amine N-H stretch</td>
<td>3414-3348</td>
</tr>
<tr>
<td>Hydroxyl stretch</td>
<td>3600-3200</td>
</tr>
</tbody>
</table>

2.2.1.2 Fourier Transform InfraRed Spectroscopy in Near Infrared NIR

The NIR relates to electromagnetic waves with wave numbers from 4000 cm⁻¹ to 14000 cm⁻¹. The absorption of these waves is characteristic of overtone and combination of fundamental mode of vibration of molecules which are usually seen in MIR.

The sample preparation is similar to FTIR MIR. Figure 2.4 represents the change in the NIR spectrum during the curing of the resin. The blue arrows represents the epoxy function and the red one the aromatic primary amine.
Different characteristic bonds can be used to monitor the extent of reaction (Table 2.2).

The most commonly used bonds are 4530 cm$^{-1}$ for the epoxy part and 4673 cm$^{-1}$ or 5990 cm$^{-1}$ for the reference bond$^{13,16,17}$.

**Table 2.2: Main NIR characteristic peaks for an Epoxy-Amine system**

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Range of absorption of wave numbers (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Terminal epoxy ring combination</td>
<td>4535-4510</td>
</tr>
<tr>
<td>Terminal epoxy resin overtone</td>
<td>6080-6057</td>
</tr>
<tr>
<td>Aromatic C-H combination</td>
<td>4682-4620</td>
</tr>
<tr>
<td>Aromatic C-H</td>
<td>5995-5969</td>
</tr>
<tr>
<td>Primary aliphatic amine N-H combination</td>
<td>4941-4920</td>
</tr>
<tr>
<td>Primary aromatic amine N-H combination</td>
<td>5072-5051</td>
</tr>
<tr>
<td>Primary amine N-H overtone</td>
<td>6690-6480</td>
</tr>
<tr>
<td>Secondary amine N-H overtone</td>
<td>6683-6600</td>
</tr>
<tr>
<td>Hydroxyl combination</td>
<td>4903-4750</td>
</tr>
<tr>
<td>Hydroxyl overtone</td>
<td>7000-6968</td>
</tr>
</tbody>
</table>

2.2.2 Raman spectroscopy

One of Raman spectroscopy's major advantage over other spectroscopy techniques is the ability to obtain data from a small spatial region of the sample$^{18}$ when it is used with a
confocal microscope. When scanning in a grid pattern over the surface and through the sample, a 3-D map of chemical information can be obtained. Also, the c=c bond has a much stronger signal in Raman spectroscopy than InfraRed spectroscopy.

Raman spectroscopy is similar in concept to Infrared spectroscopy with the only difference being the energy absorption mechanism. As a consequence, many bands are found in both infrared and Raman spectroscopy but some are only found in one of the two spectroscopy models.  

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Range of absorption of wave numbers (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂ of epoxide ring deformation</td>
<td>850</td>
</tr>
<tr>
<td>Epoxide ring deformation</td>
<td>907</td>
</tr>
<tr>
<td>Aromatic C-H</td>
<td>1012</td>
</tr>
<tr>
<td>Aromatic C-H (plane)</td>
<td>1190</td>
</tr>
<tr>
<td>C-H epoxide ring deformation</td>
<td>1270</td>
</tr>
<tr>
<td>Quadrant stretching of benzene ring</td>
<td>1614</td>
</tr>
<tr>
<td>C-H of epoxide</td>
<td>3001</td>
</tr>
<tr>
<td>C-H of epoxide</td>
<td>3072</td>
</tr>
</tbody>
</table>

Using the same methodology as described above, the kinetics of curing can also be followed by Raman. The epoxy moiety consumption is followed using the characteristics absorption bands at 1275 cm⁻¹ or 907 cm⁻¹ and the reference peak is usually taken as a peak characteristic of phenyl ring (1614 cm⁻¹). Some of these bonds are summarized in Table 2.3 above. Figure 2.5 represents the spectrum variation as a function of time of curing for the epoxy resin / aromatic amine system, as followed by Raman spectroscopy.
Raman is not as widely used as the FTIR for the characterization of epoxy resins. It is due to the cost of the instrument and the complexity to obtain a spectrum of good quality. Moreover FTIR spectrometers are present in almost every laboratory and Raman technique leads to similar results than Infrared spectroscopy.

2.2.3 In-situ infrared and Raman spectroscopy monitoring

The advantages of InfraRed spectroscopy and Raman Spectroscopy are the monitoring of the cure in-situ due to optic-fiber probes:

➢ Since MIR is from 4000 cm$^{-1}$ to 400 cm$^{-1}$, the transmission of those frequencies through conventional silica-type glass fibers is problematic. Only chalcogenide and metal halide fibers (Arsenic-germanium-selenium As/Ge/Se) or gold-coated waveguide setup $^{24}$ can be used. This challenge reduces the potential for industrial applications.
➢ NIR is from 14000 cm$^{-1}$ to 4000 cm$^{-1}$ which allows using inexpensive and abundant silica-type optical fibers. This technique has been widely used in the past decades for industrial applications since the apparition of FTIR –NIR. 

➢ Raman can also be used for in-situ monitoring. The use of classic optical fiber is possible because the wave length travelling in the fiber is different from the InfraRed MIR spectroscopy (in Raman it is a high energy wavelength (laser) where in InfraRed it is the MIR or NIR wavelength).

2.2.4 High resolution NMR

2.2.4.1 Liquid-state NMR

High resolution NMR is useful to quantitatively determine the conversion before and after gelation by following the functional characteristic peaks. It is possible to obtain the NMR spectrum of the sample before gelation by dissolution in an appropriate solvent. For the product after gelation it can be ground in fine particle and dispersed in a good solvent allowing the swelling of these particles, and measurement.

2.2.4.2 Solid-state NMR

Characterization using solid state NMR can also be performed to obtain information about molecular, spatial relations and chemical determinations. Nevertheless solid state NMR is an expensive tool which is not available in every laboratory.
2.2.5 Chromatography

2.2.5.1 High Pressure Liquid Chromatography

HPLC is used to quantify the monomer remaining after a certain time of reaction. This technique is also limited to the period of pre-gelation. It is not often used.

2.2.5.2 Size Exclusion Chromatography

The SEC is used to follow the molecular weight of the soluble part of the epoxy resin before gelation. The information can be interesting for understanding the mechanism of polyaddition and checking models but this technique is not frequently used.

2.2.6 Titration

The quantification of the epoxy function with time is possible with a simple titration. The epoxy ring reacts with hydrochloric acid in stoichiometric ratio. The titration has some limitation after the gelation point due to the difficulty of hydrochloric acid (HCl) to reach the epoxy ring inside the crosslinked materials. This technique is not often used because it requires significant bench work for only one set of data.

2.3 Indirect techniques

2.3.1 Low resolution pulsed NMR

Low resolution pulsed NMR (20MHz) can be used to monitor the curing of the epoxy resin. This type of NMR is cheaper than the traditional High resolution NMR which gives a possibility for industrial application.
The pulsed NMR measures the mobility of nuclei which are active magnetically. During the curing of the epoxy resin, change in the physical state of the system occurs i.e. change in the mobility of the hydrogen nuclei. The parameter allowing the measurement of the change is a time constant $T_2^*$. The amplitude of the Free Induction Decay is a function $T_2^*$ and can be fit as in equation 2.6. Two characteristic times are extracted and plotted in Figure 2.6.

More details about the theory of this method can be found in the papers cited in this section or in *Nuclear magnetic resonance in solid polymers* published in 1993 and written by McBrierty et al.

\[ y(t_{FID}) = A_{\text{solid}} e^{\left(\frac{-t}{T_{2\text{solid}}}\right)^2} + A_{\text{liquid}} e^{\left(\frac{-t}{T_{2\text{liquid}}}\right)^2} \]  

(2.6)

![Figure 2.6: Amplitude of liquid and solid component in function of time for AY-105 and HY-4075GB from Ciba polymer](image)

The cross-over between the two curves correspond to a state transition from liquid to solid. This time is taken as the gelation point of the system, the vitrification is identified when the amplitude of the solid component becomes constant.

To compensate for inhomogeneities in the sample and magnetic field and other off-resonance effects, the Carr-Purcell-Meiboom-Gill (CPMG) method can be used and gives information about individual components within the samples.
The fitting of the exponential decay of the CPMG method is based on exponential fits like for the Free Induction Decay (FID) analysis (Figure 2.7). Two approaches can be used:

- a single exponential decay fit representing the average mobility of hydrogen nuclei

\[ y(t) = A_{\text{single}} e^{-\frac{t}{\tau_{\text{single}}}} \]  

(2.7)

- a two component fit representing a short and long decay time.

\[ y(t) = A_{\text{short}} e^{-\frac{t}{\tau_{\text{short}}}} + A_{\text{long}} e^{-\frac{t}{\tau_{\text{long}}}} \]  

(2.8)

The CPMG method is useful for determination of the curing process with more detail, where the mechanism of reaction can be separated in several periods. Below is the plot for the one component fit, the decrease of the decay time corresponds to some extent to the curing of the resin.

Figure 2.8: time decay ($\tau_2$) of CPMG one component fit with time for the system AY-105 and HY-4076GB from Ciba polymer.
2.3.2 Ultrasound

The ultrasound technique is capable of obtaining information about the macroscopic material structure as well as the mechanical properties of the materials with measurement of acoustic wave properties\textsuperscript{29}.

Piezoelectric transducers are required to monitor the ultrasound wave as a function of time. Unfortunately the later have working temperature below 60°C. Application for in-situ monitoring of high temperature cure system is limited even though some work has been done to develop piezoelectric ceramic chip\textsuperscript{29}, capable of being used at temperatures higher than 60°C.

A generator of mechanical wave (ultrasound wave) and a detector (piezoelectric chip) are required to monitor the curing. The detector can be placed in-situ\textsuperscript{29} or at the other side of the epoxy sample\textsuperscript{26}.

In Figure 2.9, the velocity and the amplitude of the ultrasound wave going through the sample changes as a function of time of curing. From this data the gel point and the stiffness can be calculated\textsuperscript{30}.

The point where the rate of the velocity and the amplitude of absorption reach their maxima (Figure 2.9) is described as the gel point\textsuperscript{26}. 
Ultrasounds are also employed for detection of defect (voids and porosity) in final products.

2.3.3 Electrical methods

This technique is the most valuable technique for on-line monitoring. For the measurement of dielectric parameters, different types of measuring cell are used. The cell is connected to a device delivering a voltage at different frequency.

2.3.3.1 Electric impedance

The complex impedance $Z$, which is composed by a real component $Z'$ and an imaginary component $Z''$, is calculated from the ratio of the voltage over the intensity of the current. The real component $Z'$ is the electric resistance (loss term) meanwhile the imaginary component is the capacitance (storage term).
Variations in the impedance of the material can be translated into changes in the structures of the resin. The different stage of curing can be observed with the impedance modulus $|Z|$ (Figure 2.10). The decrease of the dielectric response at the beginning is due to an increase in temperature (the mobility of the charge species increase). The curing reaction induces an increase in the viscosity of the sample which results in an increase of impedance. Then between the gel point and the vitrification the impedance increases dramatically (exponentially). After the vitrification the mobility of the species is reduced and the kinetics are controlled by diffusion.

![Figure 2.10: Curing stages observed by Dielectric thermal analysis](image)

**Figure 2.10: Curing stages observed by Dielectric thermal analysis**

### 2.3.3.2 Dielectric properties: permittivity

Using devices allowing the measurement of dielectric parameters, the permittivity is recorded at a known temperature and as function of time. The permittivity has a real component and an imaginary component.

$$\varepsilon = \varepsilon' + i\varepsilon''$$  \hspace{1cm} (2.9)
\[ \varepsilon'' \] is the imaginary component of the permittivity, which relates to the dissipation (or loss) of energy within the medium and \( \varepsilon' \) is the real component of the permittivity, which relates to the stored energy within the medium.

By monitoring the dielectric properties (Figure 2.11), particular aspects of the curing process can be determined. For example, the peak observed in the dielectric loss curves is due to the gelation according to Delmonte\textsuperscript{33}. A sharp transition also occurs for the dielectric constant at the same time.

\[ \text{Figure 2.11: dielectric properties versus curing time at 10kHz for system DGEBA-DDM: • 80°C cure, o 100°C cure} \]

Prediction of viscosity (before gelation) and \( T_g \) of the system can be determined from the dielectric values. For example it is known that for low molecular weight liquid the viscosity is inversely proportional to the ionic conductivity (\( \sigma \propto 1/\eta \)), Walden’s rule\textsuperscript{31}. 

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2.3.4 Viscosity

The viscosity is a useful parameter to follow during the curing of epoxy resin. The viscosity is related to the molecular weight of the polymer. The more the resin is cured, the longer the chains and the higher the viscosity (for dilute chains $\eta \propto M_w$ and for untangled chains $\eta \propto M_w^3$). The measurement is possible in the period prior to the gelation (gelation point is often defined as the time when the viscosity reaches an infinite value). The setup used for this purpose is a disposable setup (or a conventional setup with an operator that must clean it quickly and efficiently).

To obtain the viscosity a cone or parallel plate geometry can be used (Figure 2.12). In the mean time the storage ($G'$) and the loss ($G''$) modulus is recorded. The viscosity as well as the modulus is usually monitored as function of time, temperature and frequency.

![Figure 2.12: complex viscosity of DGEBA/isophorone diamnie versus time at different temperature](image)

The viscosity can be modeled as function of temperature by the Williams-Landel-Ferry (WLF) equation or the Arrhenius equation for a fixed extent of reaction. Then viscosity, which is very important for processing, can be calculated at any curing time and temperature.
2.3.5 Dynamic Mechanical Analysis

2.3.5.1 Torsional Braid Analysis

The torsional braid analysis (TBA) is a technique providing information on chemical and physical transformations over a wide range of conditions (liquid to solid). The setup uses a composite system formed by a glass braid substrate impregnated with the liquid reaction mixture (in our case: epoxy resin + hardener)\(^{36-38}\). This technique is able to simultaneously measure the storage modulus \((G')\), loss modulus \((G'')\), complex viscosity \((\eta)\) and creep factor \((\tan\delta)\). Moreover by doing this experiment at different temperatures it is possible to obtain the activation energy of the curing process\(^{38}\).

The storage modulus \(G'\) as well as the \(\tan\delta\) are used to determine the gelation point and the vitrification point\(^{39,40}\). The maxima of \(\tan\delta\) and the inflection points of the storage modulus correspond to the gelation point for the earlier one and the vitrification point for the later.

