MICROWAVE PROCESSING OF VINYL ESTERS AND VINYL ESTER/GLASS FIBER COMPOSITES

by

Ramakrishna Dhulipala

Advisor: Dr. Martin C. Hawley

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MASTER OF SCIENCE

Department of Chemical Engineering

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ABSTRACT

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Microwave Processing of polymers and polymer matrix composites has been studied as an alternative to conventional thermal processing. In further pursuance of this research area, different aspects related to the microwave processing of vinyl esters (with vinyl toluene as comonomer) and vinyl ester/glass fiber composites have been studied.

The kinetics of polymerization during thermal curing was investigated and a model, based on considering equal reactivities for vinyl groups, was formulated to represent the kinetics. The different parameters for the model were estimated based on the minimization of the square of the error between the experimental values and model predictions of the extent of cure. The same model was used for the representation of the microwave cure kinetics. The different parameters for the microwave data were found using the same procedure, but the fit was not as good as the fit for the thermal data. A possible explanation is the enhancement of the reactivity of vinyl group from vinyl ester through the interaction with microwaves.

Unidirectional 12-ply vinyl ester/glass fiber laminates were prepared and processed in a thermal oven, and in a microwave cavity using a mode-switching technique and the same cure cycle. The mechanical properties of the microwave and thermally cured laminates in flexure were compared and were found to be the same.

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ACKNOWLEDGEMENTS

I would like to thank Dr. Martin C. Hawley for his constant guidance and direction. His steadfast support provided me the confidence and strength to tide over the difficult phases of my research. I will be indebted to him for all things I have learnt under his leadership.

A work of this nature with all the associated experimental work cannot be completed in such a time frame without a lot of assistance and for this I wish to thank Susannah Travis, Gretchen Kreig and Richard F. Falk for their steady efforts during the different stages of the work.

The excellent infrastructural support and the unfettered cooperation provided by Michael Rich, Dan Hook and Brian Rook have proved invaluable to me. All my group-mates including Jianghua Wei, Valerie Adegbite, and Larry Fellows have at one time or the other been instrumental in seeing me through the taxing segments of my work. I express my gratitude to all of them.

All the people I have had a chance to interact with in the course of this work have extended their fullest possible cooperation with alacrity. I gratefully acknowledge their help while regretting my inability to credit them individually because of the numbers involved.

Last but not the least I am thankful to my family members and friends whose moral encouragement and emotional support can never be overestimated.

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NOMENCLATURE

$A^{\lambda i}$	Absorbance of the mixture at wavelength λ_i.
C_a, C_b	Concentrations of the components in moles or grams per total volume of the mixture.
l	Path length of the sample.
x	Either of the two chemical species present.
ρ_a, ρ_b	Moles or grams per unit volume of the respective pure components.
$\epsilon_a^{\lambda i}$,$\epsilon_b^{\lambda i}$	Molar or mass absorptivities of the components 'a' and 'b' at the wavelength λ_i.
λ_i, λ_j	wavelength in any region of the spectrum.

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1. INTRODUCTION

1.1 Background

Conventional processing of polymer matrix composites involves the heating of the chemically reactive precursors through convective and conductive heat transfer mechanisms. Microwave processing involves the transfer of energy to the materials by electromagnetic radiation which offers a much faster and more easily controllable method of curing polymers and polymer matrix composites. In addition microwave radiation can have an effect on the chemical reaction mechanism which can enhance curing rates under similar processing conditions and reduce processing times. An implication of such an effect would be a possible enhancement of the mechanical properties of the cured systems. Work done on epoxies and graphite/epoxy composites has given such results [1,2].

1.1.1 Microwave processing concept

Microwaves are electromagnetic waves of a frequency far less than the frequency of visible light. These are absorbed by materials depending on the materials' dielectric properties. The relations that govern the absorption of microwaves by materials are given in equation 1.1. In materials composed of components of different dielectric properties, the microwaves are absorbed non-uniformly. This results in a non-uniform power distribution across the volume of the material exposed to microwave radiation.