![Figure 2.13: isothermal run at 60°C (DGEBA-1,3-cyclohexanebis(methyl)amine)](image)

The gel time can be defined by several rheological parameters\(^{31}\):

- crossover point of storage \((G')\) and loss \((G'')\) shear modulus
- maximum of \(\tan\delta\) or the rigidity vs. time in torsional braid analysis (TBA) measurement
- \tan \delta \text{ is independent of the frequency}
- \text{change in slope of } G'' \text{ with time}
- \text{appearance of the equilibrium modulus}

It is also possible to determine the Tg with the TBA techniques. Quick temperature scans\textsuperscript{39} at different curing time allow this measurement.

2.3.5.2 Traditional setups

The DMA can be equipped with different setups (dual cantilever, 3-point bending, compression cell...) for characterization of solid materials. It is possible to use these techniques to obtain the mechanical properties such as moduli or Tg of the cured materials (it is required to be able to handle the sample in solid form. However, it is not possible to perform these characterizations with uncured resin.

2.3.6 Differential Scanning Calorimetry (DSC)

The Differential Scanning Calorimetry can be used for two different purposes:

\checkmark Firstly the DSC can be used to monitor the extent of reaction as a function of time by recording the heat of reaction\textsuperscript{2, 41-43}. Horie\textsuperscript{2} was one of the first to use the DSC to study the mechanism of epoxy / amine polymerization.

\checkmark Secondly to measure the Tg of the network.

2.3.6.1 Heat of reaction

From the DSC, the heat flow can be obtained as a function of time. The extent of reaction can be calculated as described in the following equation:

$$\alpha(t) = \frac{\Delta H(t)}{\Delta H_{fc}}$$
Where $\Delta H(t)$ is the enthalpy of the reaction at the time $t$ and $\Delta H_f$ is the enthalpy of fully cured resin.

The DSC is set at a specific temperature in isothermal mode but it is possible to study the curing in dynamic mode$^{42,43}$. DSC allows a large range of temperature generally from -100°C to 300°C.

From the DSC, it is difficult to obtain the value of $\Delta H_f$ because at the end of the run the resin is often unfully cured. For this reason, it is often required to cure at higher temperature to make sure that the cure complete. In some other cases a direct method can be used to determine the extent of cure at a specific temperature$^{43}$. Nevertheless the DSC is widely used in kinetics studies because is it easy to obtain a large amount of data.

Figure 2.14 represents the extent of reaction of an epoxy resin versus time at two different temperatures. The lower temperature has a lower extent of reaction, as expected.

![Conversion versus time at two temperatures from DSC data, system: triglycidyl-p-aminophenol and 4,4-diaminophenylsulfone$^{42}$](image)

2.3.6.2 Thermal transition temperature

The DSC is also very useful for the determination of the Tg of the resin$^2$. The Tg can be measured as a function of time of curing. For industrial applications, relation between Tg and
conversion (Figure 2.15) can be deduced. Therefore to check conversion just a Tg measurement is necessary.

2.3.7 Gel fraction / Extraction

The gel fraction can also be a parameter related to the extent of reaction and surely indicator of the gelation point. This procedure can only be performed for sample before gelation. The epoxy resin sample is taken out of the oven at different times; next the sample is placed in a Soxhlet continuous extractor to undergo an extraction (with appropriate solvent) of the uncrosslinked part. The remainder of the undissolved sample is then quantified by gravimetry.

2.4 Technique summary

The variety of techniques which are used in order to study the curing of epoxy resin is large. The main techniques used have been mentioned above. Infrared spectroscopy in MIR and the DSC are two of the most frequently used methods in research laboratories. They are simple
techniques and they provide great information about the overall extent of reaction and even the fundamental mechanism of reaction. It is quite complicated to apply these techniques (FTIR MIR and DSC) in industrial applications due to process and quality control. Scientists have developed techniques such as optic fiber for FTIR in order to monitor in-situ the reaction curing, yet they have also explored simpler and cheaper methods like ultrasound or dielectric spectroscopy and related the output signal to the extent of reaction.

Table 2.4 enumerates the different techniques described in this chapter and gives information about the output signal of the techniques and the information extracted from those signals. Moreover, cost of the device used (from 1: cheap to 5: expensive), value of data obtained for scientific complexity (from 1: easy and gives important information to 3: complex and gives little information) and accuracy/reliability (1: up to 5%, 2: 5% to 10% and 3: from 10% to larger) were estimated according to the information compiled during the conception of this literature review and my own experience.
Table 2.4: recapitulative table of the monitoring techniques of epoxy resin curing

<table>
<thead>
<tr>
<th>Device</th>
<th>Techniques</th>
<th>Information</th>
<th>Signal</th>
<th>Vale of data / complexity scientific</th>
<th>Accuracy / reliability</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>FTIR spectrometer</td>
<td>MIR</td>
<td>Extent of reaction mechanism</td>
<td>Absorption of bonds</td>
<td>1</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>NIR</td>
<td>Extent of reaction mechanism</td>
<td>Absorption of bonds</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Raman spectrometer</td>
<td>Raman</td>
<td>Extent of reaction mechanism</td>
<td>Absorption of bonds</td>
<td>3</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>NMR</td>
<td>Low resolution</td>
<td>Gelation, vitrification mechanism</td>
<td>Relation time $T_2^*$</td>
<td>2</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>High resolution Liquid</td>
<td>Extent of reaction</td>
<td>Proton peak</td>
<td>2</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>High resolution Solid</td>
<td>Extent of reaction</td>
<td>Proton peak</td>
<td>2</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>SEC</td>
<td>Size separation</td>
<td>Extent of reaction</td>
<td>Molecular weight</td>
<td>3</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>DSC</td>
<td>Isothermal/dynamic</td>
<td>Extent of reaction</td>
<td>Heat of reaction</td>
<td>1</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Ramp</td>
<td>Tg</td>
<td>Heat flow</td>
<td>2</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>rheometer</td>
<td>Cone/Plate</td>
<td>Gelation</td>
<td>Viscosity</td>
<td>3</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>DMA</td>
<td>Torsional braid analysis</td>
<td>Gelation, vitrification</td>
<td>Moduli</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Dielectric setup</td>
<td>Dielectric measurement</td>
<td>Gelation, vitrification</td>
<td>Permittivity</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Ultrasonic setup</td>
<td>Ultrasound wave analysis</td>
<td>Gelation</td>
<td>Velocity and amplitude of wave</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Soxhlet Extractor</td>
<td>Continuous extraction</td>
<td>Gelation, extent of reaction</td>
<td>Gel content</td>
<td>2</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Analytical probe</td>
<td>Titration Epoxy/HCl</td>
<td>Epoxy left in the mixture</td>
<td>Quantity of HCl</td>
<td>2</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>HPLC</td>
<td>Affinity separation</td>
<td>Extent of reaction</td>
<td>Quantity of reactant</td>
<td>2</td>
<td>1</td>
<td>3</td>
</tr>
</tbody>
</table>
Researchers also have tried to relate parameters from indirect techniques to the extent of reaction or gelation point. In cases, simultaneous measurement of two parameters has been attempted. For example, the simultaneous dynamic mechanical analysis and dielectric analysis was developed at the University of Stellenbosch, department of chemistry and polymer science in South Africa. Moreover, works have also been performed to create time transition temperature diagram to have a full description of the curing. Techniques for the monitoring of the cure of epoxy resins have been well established for some time but there is still a need to improve the ease/cost/performance balance for industrial monitoring.

The monitoring technique which gives the best ease/cost/performance balance is the FTIR spectroscopy. DSC comes in second place due to the need of determination of the final cure with another technique but otherwise it is a technique easy and very reliable to use. FTIR MIR spectrometer equipped with an ATR (for easy experiments) and DSC are two techniques that were used to measure and determine kinetics parameters of epoxy resin curing.
CHAPTER III

KINETICS MEASUREMENTS AND MODELING OF EPOXY RESIN CURING

The subject of the research was primarily focused on the development of a novel multistage curing epoxy coating. To reach this goal, the knowledge of the epoxy resin curing kinetics was an essential part. Therefore, techniques for monitoring the curing of epoxy resins have been developed. Kinetics studies were carried out in order to develop a better understanding of the curing mechanism. Additionally, a kinetic model has been established from the curing data.

3.1 Kinetics measurements

As seen in the literature review, many techniques are available to monitor epoxy resin curing. The techniques used for this work include FTIR-MIR spectroscopy, Raman spectroscopy, DSC, torsional braid and electrical impedance measurement. The majority of the curing kinetics was followed by FTIR-MIR spectroscopy because it is easy and fast to perform.

The measurements were performed using a thermoset system composed of diglycidylether of bisphenol A (DGEBA) (Figure 4.1) as epoxy resin and pentamine: tetraethylenepentamine (TEPA) (Figure 4.2) as hardener. The functionality ratio (B) between the two components is 0.8. more description about this system is described in the section 4.3.

A procedural difficulty which had been encountered was that the selected system of epoxy resin (DGEBA-TEPA) cures at room temperature. Therefore, the curing starts as soon as the reactants are mixed. Also it is difficult to work at lower temperature due to the crystallization of the DGEBA resin.
3.1.1 FTIR-MIR spectroscopy

The concept of monitoring of epoxy resin by FTIR-MIR has been well described in chapter II (section 2.2.1). In the following section, the focus is on the description of the FTIR-MIR instrument used, the procedure for its operation, and the interpretation of the results.

3.1.1.1 Setup and procedure

The Fourier Transform InfraRed spectrometer used to monitor the cure of epoxy resin was a Tensor 27 from the BRUKER Company which is equipped with an MIR source. The sampling setup used was an Attenuated Total Reflexion (ATR) with a diamond crystal from Specac (Golden Gate) which was thermoregulated. The temperature can be adjusted from room temperature to 300°C. The instrument and ATR are shown in the Figure 3.1.

![Figure 3.1: Tensor 27 from Bruker and ATR golden gate from Specac](image)

The mixture to be analyzed was prepared in a beaker and mixed manually with a spatula or a mechanical stirrer. Next, a drop of the mixture was placed directly on the diamond crystal of the ATR. To limit the spreading of the mixture, an O-ring was used as shown in Figure 3.2.
The software used to control the FTIR is called OPUS, which allows the automatic recording of spectra at different times. The configuration of the FTIR was 2 cm\(^{-1}\) for the resolution, 16 scans for the background spectrum, 16 scans for the sample spectrum and a frequency range of 400 cm\(^{-1}\) to 4000 cm\(^{-1}\).

3.1.1.2 Analysis of the spectra

The monitoring of epoxy consumption was performed by observation of the decrease of the absorption band at 914 cm\(^{-1}\), which is characteristic of the terminal epoxy ring (ring vibration). The vibration band of aromatic carbon double bond at 1606 cm\(^{-1}\) was used as reference (Figure 3.3).
Figure 3.3: FTIR spectrum of DGEBA-TEPA sample 08-msc-133

Figure 3.4 a) and b) represent the reference band and the epoxy ring band during the curing, respectively. The reference band stayed relatively constant during the cure. The variation was due to the change of state during the curing which affects the response of the FTIR ATR spectrometer. The area of the epoxy band decreased as a function of time as the epoxy moiety was consumed. The shift of the baseline was certainly due to the physical state change of the system.

a) Reference band (c=\text{aromatic} \text{ at } 1606 \text{ cm}^{-1})

b) Epoxy ring band (ring vibration 914 \text{ cm}^{-1})

Figure 3.4: Characteristic band monitored during the curing
The integration of these two bands gives access to the extent of reaction of the epoxy ring. The difficult part encountered in the integration of the bands was the choice of the baseline. In the OPUS software, a full range of baseline type is available. For example for the integration of the reference bands at 1608 cm\(^{-1}\), the baseline is selected as shown in the Figure 3.4 a). For the epoxy ring band, the baseline is taken as described by Mijovic et al.\(^{24}\) i.e. the baseline shifts during curing (Figure 3.4 b)). The baseline issue for the epoxy band is responsible for data reproducibility.

The extent of reaction is calculated as explained in the previous chapter (equation 2.5).

3.1.1.3 Experimental results

Several experiments were performed at 30°C to examine the reproducibility of the FTIR technique. Also, different temperatures were selected in order to show the influence of the temperature. The different experiments are shown in the Table 3.1: FTIR experiments. The data obtained were used in the modeling described later.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>07-msc-30</td>
<td>DGEBA/TEPA B=0.8</td>
<td>30</td>
</tr>
<tr>
<td>08-msc-131</td>
<td>DGEBA/TEPA B=0.8</td>
<td>30</td>
</tr>
<tr>
<td>08-msc-133</td>
<td>DGEBA/TEPA B=0.8</td>
<td>30</td>
</tr>
<tr>
<td>09-msc-01</td>
<td>DGEBA/TEPA B=0.8</td>
<td>50</td>
</tr>
<tr>
<td>09-msc-02</td>
<td>DGEBA/TEPA B=0.8</td>
<td>70</td>
</tr>
</tbody>
</table>

Figure 3.5 represents the extent of reaction versus time of three experiments performed in the same condition of \(T = 30°C\). The rest of the data at 50°C and 70°C are presented later in Figure 3.16.
3.1.1.4 Discussion

The experiments show a limited conversion around $\alpha = 0.7$ for a curing temperature of 30°C. The conversion of epoxy moiety is limited even with the excess of amine function because the rigidity of the system increases with the conversion and when the system reaches the vitrification point the conversion stops. The reproducibility of the data is acceptable due to uncertainty related to the FTIR, the preparation mixture or the temperature.

3.1.2 Differential Scanning Calorimeter

The DSC was used to monitor both the extent of reaction and the glass transition temperature versus time.
3.1.2.1 Setup

The DSC used was a Q2000 from TA instruments. It is equipped with an auto-sampler which is very useful for the measurement of the Tg as function of time. Hermetic aluminum pans were used. The DSC was calibrated properly with an Indium standard.

Figure 3.6: DSC Q5000 from TA instrument

3.1.2.2 Extent of reaction versus time

3.1.2.2.1 Setup

DSC was used to follow the epoxy resin curing as function of time. In fact, the curing implies a chemical reaction which is exothermic. Using DSC, the heat flow can be quantified and related to the extent of reaction (equation 3.1).

The mixture was prepared with the desired composition of DGEBA and TEPA and poured in the aluminum pan. Next, the pan was placed into the DSC running under nitrogen atmosphere. The procedure used was the following:

- First, the pan was held isothermal at the curing temperature for a specific time to allow most of the curing to occur.
Second, the pan was held isothermal at higher temperature (100°C) to push the reaction to full conversion and thus obtain the total heat of reaction. The heat flow is recorded during the experiment.

3.1.2.2.2 Analysis

The relation of the heat flow to the extent of reaction is the following:

\[
\alpha(t) = \frac{\int_0^t \text{heatflow}.dt}{\int_0^{\infty} \text{heatflow}.dt}
\]  

(3.1)

The DSC provides the heat flow as a function of time, but some data manipulation is required. An extrapolation of the heat flow to the initial time and a baseline adjustment were performed (Figure 3.7) to remove the artifacts at the beginning of the measurement.

Figure 3.7: Heat flow versus time from the DSC of 08-msc-138

The first part of the curve (from 0 to 10 hours) shows the heat flow released by the reaction at 30°C. The increase of the heat flow released during the first hours is characteristic of an autocatalytic reaction. The second part of the curve (temperature at 100°C) characterizes the
heat flow of the chemical reaction which was not possible at 30°C due to constraint of the mobility of the molecule. After the cure at 100°C the epoxy resin can be considered to be at full conversion (there is always unreacted epoxy ring even at high temperature). Using the equation 3.1 the conversion can be calculated (Figure 3.8).

However, a more accurate measurement of the extent of reaction at the end of the curing can be obtained by observing an FTIR spectrum of the sample after the experiment.

3.1.2.2.3 Experimental results

Below is Table 3.2 which summarizes the experiment carried out by the DSC.

<table>
<thead>
<tr>
<th>sample</th>
<th>Composition</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>08-msc-132</td>
<td>DGEBA-TEPA B=0.8</td>
<td>30</td>
</tr>
<tr>
<td>08-msc-137</td>
<td>DGEBA-TEPA B=0.8</td>
<td>30</td>
</tr>
<tr>
<td>08-msc-138</td>
<td>DGEBA-TEPA B=0.8</td>
<td>30</td>
</tr>
</tbody>
</table>

The conversion versus time for the three identical experiments is plotted below (Figure 3.8). Clearly, the experiment is very reproducible.

*Figure 3.8: Extent of reaction versus time obtained by DSC*
3.1.2.3 Tg versus time

By using the DSC, the Tg of the network can be measured as a function of the curing time. To perform these experiments, two methods were developed:

3.1.2.3.1 Method 1:

In this method, the reaction mixture was poured into the DSC pan. The DSC was programmed with cycles of isothermal intervals at the curing temperature and ramps between two appropriate temperatures to measure the Tg. The measurement of the Tg should be as quick as possible to limit the curing at high temperature which is faster than at low temperature.

This method allowed for the selection of a wide range of curing temperature but the curing conditions are modified by the measurement of the Tg (the epoxy resin is cured faster that is should be).

3.1.2.3.2 Method 2:

This method solves the issue of method 1 (modification of curing conditions) because a new aluminum pan was used for each Tg measurement, the number of pans required is the same as the number Tg measurement. Next, these pans were placed in the cell under the appropriate temperature condition. Then at defined times, the Tg of the materials was measured with the DSC.

This method is more accurate than the method 1 in terms of curing conditions, but labor intensive. The control temperature environment is 30°C in summer. If desired the pans could be placed in the oven, but should be manually introduced into the auto-sampler at each measurement time.
3.1.3 Analysis

The $T_g$ is extracted from the DSC data of the reversible heat capacity versus temperature plot.

3.1.4 Experimental results

Table 3.3: DSC $T_g$ experiments

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
<th>Temperature (°C)</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>08-msc-10</td>
<td>DGEBA/TEPA/GMA B=0.8/60%epoxy from GMA</td>
<td>30</td>
<td>Method 1</td>
</tr>
<tr>
<td>08-msc-13</td>
<td>DGEBA/TEPA/GMA B=0.8/60%epoxy from GMA</td>
<td>30</td>
<td>Method 1</td>
</tr>
<tr>
<td>08-msc-20</td>
<td>DGEBA/TEPA/GMA B=0.8/60%epoxy from GMA</td>
<td>30</td>
<td>Method 1</td>
</tr>
<tr>
<td>08-msc-126</td>
<td>DGEBA/TEPA/GMA B=0.8/60%epoxy from GMA</td>
<td>30</td>
<td>Method 2</td>
</tr>
<tr>
<td>09-msc-03</td>
<td>DGEBA/TEPA B=0.8</td>
<td>30</td>
<td>Method 2</td>
</tr>
<tr>
<td>09-msc-04</td>
<td>DGEBA/TEPA B=0.8</td>
<td>30</td>
<td>Method 2</td>
</tr>
</tbody>
</table>

The $T_g$ versus time of curing is important for two reason. First, with the data conversion versus time, the data can be transformed, in $T_g$ versus conversion useful for the kinetic modeling of DGEBA-TEPA described later (Figure 3.19). Secondly the $T_g$ versus time are important data for the modeling of the diffusion through these epoxy resin coatings (Figure 3.9 and Figure 3.10).
3.1.5 Torsional braid analysis

The curing behavior was followed by monitoring the change of mechanical properties. During the curing there are critical points called gel and vitrification points where the mechanical properties change suddenly. This method is able to determine these points.
3.1.5.1 Setup

The apparatus used was a DMA (Q800 from TA instrument) equipped with a dual cantilever (Figure 3.11). To perform the analysis in the pre-gel state, a glass fiber braid was used. The glass fiber braid (width: \(\frac{3}{8}\) inch) was purchased from TA instrument as well.

In order to avoid any difficulty to remove the braid from the setup, the clamp surfaces of the dual cantilever were covered with aluminium foil. The oven was closed so that temperature control can be assured. The braid was impragnated with the reaction mixture with a brush. The next step was to place the impregnated braid in the dual cantilever setup (Figure 3.12). The braid was tightened with a torque wrench which provides a control tension. The curing temperature was set at 30°C but because the DMA does not have any cooling unit, a system with dry ice and isopropanol was used to cool down the continuous flow of nitrogen. The DMA was properly calibrated before the beginning the experiment. The mechanical properties were recorded with a frequency of oscillation of 1 Hz and various amplitudes of oscillation.
3.1.5.2 Experimental results

Two experiments were performed with two different oscillations (Table 3.4).

Table 3.4: Torsional Braid analysis experiments

<table>
<thead>
<tr>
<th>Composition</th>
<th>Temperature (°C)</th>
<th>Frequency (Hz)</th>
<th>Oscillation (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>08-msc-129</td>
<td>DGEBA/TEPA B=0.8</td>
<td>30</td>
<td>1</td>
</tr>
<tr>
<td>08-msc-130</td>
<td>DGEBA/TEPA B=0.8</td>
<td>30</td>
<td>1</td>
</tr>
</tbody>
</table>

The DMA data provides a wide range of mechanical properties (such as viscosity and loss modulus), but it is interesting to plot the storage modulus and the tanδ as a function of time (Figure 3.13). The properties are useful because they have a characteristic change of value for the gel and vitrification points.
The difference of amplitude for the response of the materials between the two experiments is difficult to explain. It is either due to the difference of amplitude of oscillation and/or, the difference of the thickness of epoxy resin put into the fiber (which is not easy to control).

From the data of the tanδ, maximas are observed for both experiments at 50 and 100 μm for the oscillation parameter. In the storage modulus data, an inflexion point is noticed for both the experiments at 50 μm and 100 μm. The characteristic fluctuations are the response in mechanical properties of a physical change in the product. These changes are, according to several researchers\textsuperscript{39,40}, due to the gel point or the vitrification point.

Table 3.5: characteristic changes of mechanical properties in TBA

<table>
<thead>
<tr>
<th></th>
<th>50 μm</th>
<th>100 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tanδ maximum (hr)</td>
<td>2.45</td>
<td>2.60</td>
</tr>
<tr>
<td>Storage modulus</td>
<td></td>
<td></td>
</tr>
<tr>
<td>inflexion point (hr)</td>
<td>3.10</td>
<td>2.80</td>
</tr>
</tbody>
</table>
It is difficult to attribute the critical point to the gel or vitrification point without other information. This point will be discussed in the next section about the gelation (section 3.3).

The data of this experiment are not only a reflection of the properties of the epoxy resin, but also the properties of the glass fiber. The later dominate at the beginning of the experiment and can affect the interpretation of the data.

3.1.6 Electrical measurement

As described in the second chapter, it is possible to obtain information related to the curing process (such as the gel point or the vitrification point) with the measurement of electrical properties. The electrical impedance was measured.

3.1.6.1 Setup

The electrical impedance of thermoset polymer was recorded as a function of the curing time. A homemade cell was created with two steel plates and a Teflon sheet cut into an O-ring shape (Figure 3.14). The Teflon O-ring allowed for the measurement of electrical properties of the sample with defined dimensions. The two steel plates acted as electrodes. These electrodes were linked to a potentiostat Gamry Series G 300 potentiostat by wires (as described in Figure 3.14). The Gamry is an electronic board inside a computer and the data were recorded and analyzed using the Gamry Framework™ and the Gamry Echem Analyst software. The impedance was also recorded as function of the frequency. The range of frequency used was 1 Hz to 100 kHz.
The temperature of the experiment was room temperature. A system for the control of the temperature was not built for this work. Several options were possible, one was to put the cell in a thermoregulated oven and adapt the oven for the passage of wires. Another one was to use a thermal tape and a thermocouple linked to a control box to regulate the temperature.

The electrical properties and especially the impedance of the epoxy resin changes during the curing because the electrical properties are related to the mobility of the molecules (more specifically, the ions). As the curing stage increases, this mobility is reduced which is observed by an increase of impedance in the system. At the gel point, the molecules are all linked together, which dramatically reduces the mobility even though the material is still soft. When the $T_g$ of the thermoset reaches the curing temperature (vitrification point), the flexibility is reduced to a minimum and the impedance no longer changes.

### 3.1.7 Experimental results

Several trials were performed before obtaining an experiment with trustworthy result.

The experiment is presented in Table 3.6.

**Table 3.6: Electrical experiment**

<table>
<thead>
<tr>
<th>sample</th>
<th>Mixture</th>
<th>temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>08-msc-148</td>
<td>DGEBA-TEPA B=0.8</td>
<td>Room temperature (25°C)</td>
</tr>
</tbody>
</table>
Figure 3.15 represents the impedance modulus of sample 08-msc-148 recorded as a function of time. The temperature of the experiment was room temperature (around 25°C) because a thermoregulated system was not available. The values at 1 Hz were selected because they have the greatest variations of impedance modulus.

After about 6 hours of reaction, the impedance modulus does not vary, which can be attributed, as discussed in the second chapter, to the vitrification point. It is difficult to quantify any gel point since the early data are not stable. The information obtained from this experiment is difficult to relate to other results due to the curing at a lower temperature.
3.2 Mechanism and kinetics

The chemical reactions occurring during the polymerization are described below. The first one is the reaction of a primary amine with an epoxy ring, and the second one is similar to the first one, expect that it is a secondary amine. The last reaction is often called etherification and is a reaction between an alcohol and an epoxy ring leading to the formation of an ether moiety.

\[
R_1-NH_2 + R_2-OH \rightarrow R_1-NH-R_2 + R_2\text{OH}
\]

\[
R_1-NH-R_2 + R_2-OH \rightarrow R_1-N-R_2 + R_2\text{OH}
\]

\[
R_1-NH-R_2 + R_3-OH \rightarrow R_1-N-R_2 + R_3\text{OH}
\]

The reaction of etherification is not a predominant reaction and is slower than the other two, therefore this reaction is considered insignificant. To simplify the approach, it is often assumed that the reactivity of the primary amine and the secondary amine are similar even if the reactivity is of secondary amine is lower due to spatial hindrance. The chemical reaction of amine with an epoxy ring can be catalyzed by the alcohol produced during the curing which has for effect to increase the reaction rate. The kinetic mechanism is then reduced to two equations.
These reactions are between an amine (primary or secondary) and an epoxy ring, catalyzed or not.

The non-catalytic reaction is bi-molecular since the reaction rate is proportional to the concentration of epoxy and the concentration of amine. $k_1$ is the rate constant of this reaction.

$$\text{R}_1\text{R}_2\text{NH} + \text{R}_3\text{O} \xrightarrow{k_1} \text{R}_1\text{N}^\text{I}\text{R}_3$$

The catalytic reaction is a reaction where three molecules need to interact with each other. This is a tri-molecular reaction. The alcohol molecule acts as a catalyst and therefore is not consumed during the reaction. $k_2$ is the rate constant of this reaction.

$$\text{R}_1\text{R}_2\text{NH} + \text{R}_3\text{O} \xrightarrow{k_2} \text{R}_1\text{N}^\text{I}\text{R}_3$$

For a wider application, a system with a non-stoichiometric ratio between epoxy functions and N-H amine moieties is used to derive the kinetic equation. The functionality ratio $B$ is defined as the ratio of epoxy moieties over the N-H amine entities at the initial time.

$$B = \frac{[\text{epoxy}]_0}{[N-H \text{ amine}]_0} \tag{3.2}$$

The conversion, $\alpha$ is defined by the epoxy ring consumption as described below.

$$\alpha = \frac{[\text{epoxy}]_0 - [\text{epoxy}]}{[\text{epoxy}]_0} \tag{3.3}$$

Table 3.7: reaction table

<table>
<thead>
<tr>
<th>epoxy</th>
<th>amine</th>
<th>product</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The rate of consumption of epoxy moieties can be expressed as the sum of the two rates of consumption for each of the reaction (catalyzed and none)

\[
\frac{d\text{[epoxy]}}{dt} = k_1\text{[epoxy][amine]} + k_2\text{[ROH][epoxy][amine]}
\]

(3.4)

\[
\frac{d(C_0 \times (1 - \alpha))}{dt} = (k_1 + k_2(\alpha C_0)) \times (C_0(1 - \alpha) \times C_0(\frac{1}{B} - \alpha))
\]

(3.5)

\[
\frac{d\alpha}{dt} = (k_1 + k_2\alpha) \times (1 - \alpha) \times (\frac{1}{B} - \alpha)
\]

(3.6)

The differential equation (3.6) is a Quadrature type of differential equation. This equation is quite complicated to integrate, but the reaction constants can be found without integration.

\[
\frac{d\alpha}{dt} = k_1 + k_2\alpha
\]

(3.7)

Using equation (3.7), the data from the FTIR and DSC experiments can be fitted with linear curves to obtain the constant \(k_1\) and \(k_2\).

3.2.1.1 Experiment modeling

The data of conversion versus time obtained from the FTIR and DSC methods (Figure 3.16) are used to calculate the kinetic parameters.
3.2.1.2 Calculation of $k_1$ and $k_2$ at 30°C

To calculate the kinetic constants $k_1$ and $k_2$ at 30°C, three experiments from FTIR-MIR and two from the DSC were used. The sample names are: 07-msc-30, 08-msc-131, 08-msc-133, 08-msc-137 and 08-msc-138, and all compositions were identical.