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$$P = \frac{1}{2}\,\varepsilon_0\,\varepsilon''\,\omega\,|E|^2$$

$$\varepsilon'' = \varepsilon''_d + \frac{\sigma}{\varepsilon_0\,\omega}$$

(1.1)

P = *power dissipated as heat*
ε'' = *loss factor*
ε''_d = *dipolar contribution*
σ = *conductivity*
ω = *frequency*
ε_0 = *permittivity of vacuum*
$|E|$ = *electric field strength*

1.1.2 Microwave system

A cross section of the cylindrical cavity used for the curing of polymers and composites is shown in Figure 1.1. The microwave processing circuit that contains the cylindrical cavity is shown in Figure 1.2. A single frequency microwave power source is used that emits microwaves at 2.45 Ghz frequency. The directional couplers redirect a fraction of the power to the power meters to enable the measurement of the power supplied to the cavity and the power reflected back from the cavity. A complete description of the system is available elsewhere [3].

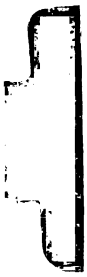

Figure 1.1

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Figure 1.2

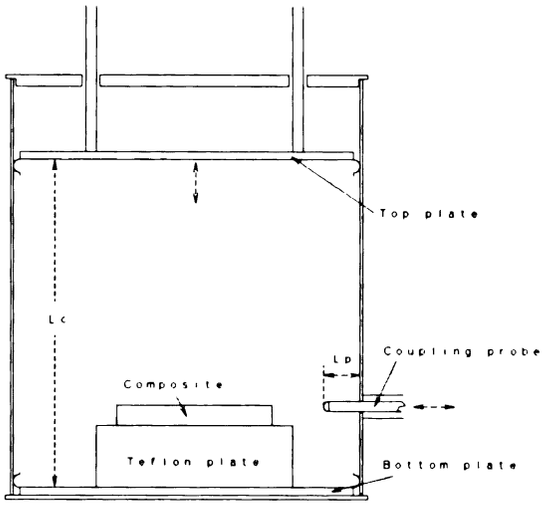

Figure 1.1 Cross section of tunable cylindrical microwave cavity

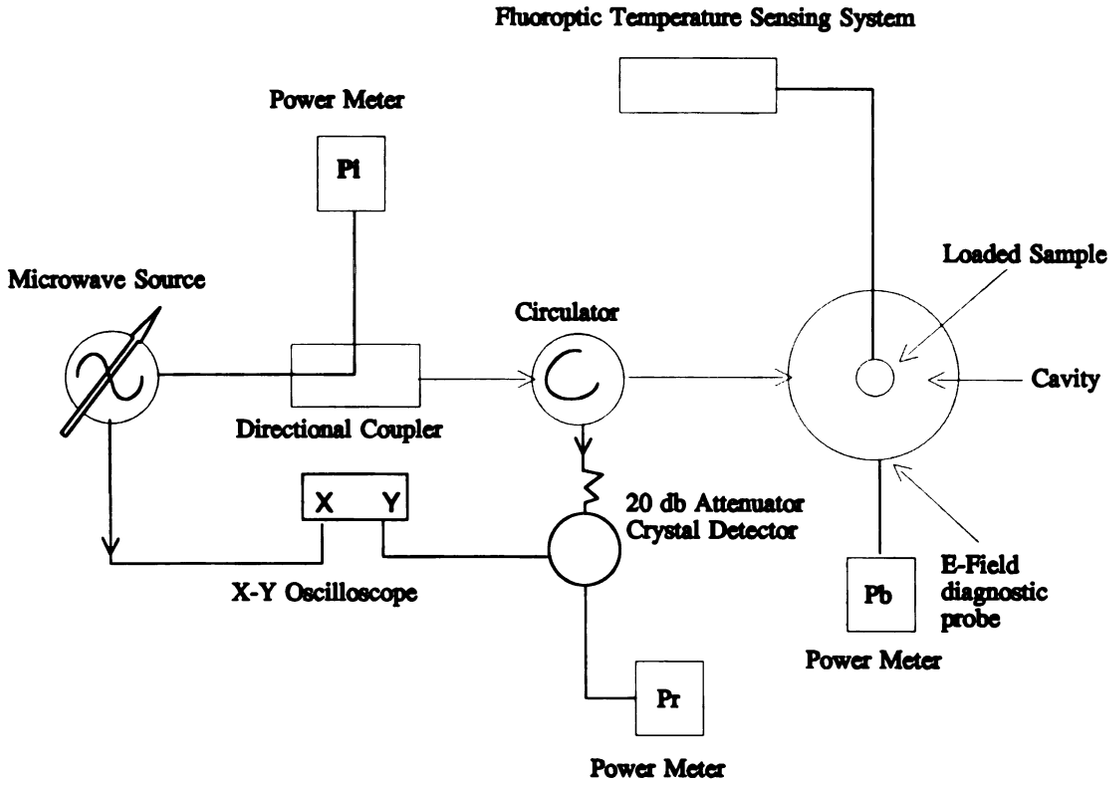

Figure 1.2 Microwave diagnostic and processing system circuit

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1.1.3 Advantages of microwave processing

Microwave processing involves direct transfer of energy to materials and this results in a greater controllability compared to thermal heating. Microwave processing involves the volumetric heating of materials and this results in rapid heating compared to the slow heat transfer controlled thermal heating. The much faster response times results in the ability to control the exothermic excursion during the processing of thermoset polymers. Temperature gradients are not necessary for heat transfer and so there is a possibility of maintaining very good temperature uniformity across the material to which energy is being transferred using microwave radiation. Preferred gradients can also be maintained to reduce voids during condensation polymerization.

1.2 Materials

1.2.1 Highlights of vinyl esters

Vinyl ester resins are noted for their high chemical resistance and toughness. They have excellent reactivity during polymerization due to the terminal vinyl unsaturations. They have very good wetting and bonding to glass reinforcements due to the secondary hydroxyls on the vinyl ester resin molecule. These materials have superior acid and hydrolysis resistance [4].

1.2.2 Vinyl ester chemistry

Vinyl ester resins are formed by reacting epoxy resins with ethylenically unsaturated carboxylic acids. The most commonly used epoxy resin is DGEBA based and

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the common carboxylic acid used is methacrylic acid. Crosslinking occurs due to the cleavage of double bonds and the formation of single bonds. The polymerization proceeds by a free radical mechanism. Vinyl ester resins typically homopolymerize sluggishly and therefore unsaturated low molecular weight monomers are added to increase their polymerization rates and also to reduce the working viscosity of the resins. Examples of the unsaturated monomers used include styrene and vinyl toluene. Figure 1.3 shows the chemical structures of a vinyl ester resin and vinyl toluene.

The free radical polymerization of vinyl esters consists of three steps occurring in parallel. Figure 1.4 illustrates the different steps of the polymerization. The initiation step involves the decomposition of the initiator and results in the production of free radicals that initiate the chain formation. The propagation reaction involves the growing chains reacting with the unreacted unsaturations and results in the increase in chain lengths. The termination reaction involves the interaction of two free radicals to form a dead chain.

The termination reaction can proceed in two different ways. In the combination form of termination the two free radical ends combine together to form a chain that has a molecular mass equal to the sum of their individual molecular masses. In disproportionation, one of the free radicals transfers a proton to the other free radical thereby becoming unsaturated while the other free radical becomes a dead chain [5].