Each data set was plotted using equation 3.7 (Figure 3.17: plot of the equation). To smooth the data, a average over three points was taken.
The different sets of data show that the linear relation between \( \frac{da}{dt} \left( \frac{1}{(1-\alpha)(1-B-\alpha)} \right) \) and \( \alpha \) is only correct up to a certain extent of conversion. This linearity is observed up to 0.5-0.6 which corresponds to the data before gelation and vitrification. Therefore after further conversion, the data show behavior characteristic of being controlled by diffusion because the viscosity of the materials are in the vicinity of infinity and only conformation changes allow further polymerization.

The linear sections were fitted by a linear relation. The slope of the fitted equation gives \( k_2 \) and the y-intercept gives \( k_1 \). The values of the constant rate of reaction are summarized in Table 3.8.
Table 3.8: rate constants of reaction at 30°C

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Method</th>
<th>( k_1 ) (hr(^{-1}))</th>
<th>( k_2 ) (hr(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>07-msc-30</td>
<td>FTIR-MIR</td>
<td>0.11</td>
<td>0.76</td>
</tr>
<tr>
<td>08-msc-131</td>
<td>FTIR-MIR</td>
<td>0.09</td>
<td>0.49</td>
</tr>
<tr>
<td>08-msc-133</td>
<td>FTIR-MIR</td>
<td>0.12</td>
<td>0.50</td>
</tr>
<tr>
<td>08-msc-137</td>
<td>DSC</td>
<td>0.09</td>
<td>0.61</td>
</tr>
<tr>
<td>08-msc-138</td>
<td>DSC</td>
<td>0.09</td>
<td>0.62</td>
</tr>
<tr>
<td>average</td>
<td></td>
<td>0.10</td>
<td>0.60</td>
</tr>
</tbody>
</table>

The non catalytic constant \( k_1 \) is equal to 0.10 hr\(^{-1}\) whereas the catalytic constant \( k_2 \) is 0.60 hr\(^{-1}\).

\[
\frac{k_2}{k_1} = \frac{0.60}{0.10} = 6
\]

The catalytic path is six times faster than the non-catalytic path. Thus, it was essential to consider the catalytic effect for the modeling.

3.2.1.3 Calculation of \( k_1 \) and \( k_2 \) at any temperature

According to Arrhenius, in order to be able to predict the rate constants at any temperature, the activation energy \( (E_a) \) and the pre-exponential constant \( (A) \) are required.

\[
\begin{align*}
    k &= Ae^{-\frac{E_a}{RT}} \\
    k &= Ae^{-\frac{E_a}{RT}} \\
\end{align*}
\]  \hspace{1cm} (3.8)

Therefore, to obtain these two parameters for each of the rate constant, experiments at 50°C and 70°C were performed using the FTIR-MIR method (09-msc-01 and 09-msc-02) in which the ATR was set at the desired temperature. The data analyses to obtain the rate constants were performed using the same procedure described previously. The different graphs are attached in Appendix I and II. Table 3.9 recapitulates the values of the rates constants at three temperatures: 30°C, 50°C and 70°C.
Table 3.9: rate constants at different temperature

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$k_1$ (hr$^{-1}$)</th>
<th>$k_2$ (hr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.10</td>
<td>0.60</td>
</tr>
<tr>
<td>50</td>
<td>0.34</td>
<td>2.24</td>
</tr>
<tr>
<td>70</td>
<td>1.08</td>
<td>8.67</td>
</tr>
</tbody>
</table>

Upon taking the logarithm of each side of the equation (3.13), the following equation is obtained:

$$\ln k = \ln A - \frac{E_a}{R} \times \frac{1}{T}$$  \hspace{1cm} (3.9)

Consequently, the fitting of the curve $\ln(k)=f(1/T)$ gives the two parameters (pre-exponential coefficient ($A$) and activation energy ($E_a$)).

Table 3.10: Arrhenius plot for $k_1$ and $k_2$

The three data points for both the catalytic path and non-catalytic path are aligned, which confirms the Arrhenius behavior of the rate constants. The parameters of the Arrhenius equation for both rate constants are reported in the following table (Table 3.11).
Table 3.11: activation energy and pre-exponential coefficient of rate constants

<table>
<thead>
<tr>
<th></th>
<th>Activation energy (kJ/mol)</th>
<th>Pre-exponential coefficient (hr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 )</td>
<td>51.0</td>
<td>6.23*10⁷</td>
</tr>
<tr>
<td>( k_2 )</td>
<td>57.8</td>
<td>5.28*10⁹</td>
</tr>
</tbody>
</table>

The activation energy values are in the same order than the values found by Xu⁶ for DGEBA/methylaniline and Fraga¹¹ for DGEBA/1,2-cyclohexane. The activation energy is higher than the activation energy usually found for polymerization of vinyl bond (~30 kJ/mol)⁶⁶.

Now that the activation energy and the pre-exponential coefficient for the two rate constants are known, it is simple to calculate the rate constant at any temperature. The linear behavior of \( \ln(k) = f(t) \) has been verified for the range of temperature from \( 30°C \) to \( 70°C \). For higher or lower temperature, an extrapolation can be done nevertheless it is better to verify with experimental data if the linearity is still respected.

### 3.2.2 Modeling of conversion

The next step after the calculation of the rate constants (\( k_1 \) and \( k_2 \)) is to solve the differential equation (3.10). It is very difficult to solve for a defined solution, but it is possible to solve the differential equation numerically. The numerical solution was performed with Maple12 from Waterloo Maple Inc., for which the details of the commands are in ANNEXE III. The solution provides the extent of reaction as a function of time at any temperature.

Using the model developed above, a model curve of curing at several temperatures (\( 30°C \), \( 50°C \) and \( 70°C \)) was calculated. Figure 3.18 represents the model curves at three temperatures and the experimental data at these temperatures.
Clearly, the model nicely predicts the extent of conversion from zero to a certain value. These values are the same that have been encountered in the calculation of the rate constants (plot of equation 3.7). After this value, the rate of conversion decreases dramatically and the model is completely incorrect. This is because the approach does not take into account the effect of the change of viscosity or change of state. The model needs to be completed in order to express the behavior at late conversion.

3.2.3 Diffusion controlled kinetics

A diffusion controlled model for the epoxy-amine cure has been proposed by Yong et al. but has not been utilized because it requires data about the diffusion from dielectric measurement. Although, Yong's proposal has inspired some of this work.
The $T_g$ of the system is important to know for the modeling of the diffusion control curing.

3.2.3.1 $T_g$ versus conversion

The curve of the glass transition temperature of the network as a function of the conversion was computed by combination of the data from the Figure 3.10 and the data at 30°C from Figure 3.16. The $T_g$ for the high conversion was determined by performing several ramps of temperature up to 200°C in order to obtain the maximum curing (which means the maximum $T_g$). Its conversion was obtained by FTIR.

\[
y = -2977x^6 + 6688x^5 - 4844x^4 + 1200x^3 + 68x^2 + 50x + 234
\]

\[R^2 = 0.997\]

![Figure 3.19: $T_g$ versus conversion for DGEBA/TEPA](image)

The data was fitted with a 6th order polynomial curve in order to have an adequate data fitting.

\[T_g(\alpha) = -2977\alpha^6 + 6688\alpha^5 - 4844\alpha^4 + 1200\alpha^3 + 68\alpha^2 + 50\alpha + 234\]

(3.10)

The equation above relates the glass transition temperature of the system with the conversion at any temperature since it is independent of temperature.
3.2.3.2 Critical point

It is critical to understand why the reaction rate decreases dramatically after a certain conversion value called the critical point (Cp). This value was determined by observation of the point where the rate of reaction starts to decrease \( (\frac{\Delta t}{\Delta \gamma}) \). Each conversion at its critical points was converted to Tg of the network using the equation (3.10). The data are summarized in the table below.

<table>
<thead>
<tr>
<th>Experimental Temp (°C)</th>
<th>Conversion at Cp</th>
<th>network Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.61</td>
<td>30</td>
</tr>
<tr>
<td>50</td>
<td>0.69</td>
<td>49</td>
</tr>
<tr>
<td>70</td>
<td>0.76</td>
<td>71</td>
</tr>
</tbody>
</table>

Since the Cp corresponds to a network Tg equivalent to the curing temperature, the Cp is the vitrification point. This can be well understood since the reaction mixture starts as a liquid and the viscosity increases gradually with the extent of the reaction. At the vitrification point, the mobility of the network is restrained which results in a decrease of the rate of reaction.

One might mistake the Cp for the gel point, because at this point the molecular weight is theoretically infinite. With such product, one might expect the reaction to stop but the flexibility of the network is still sufficient for farther polymerization. The gel point is independent of the curing temperature, unlike Cp (by consequence the Cp is the vitrification point).
3.2.3.3 Concept of modeling

The system can be separated into two parts: the first one where the reaction mixture respects the laws of the kinetics in solution and the second part where the kinetics is controlled by diffusion. The change of behavior appears at the vitrification point.

The model needs to express the change of behavior at the vitrification point. To do so, an apparent rate constant was used as defined in equation (3.11).

\[
\frac{da}{dt} = k_{app} \times (1 - \alpha) \times \left( \frac{1}{B} - \alpha \right)
\]  

(3.11)

The apparent constant should be equal to the rate constant in solution at the beginning of polymerization and up to the vitrification point, at which time the apparent constant should then equal the rate constant in diffusion control.

The rate constant in solution was well defined previously.

\[
k_{solution} = k_1 + k_2 \alpha
\]  

(3.12)

The system can also be seen as two successive paths. At the beginning one is negligible because as the reaction progresses, the second path becomes smaller and the limiting one. Figure 3.20 represents the evolution of the rate constants during the curing. Before the vitrification, the solution rate constant is limiting and after the diffusion rate constant is limiting.

Figure 3.20: rate constants scheme
An analogy can be made between the rate constant for a reaction and the conductance of a resistor. The current is assimilated to the rate of reaction. The voltage (which is a difference of potential) is also comparable to the concentration of reactants. The higher the conductance, the higher the current, which is analogous with a higher constant of reaction resulting in a higher rate of reaction. Using this analogy, the apparent rate constant is equal to the inverse of the sum of the inverse of the rate constants, as shown in equation (3.13).

\[
k_{app} = \frac{1}{1/k_{solution} + 1/k_{diffusion}}
\]  

(3.13)

This equation clearly shows that the apparent constant of reaction is strongly affected by the value of the lower rate constant.

Now that the two parts of the curing are related by \( k_{app} \). The next thing to do is to define the diffusion rate constant.

The diffusion rate constant must be very large before the vitrification in order to be kinetically insignificant. Then, the diffusion rate constant must become very small at the vitrification point. The constant is composed of two terms in the model:

The first one is in relation to the state of the mixture (viscosity), which allows the major variation of the constant. This part has been built from a mathematic point of view. The use of an inverse function \( 1/x \) with a change centered around \( (T-Tg) \) was used. The expression was also given an exponent in order to increase the change of value.

The second term is a more traditional concept of Arrhenius which is dependent on the temperature.
The first term is composed of the curing temperature T, the Tg of the mixture which is described by equation (3.15) and a coefficient γ which allows to adjust the rate of change of $k_{diff}$ close to the vitrification point.

The activation energy and the pre-exponential constant of the diffusion rate constant are two other parameters to take in account because of the effect of the temperature on the energetic level of the molecules.

The new differential equation is the following.

$$\frac{d\alpha}{dt} = \frac{1}{k_{chemistry} + k_{diffusion}} \times (1 - \alpha) \times \left(\frac{1}{B} - \alpha\right)$$

To obtain the value of these parameters, several trials have been performed to fit the experimental data until the fit was correct. For each trial the numerical solution of the differential equation has been calculated. Using the experimental data at 30°C, 50°C and 70°C, the parameters γ and $C_{diff}$ were determined. Firstly γ has been fixed at 75 after optimization (good curvature of the conversion versus time). Secondly, values for the parameter $C_{diff}$ at the different temperature were found to achieve appropriate fitting.
These values are summed up in Figure 3.16 and provide a good fit of the experimental data (Figure 3.21: Experimental data with full model curing).

Table 3.13: diffusion rate constant parameters

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>( \gamma )</th>
<th>( C_{\text{diff}} ) (hr(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>75</td>
<td>1</td>
</tr>
<tr>
<td>50</td>
<td>75</td>
<td>100</td>
</tr>
<tr>
<td>70</td>
<td>75</td>
<td>10000</td>
</tr>
</tbody>
</table>

The values of \( E_{\text{diff}} \) and \( A_{\text{diff}} \) were determined by linear fitting of the curve \( \ln(C_{\text{diff}}) = f\left(\frac{1}{T}\right) \). These parameters allow the model to work for any temperature between 30°C and 70°C.

Table 3.14: diffusion rate constant parameters for any temperature

<table>
<thead>
<tr>
<th>Parameter value</th>
<th>( \gamma )</th>
<th>( E_{\text{diff}} ) (J/mol)</th>
<th>( A_{\text{diff}} ) (hr(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>75</td>
<td>198705</td>
<td>1.64x10(^34)</td>
</tr>
</tbody>
</table>

The final model (taking into account the diffusion control after the vitrification point) works for the DGEBA-TEPA system with a functional ratio of \( B=0.8 \) between the temperature of
30°C and 70°C. The differential equation is shown below and can be numerically solved for any temperature.

\[
\frac{dx}{dt} = \frac{1}{k_1 + k_2a + \frac{1}{1.65 \times 10^{14} \times e^{-\frac{9510}{T}} \left(-2977a^4 + 6688a^3 - 4844a^2 + 1200a + 50a + 234\right)^2/7}} \times (1 - a) \times \left(\frac{1}{b} - a\right)
\]

(3.18)

This model can be used for different functional ratios but will need to be tested with experimental data to check its validity. The model is not only for the DGEBA-TEPA system, with proper information and data, it can be adapted to other thermosets polymers.
3.3 Gelation

The system studied here is a mixture of DGEBA (f=2) with TEPA (f=7) with a functionality ratio of 0.8 (excess of amine function). It is equivalent to 0.357 mole of TEPA for one mole DGEBA.

To predict the gel point i.e. the conversion at which the network becomes infinite, two approaches can be used:

- Carothers approach
- Statistical approach

3.3.1 Carothers approach

This approach is based on the calculation of the number average molecular weight \( M_n \). The gel point is then derived by calculating the limit when \( M_n \) tends to infinity. Carothers (1936) derived a relationship between the extent of reaction at the gel point \( (p_c) \) and the average functionality \( (f_{av}) \) for a stoichiometric mixture in term of functionality.

\[
p_c = \frac{2}{f_{av}}
\]  \hspace{1cm} (3.19)

Pinner (1956) derived an average functionality for the nonstoichiometric mixtures. In the system used, the epoxy ring moiety being in default, the average functionality is defined as:

\[
f_{av} = \frac{2(N_{DGEBA} \times f_{DGEBA})}{N_{DGEBA} + N_{TEPA}}
\]  \hspace{1cm} (3.20)

\(N_{DGEBA}\) and \(N_{TEPA}\) represent the quantity of matter of DGEBA and TEPA respectively. In the approach, the extent of reaction depends on the deficient reactant, therefore the functionality of the TEPA is not taken into account.
\[
p_c = \frac{2}{2 \times 1 \times 2 \times 1 + 0.357} = 0.68
\]

### 3.3.2 Statistical approach

This approach uses a statistical method to derive an expression for predicting the extent of reaction at the gel point by calculating the conversion when the weight average molecular weight \(M_w\) approaches infinite size\(^{46}\).

\[
p_c = \frac{1}{\sqrt{r \times (f_{TEPA} - 1) \times (f_{DGEBA} - 1)}} \quad (3.21)
\]

\[
p_c = \frac{1}{\sqrt{0.8 \times 6 \times 1}} = 0.456
\]

<table>
<thead>
<tr>
<th>Approach</th>
<th>Conversion at gel point</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carothers</td>
<td>0.68</td>
</tr>
<tr>
<td>Statistical</td>
<td>0.46</td>
</tr>
</tbody>
</table>

Table 3.15: theoretical gel points

The two approaches predict the extent of reaction at the gelation and lead to two different results. The Carothers approach predicts the gel point based on the number average molecular weight becoming infinite. It is obvious that the predicted value is too large because chains larger than \(M_n\) are presented in the system and will reach the gel point before those of size of \(M_n\). The statistical approach is more accurate in calculating this point because it is based on the \(M_w\) and is more representative of the time when the distribution curve extends into the infinite region. Other models based on \(M_z\), \(M_{z+1}\) and so on represent more the first chains reaching infinity but if only a little percentage is infinite, the system will still behave as liquid and not gel. The statistical model has been shown to be the closest to the experiment.
3.3.3 Experimental data

The data from the FTIR, DSC and electrical experiments do not provide information about the gel point. The only data which do provide information on the gel point are from the torsional braid analysis.

The times defined in Table 3.5 can be transformed to conversion by use of Figure 3.16. The average of these times is 2.73 hours, which is approximately 43% for the conversion of the epoxy. The statistical approach gives a gel point at 46%. It may be concluded that the physical change observed in the torsional braid analysis experiments is an indication of the gelation.

3.4 Conclusion

Techniques to monitor the curing of epoxy resin have been employed (FTIR MIR, DSC, DMA and electrical impedance measurements) and have been used as experimental data for modeling. The model described above predicts the curing behavior from the beginning to the fully cure point. The model can be used between the temperature of 30°C and 90°C. Moreover the critical point has been confirmed to be the vitrification point.
CHAPTER IV

SECOND CURING STAGE OF THE FIRST LAYER

The purpose of this chapter is to find an appropriate formulation for the first layer suitable to being cured to an adequate extent in the first stage of curing and to being reinitiated by the second stage. A formulation is described allowing the incorporation of a vinyl bond within the first layer epoxy / amine. Tests on the second curing stage of the first layer are also described.

4.1 Epoxy resin system

The paints used by the Navy are formulated with numerous additives to improve a variety of properties. To perform this study a simpler system was selected. The base of the paint stays the same in order to keep the established excellent anticorrosion properties of epoxy based coatings. The formulation used consists of two components without filler: the epoxy resin and the hardener.

The epoxy resin used is diglycidylether of bisphenol A (DGEBA). The molecular weight of the resin is 342-350 g/mol which corresponds to Figure 4.1 with n=0. The resin is commercially available from Dow Chemical under the name DER 332. Resins with higher n values are solid at room temperature, and consequently curing at room temperature is not possible.
Figure 4.1: Diglycidylether of bisphenol A (DGEBA)

The hardener is a pentamine: tetraethylenepentamine (TEPA) (Figure 4.2). It is commercially available from Acros Organics with a purity of 95%.

Figure 4.2: Tetraethylenepentamine (TEPA)

The reaction between the amine TEPA and the epoxy DGEBA occurs at room temperature. These two components form the base of the first and second layer.

The coatings generally used by the Navy relevant to this project have a glass transition temperature between 40 and 50°C. It is above the room temperature to obtain a hard coating and to provide good properties against the diffusion of species responsible for the corrosion. It should also not be too high otherwise the coating becomes brittle and cracks are easily formed, which can lead to loss of barrier properties.

4.2 Incorporation of vinyl bond in the first layer

For the second stage of curing of the first layer, vinyl bonds have to be incorporated in the coating. The incorporation of the vinyl bonds can be either by reaction of the epoxy moiety or the amine moiety.
4.2.1 Modification of the Hardener

First, modification of the hardener has been tried without great success. The idea was to react a fraction of the amine present in TEPA with a halogenostyrenic product like 4-bromostyrene or 4-vinylbenzyl chloride and forms a product with vinyl and amine moieties. The syntheses of the products are not easy and lengthily. Moreover it adds a chemical reaction step to the formulation of the paint.

4.2.2 Third component

The previous idea of modification of hardener was abandoned in favor of the use of glycidylmethacrylate (GMA) (Figure 4.3) as a co-monomer during the first curing stage. The later is composed of an epoxy and a vinyl group. The epoxy group can react with the amine which allows the molecule to be linked to the network.

![Figure 4.3: Glycidylmethacrylate (GMA)](image)

This novel approach simply involves adding the GMA directly to the mixture of epoxy resin and hardener allowing the vinyl functionality to be copolymerized into the matrix. During the preparation of the paint the epoxy resin (DGEBA and GMA) and the hardener are mixed and the mixture is applied on the substrate. Epoxy groups from both DGEBA and GMA react with the amine of the hardener. When the first curing stage is done, it leads to the formation of a network with residual vinyl groups (Figure 4.4: curing steps of the first layer).
The second curing step is the free radical polymerization of the vinyl bonds. For this, a free radical initiator is required. The free radical initiating system is described in chapter V.

4.3 Coating formulation

First, a study of the DGEBA-TEPA system was performed in order to characterize the network in term of the influence of the functionality ratio on the glass transition temperature.

4.3.1 T<sub>g</sub> versus functionality ratio for DGEBA-TEPA system

DGEBA has two epoxy moieties which give a functionality of two. TEPA is composed of two primary amines and three secondary amines. The functionalities are one and two for the secondary amine and primary amine respectively. Therefore, the total functionality of TEPA is seven.

The functionality ratio (B) is defined as the number of mole of DGEBA (n<sub>DGEBA</sub>) multiplied by functionality of DGEBA (f<sub>DGEBA</sub>) divided by the number of moles of TEPA (n<sub>TEPA</sub>) times the functionality of DGEBA (f<sub>TEPA</sub>)(equation 1.3).

\[
B = \frac{n_{DGEBA} \times f_{DGEBA}}{n_{TEPA} \times f_{TEPA}}
\]  
\[\text{(4.1)}\]

76
Mixtures having different ratios of functionality were performed by mixing both components (DGEBA and TEPA) together with a mechanical stirrer during five minutes. The mixtures were left to cure at room temperature (25°C) during approximately one week. The products were hard after less than a day but the curing time was longer in order to allow a more complete cure. The measurements of Tg of the cured epoxy resin were performed on a DSC Q2000 from TA instrument, a ramp from 20°C to 250°C at 3°C/min in temperature modulated mode. The results are summarized in Figure 4.5.

![Graph showing Tg as a function of functionality ratio for DGEBA/TEPA system](image)

*Figure 4.5: Glass transition temperature as function of functionality ratio for DGEBA/TEPA system*

A maximum in the value of Tg is observed for a functionality ratio around 0.8 and is roughly 130°C. This ratio is then the maximum crosslinking density reachable at room temperature. At ratios lower than 0.8 the network has a lower Tg. This can be explained by a lower crosslinking density because of an excess of amine function in the network compared with the 0.8 mixture. With the same argument, for a functionality ratio higher than 0.8, the network has an excess of epoxy groups.
The highest Tg is not obtained for a functionality ratio of 1 because some of the secondary amines in the TEPA have restricted mobility and are difficult to reach by the epoxy after reaction of others amines present around. It is most likely that the functionality ratio for the highest Tg shifts to a higher value when the temperature of curing is higher. At higher temperature the mobility of the moiety increases and some moieties that were not able to react at room temperature are then able to.

4.3.2 DGEBA-GMA-TEPA system formulation

In order to be able to create novel epoxy resin coatings with two curing stages and with appropriate Tg, the incorporation of GMA was evaluated. The requirement for the properties after the first stage of curing is a tack and sag free while minimizing the Tg in order to obtain better adhesion between the two layers. To have a tack and sag free coating the Tg has to be higher than room temperature. The target Tg was set to 35°C.

The addition of GMA to the mixture will lower dramatically the crosslinked density due to the functionality of one for GMA. According to the study of DGEBA-TEPA system, the reactivity of some of the amine is limited and the optimum functionality ratio is 0.8. In the system DGEBA-GMA-TEPA the functionality ratio is kept at 0.8 in order to obtain a network with the higher crosslinked density possible. Variation in ratio of DGEBA-GMA allows us to tune the Tg of the network after the first curing stage.

Mixtures of DGEBA-GMA-TEPA have been performed with a constant functionality ratio of 0.8 and variation of the percentage of epoxy moiety from GMA called: %GMA. The Tg of the samples were measured using the same method as described previously and after 48 hours of curing at room temperature. The results are expressed in Figure 4.6.
The $T_g$ decreases dramatically when some of the DGEBA is replaced by GMA. Using Figure 4.6, the target first layer composition can be determined to have a percentage GMA of 60% in order to achieve the target $T_g$ of 35°C. This composition is a mixture with functionality ratio of 0.8.

4.3.3 Formulation of the layers

The first layer is composed of DGEBA-GMA-TEPA in the proportion described in Table 4.1. The composition of the second layer is taken as a mixture of DGEBA-TEPA with a functionality ratio of 0.8. The second layer $T_g$ after curing being high (130°C), it could be adjusted by changing the functionality ratio B.

| Table 4.1: Mass and molar percentage composition of the layers |
|-----------------|-----------------|-----------------|
| Mass percentage |                  | Molar percentage |
| DGEBA | TEPA | GMA | DGEBA | TEPA | GMA |
| 36    | 19   | 45  | 20    | 19   | 62  |
| 84    | 16   | 0   | 74    | 26   | 0   |
4.4 Monitoring of the curing stages

From the previous section the appropriate compositions of the layers have been determined. Monitoring of the curing process is an important tool which allows numerous experiments for measuring the curing kinetics of the new coating. The kinetics data are useful for the optimization of the formulation.

4.4.1 Fourier Transform InfraRed spectroscopy techniques

The curing has been followed by Fourier Transform InfraRed spectroscopy (FTIR) (instrument: Bruker Tensor 27 diamond ATR) as described in chapter II and in more details in the chapter III.

To monitor the consumption of the epoxy and vinyl moieties characteristics bonds have been selected. The epoxy bond at 907 cm\(^{-1}\) and the vinyl bond at 1639 cm\(^{-1}\) were selected for the consumption of the species. The bond at 1609 cm\(^{-1}\) characteristic of the aromatic double bond is used as reference for the monitoring of the second layer. For the monitoring of the first layer the carboxylic bond at 1720 cm\(^{-1}\) is preferred due to the overlap of the aromatic double bond band.
The experiments were performed at a control temperature with a thermoregulating ATR plate. The extent of reaction of the different bonds are calculated as described by the equation (1.9)

$$\alpha = 1 - \frac{\tilde{A}_{t_{\text{epoxy or vinyl}}}}{\tilde{A}_{t_{\text{ref}}}} = \frac{\tilde{A}_{t_{\text{epoxy or vinyl}}}}{\tilde{A}_{t_{\text{ref}}}}$$

(4.2)

Where $\tilde{A}$ is the integrated area of the respective peaks
4.4.1.1 Curing time of the first stage of the new first layer system

The curing was monitored by FTIR. After 12 hours the first layer of the coating reached 90% maximum cure for the first step of curing. This reduction in reactivity from 3 to 12 hours can be explained by a lower reactivity of GMA than DGEBA with TEPA.
4.4.1.2 Curing time of the second layer system

The final cure of the mixture of DGEBA-TEPA (second layer) with a functional ratio equal to 0.8 was followed at 30°C. After 3 hours, 90% of the plateau in the cure was reached (Figure 4.11). The final epoxy conversion of the second layer is about 70%. This method is quite effective to monitor the extent of epoxy curing.
4.4.2 Second curing stage of the first layer

The second stage of curing of the first layer is possible due to the presence of vinyl bonds within this first layer. The polymerization of the vinyl bonds is performed by free radical polymerization. The polymerization is initiated by diffusion of an initiator from the second layer into the first one is described in the next chapter.

This chapter is dedicated to the study of the free radical polymerization in the first layer (Figure 4.12). The goal being to prove that it is possible to further polymerize the coating after the first curing stage.

A thermal initiator was used to carry out the polymerization after the cure of the epoxy resin. AIBN is an oil soluble free radical initiator with a significant decomposition only above 50°C. The half life time at 80°C is 1 hour and more than 20 days at 30°C ($k_d = 2 \times 10^{-4} \text{ s}^{-1}$ (80°C); $k_d = 4 \times 10^{-7} \text{ s}^{-1}$ (40°C))

4.4.2.1 FTIR monitoring

Mixtures of DGEBA-GMA-TEPA (composition of the first layer) with AIBN were performed to test the polymerization of the vinyl groups. First, the reaction mixture is placed on the ATR of the FTIR and left for half a day at 30°C to allow the first curing stage to be performed.
Next, the temperature of the ATR is increased to 80°C (the temperature is reached within a couple minutes) to allow the decomposition of AIBN and the free radical polymerization to be completed.

The composition of the mixture of the first experiment is described in Table 4.2 and the results are expressed in Figure 4.13.

<table>
<thead>
<tr>
<th>Sample</th>
<th>DBEGA (mass %)</th>
<th>TEPA (mass %)</th>
<th>GMA (mass %)</th>
<th>AIBN (%/monomer)</th>
<th>B</th>
<th>% epoxy from GMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>07-msc-69</td>
<td>34</td>
<td>15</td>
<td>51</td>
<td>1.32</td>
<td>0.8</td>
<td>60</td>
</tr>
</tbody>
</table>

*Figure 4.13: Monitoring of the two curing stages of the first layer (07-msc-69)*

The curing of epoxy function reached 90% after 24 hours, then when the temperature is increased to 80°C, the mobility increases allowing 100% of conversion for the epoxy.
The vinyl moiety is converted at about 10% during the period of the first curing stage. The reaction of the vinyl at 30°C is either due to some side reaction between the amine and the vinyl or because of free radical polymerization performed by radical from AIBN. When the temperature is changed to 80°C, the conversion of the vinyl went up to 50%. The increase in term of conversion is most likely due to the polymerization, the limitation to 50% of the polymerization can be attributed to the fact that the mobility of the reacting species decreases as the crosslinked density increases.

In order to test if the mobility is a problem to reach full conversion of the vinyl polymerization, a mixture with a higher percentage of GMA was made. At the same time the quantity of AIBN was also increased (Table 4.3).

<table>
<thead>
<tr>
<th>Sample</th>
<th>DBEGA (mass %)</th>
<th>TEPA (mass%)</th>
<th>GMA (mass %)</th>
<th>AIBN (%/monomer)</th>
<th>B</th>
<th>% epoxy from GMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>08-msc-160</td>
<td>21</td>
<td>19</td>
<td>60</td>
<td>6.7</td>
<td>0.8</td>
<td>75</td>
</tr>
</tbody>
</table>

The experiment was performed similarly to the previous one described. The results of this test are graphically represented by the Figure 4.14.
The epoxy conversion follows the same trend as in the previous experiments. However, the vinyl conversion in the first part of the curing was higher (up to 25%). The increase could be due to the larger quantity of AIBN put in the mixture. The conversion during the second stage of curing is up to 60% which is higher than for the experiment with 60% epoxy from GMA. In this experiment 75% of the epoxy is from GMA which provided more vinyl bonds.

In retrospect, it would have been good to do a reference experiment i.e. an experiment following the sample procedure but without the AIBN.

The FTIR is able to monitor the disappearance of the vinyl bond but does not tell whether the vinyl bonds really polymerize or whether the vinyl bonds react with a radical and do not propagate. The DSC experiments were performed with the goal of answering this question.
4.4.2.2 DSC experiments

The $T_g$ of the network is an easy physical property to measure and obtain an idea about the degree of crosslinking within a network. The higher the crosslinking density, the higher the $T_g$ for a defined system.

A series of experiment with variations in the percentage of epoxy from GMA has been carried out. For each percentage, four samples were made, two with AIBN and two without were used as reference points for comparison. The samples were cured at 30°C for approximately one day. The $T_g$ of one sample with AIBN and one without AIBN was measured. The two samples remaining were cured further at 80°C for 2 hours and then the $T_g$ was measured. Four samples were required because the measurement of the $T_g$ modified the condition of curing. The results are summarized in the Figure 4.1.

<table>
<thead>
<tr>
<th>sample</th>
<th>AIBN (%/monomer)</th>
<th>B functionality ratio</th>
<th>% epoxy from GMA</th>
<th>$T_g$ (°C) after curing at 30°C during a day</th>
<th>$T_g$ (°C) after curing at 30°C during a day following by 2 hours at 80°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>08-msc-159</td>
<td>0</td>
<td>0.8</td>
<td>75</td>
<td>-3</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td></td>
<td>78</td>
<td>-9</td>
<td>42</td>
</tr>
<tr>
<td>08-msc-144</td>
<td>0</td>
<td>4.38</td>
<td>81</td>
<td>6</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>1.9</td>
<td></td>
<td>81</td>
<td>11</td>
<td>35</td>
</tr>
<tr>
<td>08-msc-146</td>
<td>0</td>
<td></td>
<td>87</td>
<td>1</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>1.7</td>
<td></td>
<td></td>
<td>0</td>
<td>23</td>
</tr>
</tbody>
</table>

The sample without AIBN showed an increase in the $T_g$ when they were heated at 80°C. This confirms that the conversion of epoxy is pushed forward when the samples are heated. Moreover need for a reference is confirmed otherwise some of the effect of epoxy conversion would have been attributed to the free radical polymerization.
The $T_g$s of the samples after the first curing stage were similar to the samples with and without AIBN (the accuracy of the $T_g$ measurement is about 5°C). The $T_g$s after the second stage of curing show a difference when there is AIBN or not. The differences of $T_g$ after the two stages are plotted for better understanding (Figure 4.15).

![Figure 4.15: Tg difference between experiment with and without AIBN](image)

From Figure 4.15, it is easy to conclude that the presence of AIBN in the system created a network with higher crosslinking density after the end of the second curing stage. The small difference of $T_g$ after the first curing stage showed that the AIBN did not react appreciably before the increase of temperature.
4.4.3 Gelation of the first layer

The incorporation of GMA as co-monomer in the first layer formulation decreases the crosslinked density of the materials during the first curing stage.

The extent of reaction of epoxy at the gel point can be calculated using the statistical approach. The gel point is calculated as described by equation 3.22. The average epoxy functionality is calculated as described by equation 4.3.

\[
N_{\text{GEBA}} X^{fp_{\text{GEBA}}} + N_{\text{GMA}} X^{fc_{\text{GMA}}} = \frac{N_{\text{DGEBA}} X^{2} f_{\text{DGEBA}} + N_{\text{GMA}} X^{2} f_{\text{GMA}}} {2} + \frac{6 X 1} {2 + 6 X 1} \]

The gel point of the first layer is the following.

\[
f_{av_{\text{epoxy}}} = \frac{N_{\text{DGEBA}} X^{2} f_{\text{DGEBA}} + N_{\text{GMA}} X^{2} f_{\text{GMA}}} {N_{\text{DGEBA}} X^{2} f_{\text{DGEBA}} + N_{\text{GMA}} X^{2} f_{\text{GMA}}} 
\]

\[
f_{av_{\text{epoxy}}} = \frac{2 \times 2^{2} + 6 \times 1^{2}} {2 \times 2 + 6 \times 1} = 1.4
\]

The gel point of the first layer is the following.

\[
p_{c} = \frac {1} {\sqrt {0.8 \times (7 - 1) \times (1.4 - 1)}} = 0.72
\]

The gel point of the first layer with B=0.8 and % $\gamma_{\text{GMA}}$ =60% is 0.72 which means that after the first curing stage, the first layer is a crosslinked materials because the epoxy conversion reaches 0.85. The second curing stage further increases the crosslinked density of the network.

If for some reasons, the % $\gamma_{\text{GMA}}$ has to be increased the gel point will be more difficult to reach due to the mono functional monomer content increases.

The value of the $T_{g}$ of the first layer after the first curing stage is a requirement that cannot be changed. If the mechanical and chemical properties of the first layer are not adequate, the crosslinked density of the network can be adjusted without changing the $T_{g}$ after the different curing stages by using another GMA-like monomer with longer spacer between the epoxy and
vinyl group in order to provide more flexibility. Then to reach the same $T_g$, a higher crosslinked density will be required which can provide better properties.

4.5 Conclusion

According to the experiment performed, the polymerization of the vinyl moieties is possible after the first stage of curing. The conversion is not complete but enough to produce the change in the $T_g$ of the coating which is sought. A refinement of the formulation of the first layer has to be done. On one hand the polymerization is more effective when the quantity of GMA is higher. On the other hand, too much GMA in the coating can affect the mechanical properties of the coating.

These experiments show that the hybrid epoxy / free radical polymerization is possible. Nevertheless the polymerization of the vinyl bond was performed at 80°C because of the use of AIBN. This temperature also allows a higher mobility of the molecule than at room temperature. The polymerization of the vinyl bond has to be tested at 30°C. In order to test this, potentially a UV-initiator like 2,2-dimethoxy-2-phenylacetophenone (DPAP) could be used. Which can be cured at room temperature at room temperature following by a UV exposure.

The incorporation of GMA in large quantity in the formulation of the first layer could affect the anticorrosion properties and mechanicals properties of the coating. Studies to characterize these properties will have to be performed.
CHAPTER V

ROOM TEMPERATURE FREE RADICAL INITIATOR SYSTEM

As described in the previous part, the first layer of the coating needs to undergo a free radical polymerization triggered by the application of the second layer. A production of free radicals in the first layer is required to perform the second stage of curing of that layer. This generation of free radicals can be achieved by the use of room temperature initiator systems.

Two ideas for the initiation of the vinyl polymerization have been explored.

- The first one is to use a room temperature initiator which is placed in the second layer and diffuses into the first one when the second one is applied. These systems have been called single initiator systems.
- The second idea is to use a high temperature initiator which can be activated at room temperature by a secondary catalyst substance. The initiator and the secondary substance will be placed either in the first layer or second layer. These systems have been called dual initiator systems.

5.1 Single initiator systems

Monomolecular free radical initiators which activate at room temperature are of two varieties. One kind is UV-initiator and the other is thermal initiator. The thermal initiators for this work will decompose at around room temperature. The UV-initiators have not been used in this project due to difficulties related to the nature of the application of the coating (wide surface areas and high energy usage), however they are an investing option to consider for future work.
5.1.1 Azo initiator

There are a wide range of azo initiators. Some are water soluble and some are oil soluble. Their temperature of thermal decomposition has been tuned with functional groups and these initiators are available with a $T_{\text{half life}_{10h}}$ from 30°C to more than 100°C.

One idea is to use a room temperature azo initiator known as 2,2'-Azobis(4-methoxy-2,4-dimethyl valeronitrile) (Figure 5.1), or as called by Wako: V70. It is an oil soluble azo initiator with a $T_{\text{half life}_{10h}}$ of 30°C.

![Figure 5.1: V70 oil soluble azo initiator](image)

Before testing the ability of V70 to diffuse from the second to the first layer, a model with azobisisobutyronitrile (AIBN) (Figure 5.2) was studied to see if an azo initiator can initiate the free radical polymerization.

![Figure 5.2: AIBN azo initiator](image)

AIBN has a $T_{\text{half life}_{10h}} = 80°C$. The effect of TEPA on the azo initiator was first tested. Mixtures of MMA, TEPA and AIBN were made. The first one was directly heated to 80°C, where the second one was set on the bench at room temperature for one day and then heated to 80°C. The results of these experiments are summarized in the Table 5.1
Table 5.1: AIBN experiments

<table>
<thead>
<tr>
<th>Sample</th>
<th>temperature</th>
<th>MMA (mass %)</th>
<th>TEPA (mass %)</th>
<th>AIBN (mass %)</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>08-msc-18</td>
<td>RT</td>
<td>81</td>
<td>18</td>
<td>1</td>
<td>Still liquid after a day</td>
</tr>
<tr>
<td>08-msc-19</td>
<td>80°C</td>
<td>81</td>
<td>18</td>
<td>1</td>
<td>Became hard after 2 hours of heating</td>
</tr>
<tr>
<td>08-msc-18</td>
<td>RT 1 day then 80°C</td>
<td>81</td>
<td>18</td>
<td>1</td>
<td>Became hard after 2 hours of heating</td>
</tr>
</tbody>
</table>

It is clear from the results that AIBN can initiate the polymerization. There is no apparent effect of the amine on the initiator. Because the bond (N=N) exists in both initiators and is responsible for the creation of radicals, the behavior of V-70 is assumed to be the same. The azo-initiator, V-70, is a potential provider of free radicals for the polymerization within the first layer.

The single initiator systems have three different phases: the diffusion phase from the second layer, the decomposition phase and the curing phase of the second layer. To obtain an efficient coating system, these phases need to have appropriate durations. These parameter requirements are complex and thus difficult to obtain.

The V-70 initiator was left aside because of its numerous drawbacks, such as the storage temperature and the addition of another time parameter as compared to the dual initiator system (see below).

5.2 Dual initiator system

A dual initiator system is composed of two molecules. The first one is a high temperature initiator and the second one is an activator. The activator reacts with the initiator and allows the production of radicals at room temperature.
One of the components is placed in the first layer while the other one is in the second layer. The diffusion of the component in the second layer into the first layer enables the interaction between the two molecules which leads to the formation of radicals for the free radical polymerization.

The advantage of the use of a dual system over of single initiator system is the disappearance of the decomposition phase, because the radicals are produced only in presence of both components.

There are many dual systems available, one of them which was not conclusive for the project and one promising which is described below.

5.2.1 MethylEthylKetone Peroxide/cobalt complex

MethylEthylKetone Peroxide (MEKP) (Figure 5.3) is a peroxide which has a high decomposition temperature. In the presence of a cobalt complex like cobalt naphthenate (Figure 5.4) or cobalt octate (Figure 5.5), it can decompose more rapidly at room temperature. This property can be used for the initiation of the polymerization. The MEKP can be placed in the first layer and the cobalt complex in the second layer. The complex diffuses into the first layer. The opposite can also be done by switching the MEKP and cobalt complex.

\[
\text{HO-}\text{O-}\text{O-O-}\text{OH} + \text{O-O-}\text{OH}
\]

*Figure 5.3: methylethylketone peroxide*
First the system with the cobalt naphthenate was tested. Several mixtures of GMA, MMA, TEPA, MEKP and cobalt complex were tested.

From these experiments, the conclusion was made that MEKP by itself cannot generate radicals. Even without the amine component, the MEKP can produce radicals when it is associated with cobalt complex. The cobalt complex is not soluble in GMA, but it can still act as a catalyst. The amine seems to modify the complex of cobalt (change of color purple to brown at the introduction of the amine in the system). When amine is present in the system, radicals are no longer produced.

This dual system was interesting, but because of the solubility issue of the complex and the incompatibility of the amine with the complex, the combination of MEKP / cobalt complex was abandoned.
5.2.2 Benzoyl peroxide and Dimethylparatoluidine

Qui et al. reported that Benzoyl peroxide (BPO) (Figure 5.6) is activated by an aromatic tertiary amine with electron-rich substituent on the N atom\textsuperscript{51}. The redox system BPO/Dimethylparatoluidine (DMPT) (Figure 5.7) has been studied for dental applications where there is room temperature polymerization of MMA based or GMA based materials\textsuperscript{52}.

![Figure 5.6: benzoyl peroxide](image)

![Figure 5.7: Dimethylparatoluidine](image)

BPO has a temperature of decomposition much higher than room temperature (80°C\textsuperscript{48}), but in presence of DMPT, BPO can produce radicals at room temperature.

5.2.2.1 Reaction

The reaction of BPO with DMPT produces two radicals and one molecule of benzoic acid as described in

Figure 5.8. The DMTP acts as a reactant because for each molecule of BPO, one molecule of DMPT is consumed.
5.2.2.2 Radical production

Experiments were carried out with MMA to test the system. A mixture of MMA with 1% in mass of each component (BPO and DMPT) was added. The dual system can give radicals at room temperature because the polymerization occurred in less than two hours.

5.2.2.3 Stability of BPO with the aliphatic amines

Since BPO is able to produce radicals in the presence of aromatic tertiary amine, one may theorize that it would not be able to do the same with aliphatic primary, secondary and tertiary amines. This part aims to check the stability of BPO with the amine present in the first and second layer (except DMPT).

In the epoxy resin coating there are significant amines present, the majority of which are primary, secondary and tertiary amine with a heteroatom (N or O) in γ-position. Figure 5.9 shows specific amines (ethanolamine, diethanolamine and triethanolamine) used as models for the amines present in the coating.

Figure 5.8: reaction between DMPT and BPO\textsuperscript{52}
Kinetic experiments were performed to check the stability of BPO in presence of the model amines. The decomposition of BPO was followed by $^1$H NMR using a Varian 500 MHz. An equimolar solution of BPO and anime in CDCl$_3$ at about $2 \times 10^{-3}$ mol/L was used. The experiments were run at 25°C and a NMR spectrum was taken at different times in order to obtain the evolution of the decomposition of BPO as a function of time.

Figure 5.9: Equivalent amine to amine present in the coating
5.2.2.4 BPO-ethanolamine

Figure 5.10 shows the evolution of the mixture of BPO-ethanolamine as a function of time.

The blue highlighting corresponds to the BPO peaks. The experiment of BPO-ethanolamine shows a certain stability of the BPO, while an unexpected result occurs for the ethanolamine which is difficult to explain. There are also some peaks which appear and disappear in the aromatic region.
5.2.2.5  BPO-diethanolamine

Figure 5.11 shows the evolution of the mixture BPO-ethanolamine as a function of time.

<table>
<thead>
<tr>
<th>Time</th>
<th>ppm (1)</th>
<th>ppm (11)</th>
</tr>
</thead>
<tbody>
<tr>
<td>t = 2days</td>
<td>1.07</td>
<td>4.50</td>
</tr>
<tr>
<td>t = 1 day</td>
<td>1.00</td>
<td>4.00</td>
</tr>
<tr>
<td>t = 83 min</td>
<td>1.00</td>
<td>3.50</td>
</tr>
<tr>
<td>t = 37 min</td>
<td>1.00</td>
<td>3.00</td>
</tr>
<tr>
<td>t = 3 min</td>
<td>1.00</td>
<td>2.50</td>
</tr>
</tbody>
</table>

Figure 5.11: H^1 NMR experiment of BPO-diethanolamine

The BPO-diethanolamine experiment highlights the degradation of the BPO in molecule which cannot identify as benzoic acid because the aromatic peak of acid benzoic are the following 8.12 ppm, 7.62 ppm and 7.45 ppm in CDCl₃ (according to the web data base SDBS). The peaks of this molecule are certainly the one of the ionic form of the benzoic acid because of the shift to the left (low fields)⁵. The degradation is less than 50% in one day and less than 15% in more than an hour.
5.2.2.6 BPO-triethanolamine

Figure 5.11 shows the evolution of the BPO-ethanolamine mixture as a function of time.

Figure 5.12 shows the evolution of the BPO-triethanolamine mixture as a function of time.

The BPO-thiethanolamine experiment shows the stability of BPO in presence of aliphatic tertiary amine. The BPO stability in presence of aliphatic tertiary amine is encouraging because this type of amine is increasing concentration in the coating during the curing.

5.2.2.7 Conclusion about the stability with the model amines

According to the set of NMR experiments, most of the BPO is stable for a couple of hours in the presence of ethanolamine, diethanolamine and triethanolamine in stoichiometric
quantities. However, it is difficult to explain the difference of reactivity of the diethanolamine compared to the triethanolamine or ethanolamine. In order to obtain more accurate and reliable information more experiments are required.

5.2.3 BPO/DMPT kinetics

An experiment was performed with BPO and DMPT in order to obtain information about the rate of decomposition. The decomposition of BPO was followed by $^1$H NMR as performed previously.

Figure 5.13: $^1$H NMR experiments of BPO-DMPT
The characteristic peaks of BPO and benzoic acid are highlighted in red and blue, respectively. By integration of the peaks, the extent of reaction can be calculated (Figure 5.14).

\[
y = 1.86x \\
R^2 = 0.9476
\]

Figure 5.14: conversion and kinetics of BPO-DMPT

The rate of decomposition of BPO by DMPT is a second-order reaction \(^5^4\). The rate constant of decomposition is equal to 0.26 L.mol\(^{-1}\).s\(^{-1}\) at 25°C since \(\frac{\alpha}{1-\alpha} = [BPO]_0 kt\). The half life time is less than one hour for a small initial concentration, and then since \(t_{1/2} = \frac{1}{[BPO]_0 k\alpha}\) the value would only be shorter.

If after testing the time of decomposition is too long or too short, it can be adjusted due to the availability of a wide range of activators that have different rates of reaction \(^5^4,^5^5\).

5.2.4 BPO-DMPT in the coating

In this section, the stability of BPO in the coating has been studied. In order to follow the experiment by NMR, an adaptation of the coating was made. DGEBA which is a difunctional monomer, was replaced by an epoxy octane. This allowed the mixture to stay liquid during the experiment, and thus allows for more clarity in the aromatic region of the spectrum.
Mixtures of epoxy octane, TEPA, BPO and DMPT in CDCl$_3$ were tested following the same procedure described previously. Below are the spectra of the experiment without and with DMPT.

Table 5.2: BPO in coating experimental sample

<table>
<thead>
<tr>
<th>sample</th>
<th>Epoxyoctane (mg)</th>
<th>TEPA (mg)</th>
<th>BPO (mg)</th>
<th>DMPT (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>08-msc-162</td>
<td>50.0</td>
<td>13.3</td>
<td>12.7</td>
<td>0</td>
</tr>
<tr>
<td>08-msc-163</td>
<td>50.0</td>
<td>13.3</td>
<td>12.7</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Figure 5.15: NMR spectra of 08-msc-162
Figure 5.16: NMR spectra of 08-msc-163

For both experiments, the product of degradation is the same as in presence of diethanolamine which is most likely the ionic form of the benzoic acid.
The experiment shows a rate of decomposition of BPO slightly higher in presence of DMPT. TEPA, being in large excess as compared to the BPO, shows a high rate of decomposition even if the rate constant is low. This allows for the conclusion that TEPA may pose a problem for the DMPT-BPO system because the BPO in the second layer is decomposed too fast and the molecules do not have time to reach the core of the first layer.

5.2.4.1 Conclusion on the stability of BPO in the coating

Preliminary results show that BPO is reasonably stable in the presence of aliphatic primary and tertiary amines whereas it undergoes a slow decomposition in contact with secondary amine. The stability of BPO in the condition of the coating (i.e. high concentration of TEPA) required more investigation, but at this point the DMPT needs to be in the first layer and the BPO in the second. In this configuration, even with some loss due to the TEPA, a part of the
BPO can reach the first layer. In the opposite configuration, the BPO would have all the time necessary to be decomposed by the amine in presence which is not acceptable.
5.3 Diffusion of initiator molecule in the resin

This section has the goal of analyzing the different steps of a diffusion model for the initiator through the resin. The system is very complex, particularly because many parameters depend on time and the layer physical state changes. Moreover, when the molecules enter into the first layer they degrade which reduces the diffusion rate. In this work, the model focuses on the self-diffusion. The appropriate approach would have been to study the diffusion of a molecule having interaction with the matrix. This approach is very complex but essential to obtain a full understanding of the phenomenon.

Several systems are described from the simplest form to the most complex. Estimation of diffusivity is made in order to obtain some information through the solution of the models and to conclude about the feasibility of the diffusion.

5.3.1 Description of the system

5.3.1.1 Geometric factor

The system is composed of two layers with a defined thickness in the x-direction. The assumption of infinite dimension in the y and z direction can be easily established since the thickness is in hundreds of micrometers and the two other directions are in meters (Figure 5.17).
Due to the infinite dimension in y and z direction, there are two symmetric planes $(x,y)$ and $(x,z)$. Thus, the system is reduced to a 1D system (Figure 5.18).

The system is now well defined in terms of spatial dimension. The next step is to identify the diffusion parameters and subsequent parameters which influence the diffusion in order to model each part of the system.

5.3.1.2 Physical factors

To model the diffusion of the molecule from the second layer into the first layer, the diffusivity has to be known in both of the layers. The system is described from its simplest form to its most complicated, and each model is described below (as well as in Figure 5.19).
Model 1: the diffusivity in the layers is the same and is constant with time.

Model 2: the diffusivity in the first layer is different than in the second layer.

Model 3: the diffusivity in the first layer is a function of time and depth constant and the diffusivity in the second layer is a function of time. The diffusivity is related to the structure of the network and it can be expressed as a function of the $T_g$. The $T_g$ is related to the extent of reaction and then to the time.

5.3.1.3 Chemical factor

The model aims to describe the diffusion of a molecule present in the second layer into the first layer. The composition of the system, at the time $t = 0$ and infinite time, is shown in Figure 5.20.
5.3.3 Mathematic solution

The solution of the diffusion equations has been solved only for model 1, which is the simplest. Model 1 requires only one value of the diffusivity for both layers. The 1D system is well known and has already been solved. Equation 5.1 is the solution of the differential equation derived from Fick’s Second Law.

\[
\frac{C(x)}{C_0} = \frac{1}{2} \sum_{n=-\infty}^{\infty} \left( \text{erf} \left( \frac{h + 2nl - x}{2\sqrt{Dt}} \right) + \text{erf} \left( \frac{h + 2nl + x}{2\sqrt{Dt}} \right) \right)
\]  \hspace{1cm} (5.1)

\( \frac{C(x)}{C_0} \) is the ratio between the concentration of the molecule at the distance \( x \) and the concentration in the second layer at the time \( t = 0 \).

5.3.4 Selection of value for the diffusivity

Model 1 considers only one diffusivity for both layer, the problem is that the first layer is in a solid state with at \( T_g \) around room temperature while the second layer at the early time is a liquid and becomes a solid.
It is well accepted that the diffusivity in the liquid is about $10^{-5}$ cm$^2$/s. The diffusivity at the time $t=0$ in the second layer is assumed to be as the same.

Deng et al.\cite{Deng2011} performed a study where they described the evolution of the self-diffusion coefficient with the extent of reaction (Figure 5.21) for a system composed of DGEBA as the epoxy resin and 4,4'-diaminodiphenylmethane as the curing agent. Deng used normalized diffusivity, which is normalized with the diffusivity of the system at $t=0$ (for the Model 1 it is $10^{-5}$ cm$^2$/s).
The system used by Deng consists of a curing agent which is an aromatic amine. For Model 1, the same behavior has been assumed.

The algorithm represented by Figure 5.22 was followed to obtain the diffusivity of the Model 1 coating at different time.

![Figure 5.22: algorithm to obtain the coating diffusivity](image)

Deng's system can be used to predict the coefficient of diffusion of the first layer. The first layer has a Tg around room temperature. The diffusion coefficient is estimated to be between $10^{-8}$ and $10^{-9}$ cm$^2$/s.

For the second layer, there is an evolution of the diffusivity due to the curing. The curing time of the second layer is approximately 5 hours, as shown previously in chapter I. The majority of the diffusion of the molecules must occur before these 5 hours because at that point the second layer is fully cured (unlike the first one) and thus the diffusivity is significantly reduced. The point defined by a time of 2.5 hours at the middle of the first layer (i.e. $x=0.375$) has been selected as a reference point for discussion.
Using a curve developed in Chapter III, the conversion is related to the $T_g$ of the network. Now, still by using the plots of Deng, the diffusivity in the second layer as a function of time can be obtained.

For example: At $t=2.5$ hours, the $T_g$ is about $0 \degree C$, which gives a diffusivity of $5 \times 10^7 \text{ cm}^2/\text{s}$ after using the graphs (Figure 5.21)

Figure 5.23 shows the results of the estimation of the diffusivity in both layers as a function of time.

![Diffusivity in layers as a function of time](image)

**Figure 5.23: diffusivity in the layers as a function of time**

### 5.3.5 Simulation

Model 1 is used to calculate the value of the normalized concentration at the reference point with different values of diffusivity. The software, Maple, has been used for all calculations, and a calculus sheet is enclosed in Appendix E. The results of the computation are summarized in Figure 5.24.
The normalized concentration at the reference point should be 0.25, which means 50% of the maximum concentration is reached. \( \frac{C(x)}{C_0} \) could be lower, but not too much, since otherwise the load of the diffusing molecule is too large in the second layer.

The diffusion is a physical phenomenon which is limited by the lowest diffusivity. Thus, only the value of the diffusivity in the second layer is important for Model 1. This diffusivity is in the range between \( 10^{-8} \) and \( 10^{-9} \) cm\(^2\)/s, but perhaps the diffusivity may be increased in order to adapt the model to the real system. The diffusivity in the second layer at the early stage of curing is very high, which provides a uniform concentration in the second layer.

By combination of Figure 5.24 and Figure 5.23, one can conclude that the diffusion of the molecule through the first layer occurs at an adequate rate. This result is obtained using a self-diffusion approach. It is encouraging that the diffusion rate is adequate because when considering the interaction with the matrix and the degradation in the first layer this rate will
decrease. If it would not have been an adequate rate for the self-diffusion the real system would not have a chance to work.

5.3.6 3D simulation

Using Maple, it is possible to obtain 3D plots. Below is a 3D plot which can be created using Model 1 with a self-diffusivity of $10^8 \text{ cm}^2/\text{s}$.

![3D plot](image)

*Figure 5.25: 3D plot obtained with Maple for $D = 10^8 \text{ cm}^2/\text{s}$*

Figure 5.25 shows the evolution of the normalized concentration as a function of time. The profile at $t = 0$ evolves to the smoother shape. At 2.5 hours the concentration in the first layer (from 0.25 to 0.5 mm) is 0.5 at the interface of the layer and decreases to the value of 0.1 at the interface of coating/steel, which is an acceptable concentration.
5.4 **Full system tests**

A system was entirely defined in which the compositions of the first layer, as well as the initiating system were selected as a function of the different requirements. The different curing stages were tested separately. In this part, experiments to follow the second curing stage in the first layer in the application condition were performed in order to test the formulation.

5.4.1 **FTIR experiments**

FTIR was used because it can be used with experiments which are simple to execute. DMPT present in the first layer is half the molar quantity of the BPO present in the second layer. A first layer mixture was cured in bulk, and then the product was cut (shaved) to obtain a film of 250 μm (difficult task). The film was placed on the ATR diamond, onto which a drop of the second layer mixture was placed (Figure 5.26). The spectra were recorded as a function of time to monitor the vinyl bond.

The composition of the two coating layers is summarized in Table 5.3.

<table>
<thead>
<tr>
<th>Mass %</th>
<th>DGEBA</th>
<th>TEPA</th>
<th>GMA</th>
<th>DMPT (%/GMA)</th>
<th>BPO (%/GMA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>First layer</td>
<td>34</td>
<td>15</td>
<td>51</td>
<td>3</td>
<td>-</td>
</tr>
<tr>
<td>Second layer</td>
<td>84</td>
<td>16</td>
<td>0</td>
<td>-</td>
<td>5</td>
</tr>
</tbody>
</table>

**Table 5.3: composition of coating layers**

DGEBA, TEPA and BPO

DGEBA, TEPA, GMA and DMPT

*Figure 5.26: FTIR experiment of the full system*
Several trials have been performed, but no changes in the vinyl bond were observed. This method is limited due to the fact that the ATR diamond has only a couple of microns of penetration depth for the sample analysis. Then, even if there is vinyl polymerization in the part close to the second layer, it is not possible to verify this with the ATR.

5.4.2 DSC experiments

To obtain information about the vinyl polymerization in the part near the interlayer, \( T_g \) measurements can be performed on the part of the first layer which is close to the second layer. If the \( T_g \) increases it means that the polymerization occurs. Such an experiment is difficult to carry out due to the difficulty of extraction of a small quantity of coating close to the interface. This analysis would have been useful to verify the diffusion of BPO. Due to the lack of time and the difficulty of sample preparation, it has not been possible to perform the experiment.

5.4.3 Raman experiments

For future investigation the confocal Raman spectrometer can be a very useful device. The initiator concentration (within the second layer or diffusing into the first layer) is too low for monitoring. However the evolution of the concentration of the vinyl moieties can be followed as a function of time and depth. The resolution of the Raman spectrometer is 10 \( \mu m \) which is sufficient to obtain a concentration profile through the layers.

5.5 Conclusion

Finding an appropriate initiator system is not a simple task. Single initiator systems have been excluded due to their disadvantages compared to the dual system. The DMPT/BPO system seems to be an adequate choice, despite the instability of BPO in the presence of TEPA. More
study is needed to better understand the efficiency of this system in the epoxy resin coating. However, a preliminary diffusion model of the molecule in the coating has been established. A rendition of the simplest model (with some estimation of the diffusivity) allowed some prediction through calculation to conclude that the diffusion of the molecule could be possible in the required time. The initiation of the free radical polymerization in the first layer is triggered by the application of the second layer, and is possible according to the results found. An experiment was carried out to simulate the novel application process but the results are not conclusive. Additional study on this aspect is required in order to clarify some points.
CONCLUSIONS

In the present thesis, a novel epoxy coating was developed in order to improve the application process of anticorrosion paint. The new coating is composed of two layers. The first layer cures in two stages. The first stage is conventional epoxy cure whereas the second stage is a free radical polymerization. The second stage of the first layer allows an unlimited overcoat window. This curing stage is activated upon application of the second layer with the diffusion of a free radical initiator from the second layer into the first layer. The curing of the second layer is also an epoxy cure. The following achievements have been obtained.

- Glycidyl methacrylate (GMA) has been successfully incorporated into an epoxy based resin. GMA was linked to the polymeric network through its epoxy moiety and provides a vinyl bond required for a second curing stage in the first layer.
- A formulation for the first layer was found in accordance with the two step curing criteria. The composition is 34% Diglycidyl ether of bisphenol-A (DGEBA), 15% Tetraethylenepentamine (TEPA) and 51% GMA in mass percentage.
- The free radical polymerization of the vinyl bond within the network has been tested at 80°C using AIBN as initiator. The crosslinked density increased as a result of this second polymerization.
- The benzoyl peroxide – dimethyl-para-toluidine (BPO-DMPT) system has been selected (from a choice of many) to initiate the vinyl polymerization of the second stage. The system provides radicals when the two components are in contact. BPO showed adequate stability in the presence of certain amines and unclear behavior in presence of TEPA.
• Diffusion predictions were carried out based on self-diffusion and an uniform diffusivity of the coating double layer across the thickness. The results showed the possibility of BPO diffusing from the second layer into the first layer within the time scale of the curing of the second layer.

• Methods to monitor the curing of epoxy have been developed with the instruments available in the laboratory. More particularly, the FTIR MIR method using the ATR diamond was a great success to obtain kinetics data rapidly, reproducibly and accurately.

• Modeling of the curing kinetics has been performed from experimental data. The model predicts the extent of reaction as a function of time for a range of temperature between 30°C and 90°C. The model includes the diffusion control behavior after the vitrification point in order to improve accuracy of the model.

When the first layer is a modified epoxy based resin, the second layer remains a conventional epoxy resin.

While significant progress has been achieved, a fully functional system has not been finalized. Because of the restriction of the free radical chemistry, it remains a challenge to find an effective room temperature redox free radical system.
RECOMMENDATIONS

The polymerization of the vinyl bonds had been tested at 80°C and showed that polymerization is possible. It may be of interest to verify that polymerization can occur at 30°C. For this purpose, an UV initiator can be incorporated in the first layer, for which UV exposition (after the curing of the first stage) can be performed to initiate the second curing stage.

The formulation of the first layer (DGEBA/TEPA/GMA) can be adjusted to obtain different $T_g$s for the first layer after each curing stage.

The influence of GMA as component of the first layer on the mechanical properties and anticorrosion properties has to be quantified.

It will be helpful to carry out more investigation on the BPO in presence of the coating.

More studies and experiments have to be performed on the vinyl polymerization within the first layer initiated by the diffusion of BPO. Since the FTIR method is limited to the first microns, DSC experiments may be more useful for the optimization of the formulation or as described in the section 5.4.3 the confocal Raman spectrometer is recommended for the study of the initiator diffusion.

In order to have a greater understanding of the epoxy resin curing new monitoring techniques can be developed such as Raman or solid state NMR. Adhesion testing between the layers could be done to determine the effectiveness of the novel coating.

Even though very encouraging results were obtained, a significant amount of work is required in order to further establish a viable coating.


APPENDIX A

Sample: 09-msc-01
Curing of epoxy resin at 50°C (DGEBA/TEPA) B=0.8

Figure 1: conversion versus time for 09-msc-01

\[ y = 2.2364x + 0.3437 \]
\[ R^2 = 0.9954 \]

Figure 2: kinetic analysis for 09-msc-01

At 50°C
\[ k_1 = 0.34 \text{ hr}^{-1} \]
\[ k_2 = 2.23 \text{ hr}^{-1} \]
APPENDIX B

Sample: 09-msc-02
Curing of epoxy resin at 70°C (DGEBA/TEPA) B=0.8

![Graph of conversion versus time for 09-msc-02](image)

Figure 1: conversion versus time for 09-msc-02

![Graph of kinetic analysis for 09-msc-02](image)

Figure 2: kinetic analysis for 09-msc-02

At 70°C
\[ k_1 = 1.08 \text{ hr}^{-1} \]
\[ k_2 = 8.67 \text{ hr}^{-1} \]
APPENDIX C

restart
with(DEtools, odeadvisor, syngen)  
[odeadvisor, syngen]  \hfill (1)

\[ R := 8.314 \]

8.314

\textbf{Temperature de reaction in celcius}

\[ Tc := 50 \]

50  \hfill (3)

\[ T := Tc + 273 \]

323  \hfill (4)

\textbf{None catalytic rate constant}

preexponential constant in Hr-1
\[ A1 := 62332904 \]

62332904

energy of activation in J/mol
\[ Ea1 := 50993 \]

50993

\[ k1 := A1 \cdot \exp\left( - \frac{Ea1}{R \cdot T} \right) \]

0.353163070  \hfill (7)

\textbf{catalytic rate constant}

preexponential constant in Hr-1
\[ A2 := 5284268309 \]

5284268309

energy of activation in J/mol
\[ Ea2 := 57783 \]

57783

\[ k2 := A2 \cdot \exp\left( - \frac{Ea2}{R \cdot T} \right) \]

2.388609673  \hfill (10)

ratio of epoxy function over N-H amine
\[ B := 0.8 \]

0.8  \hfill (11)

\textbf{Differential Equation}
\[ DE := \text{diff}(\alpha(t), t) = (k1 + k2 \cdot \alpha(t)) \cdot (1 - \alpha(t)) \cdot \left(\frac{1}{B} - \alpha(t)\right) \]

\[ \frac{d}{dt} \alpha(t) = (0.3531643070 + 2.388609673 \alpha(t)) \cdot (1 - \alpha(t)) \cdot (1.250000000 - \alpha(t)) \]

\[ \text{evalf}(DE) \]

\[ \frac{d}{dt} \alpha(t) = (0.3531643070 + 2.388609673 \alpha(t)) \cdot (1 - \alpha(t)) \cdot (1.250000000 - \alpha(t)) \]

**type of the differential equation**

\[ \text{odeadvisor}(DE) \]

\[ \{\text{_quadrature}\} \]

**Numeric solution of the differential equation**

\[ \text{numericsolution} := \text{dsolve}\{\{DE, \alpha(0) = 0\}, \alpha(t), \text{numeric}\} \]

\[ \text{proc}(x \text{if} 45) \ldots \text{end proc} \]

\[ \text{plots}[\text{odeplot}](\text{numericsolution}, [t, \alpha(t)], t = 0 .. 10) \]

**values of the numeric solution**

\[ A := \text{numericsolution}(1) \]

\[ [t = 1..\alpha(t) = 0.610828889852415458] \]
restart

\texttt{with(DEtools, odeadvisor, syngen)}

\begin{align}
R & := 8.314 \\
8.314
\end{align}

\textit{Temperature de reaction (°C)}

\begin{align}
T_c & := 70 \\
70
\end{align}

\begin{align}
T & := T_c + 273 \\
343
\end{align}

\textbf{Non-catalytic rate constant}

\textit{pre-exponential constant in Hr-1}

\begin{align}
A_1 & := 62332904 \\
62332904
\end{align}

\textit{energy of activation in J/mol}

\begin{align}
E_{a1} & := 50993 \\
50993
\end{align}

\begin{align}
k_1 & := A_1 \cdot \exp\left(-\frac{E_{a1}}{R \cdot T}\right) \\
1.068652018
\end{align}

\textbf{Catalytic rate constant}

\textit{preexponential constant in Hr-1}

\begin{align}
A_2 & := 5284268309 \\
5284268309
\end{align}

\textit{energy of activation in J/mol}

\begin{align}
E_{a2} & := 57783 \\
57783
\end{align}

\begin{align}
k_2 & := A_2 \cdot \exp\left(-\frac{E_{a2}}{R \cdot T}\right) \\
8.375944606
\end{align}
functionality ratio
\[ B := 0.8 \]  \hspace{1cm} 0.8 \hspace{1cm} (11)

**Diffusion**

\[
\begin{align*}
kdiff & := \frac{1.64 \cdot 10^{34} \cdot \exp\left(-\frac{198705}{R \cdot T}\right)}{\left(-2977 \alpha(t)^6 + 6688 \alpha(t)^5 - 4844 \alpha(t)^4 + 1200 \alpha(t)^3 + 68 \alpha(t)^2 + 50 \alpha(t) + 234\right)^{75}} \\
& \times \frac{1.26039395 \cdot 10^{164}}{\left(-2977 \alpha(t)^6 + 6688 \alpha(t)^5 - 4844 \alpha(t)^4 + 1200 \alpha(t)^3 + 68 \alpha(t)^2 + 50 \alpha(t) + 234\right)^{75}}
\end{align*}
\]  \hspace{1cm} (12)

**Differential Equation**

\[
\begin{align*}
DE & := diff(\alpha(t), t) = \frac{1}{k_l + k_r \cdot \alpha(t)} \cdot (1 - \alpha(t)) \cdot \left(\frac{1}{B} - \alpha(t)\right) \\
& + \frac{1}{kdiff} \left(1.2500000000 - \alpha(t)\right) \\
& + \frac{1}{1.066852018 + 8.375944606 \alpha(t)} \left(-2977 \alpha(t)^6 + 6688 \alpha(t)^5 - 4844 \alpha(t)^4 + 1200 \alpha(t)^3 + 68 \alpha(t)^2 + 50 \alpha(t) + 234\right)^{75}
\end{align*}
\]

\[
\begin{align*}
evalf(DE) & := \frac{1}{1.066852018 + 8.375944606 \alpha(t)} \left(-2977 \alpha(t)^6 + 6688 \alpha(t)^5 - 4844 \alpha(t)^4 + 1200 \alpha(t)^3 + 68 \alpha(t)^2 + 50 \alpha(t) + 234\right)^{75}
\end{align*}
\]

**Numeric solution of the differential equation**

\[
\begin{align*}
numericsolution := dsolve\{DE, \alpha(0) = 0\}, \alpha(t), \text{numeric} \\
& \text{proc}(...) \text{ end proc}
\end{align*}
\]

\[
\begin{align*}
\text{plots[odeplot]}(\text{numericsolution}, [t, \alpha(t)], t = 0..10)
\end{align*}
\]
values of the numeric solution

\[ A := \text{numeric solution}(23) \]
\[ t = 23, \alpha(t) = 0.926980980201839166 \]  

Exportation of the data

\[ H := \text{plots[odeplot]}(\text{numeric solution}, [t, \alpha(t)], t = 0..10) \]
\[ \text{PLOT(...)} \]

\[ G := (\text{op}((\text{indets}(H,\text{Array})))): \]

\[
\begin{bmatrix}
50 \times 2 \text{ Matrix} \\
\text{Data Type: float}_8 \\
\text{Storage: rectangular} \\
\text{Order: C_order}
\end{bmatrix}
\]

with(ExcelTools)

\[ \text{Export}(G) \]
APPENDIX E

restart
the diffusion coefficient is considered constant
\[ D_i := 3.6 \cdot 10^{-3} \]
\[ 0.003600000000 \] \hspace{1cm} (1)

thickness of the 2 layers,
\[ l := 0.5 \]
\[ 0.5 \] \hspace{1cm} (2)

thickness of the second layer,
\[ h := 0.25 \]
\[ 0.25 \] \hspace{1cm} (3)

Normalized concentration
\[ C := 0.5 \cdot \sum_{n=-\infty}^{\infty} \left\{ \text{erf} \left( \frac{(l + 2 \cdot n \cdot l - x)}{2 \cdot (D_i \cdot t)^{0.5}} \right) + \text{erf} \left( \frac{(h - 2 \cdot n \cdot l + x)}{2 \cdot (D_i \cdot t)^{0.5}} \right) \right\} \]
\[ 0.5 \left\{ \sum_{n=-\infty}^{\infty} \left[ \text{erf} \left( \frac{8.333333335 \cdot (0.2500000000 + n - 1.0)}{\sqrt{t}} \right) \right] + \text{erf} \left( \frac{8.333333335 \cdot (0.2500000000 - 1.0 + x)}{\sqrt{t}} \right) \right\} \] \hspace{1cm} (4)

plot3d(C, x = 0 .. 0.5, t = 0 .. 5);

\[ \text{evalf} \left( \text{evalf} \left( C \mid (t = 2.5, x = 0.375) \right) \right) \]
\[ 0.1783397989 \] \hspace{1cm} (5)