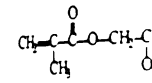

Figure 1.3

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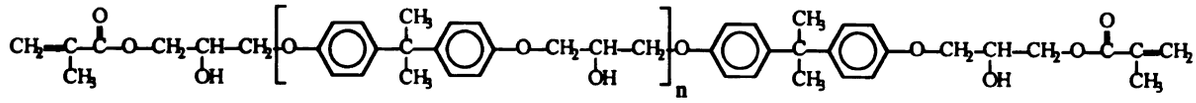
Figure 1.4



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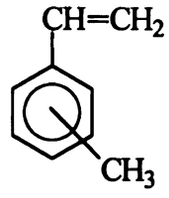

vinyl toluene

Figure 1.3 Chemical structures

Initiation

$$I \xrightarrow{K_d} 2\,R\bullet$$

Propagation

$$R_1\bullet + M_1 \xrightarrow{K_{11}} R_1\bullet$$
$$R_1\bullet + M_2 \xrightarrow{K_{12}} R_2\bullet$$
$$R_2\bullet + M_1 \xrightarrow{K_{21}} R_1\bullet$$
$$R_2\bullet + M_2 \xrightarrow{K_{22}} R_2\bullet$$

Termination

$$R_n\bullet + R_m\bullet \longrightarrow R_{n+m}$$
$$R_n\bullet + R_m\bullet \xrightarrow{K_t} R_n + R_m$$

Figure 1.4 Reaction mechanism of vinyl ester resins

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1.3 Thesis objective

The overall goal of the research group is to use microwave technology to process polymer matrix composites in a microwave cavity and to produce composites with properties similar to or better than autoclave processed composites. To achieve this goal a comprehensive understanding of the fundamentals must be attained. This involves the study of different aspects of the processing with different materials. For this work two important aspects have been identified: (1) Neat resin studies to understand the interaction of microwaves with polymers and (2) Studies on composite laminates to understand the macro-level aspects related to the microwave processability of composites. These relatively fundamental studies are expected to give a better insight into the mechanism of microwave curing and are hoped to assist in scaling up of the process to industrial requirements.

1.3.1 Materials used in the studies

The material used in the studies is an experimental vinyl ester resin XU-71973.00 supplied by The Dow Chemical Company, U.S.A. The resin is a methacrylic ester of Diglycidyl ether of Bisphenol-A based epoxy and contains 45% by weight of vinyl toluene as the cross linking monomer. Vinyl toluene was used because it has a higher flash point than styrene and is easier to handle in a laboratory from a safety perspective. Only BPO was used to catalyze the reaction. Glass fiber was used in the studies with composite laminates.

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1.3.2 Neat resin study

The focus of this study was to investigate the kinetics of the vinyl ester resin polymerization during thermal and microwave curing. The goal was to evolve a model to represent the kinetics of vinyl ester polymerization and estimate the different parameters during thermal curing and during microwave curing. This investigation was conducted to broaden the understanding of some of the fundamental interactions between microwaves and polymers and explain any differences in the curing rates.

1.3.3 Studies on composite laminates

The focus of this study was to process glass fiber reinforced vinyl ester resin matrix composites in the microwave cavity, with equivalent mechanical properties to thermally cured composites. Twelve ply unidirectional laminates were selected to be examined for these composite processing studies.

The goals for this study were set as follows: (1) process vinyl ester/glass fiber laminates using similar cure cycles, in a thermal oven and a microwave cavity (2) compare the mechanical properties of the samples cured in the microwave cavity and in the thermal oven with the mechanical properties of autoclave cured samples (3) evaluate the void fractions of the laminates produced (4) use the feedback of this investigation to reproducibly produce laminates in the microwave cavity with properties equivalent to those of the autoclave cured samples and (5) make a preliminary study of the aspects related to the industrial applicability of the microwave processing technology.

2. FTIR ANALYSIS

2.1 Background

Infrared spectroscopy is a well established technique for qualitative as well as quantitative studies [6,7,8]. This is a valuable tool for the analysis of polymer mixtures because of the highly specific nature of interaction between IR radiation and matter, which depends greatly on the molecular structure and environment of a substance. This technique has other advantages of being reproducible and nondestructive in its application. Fourier Transform Infrared Spectroscopy (FTIR) has many advantages for the present system because the morphological changes accompanying the crosslinking reaction make the application of other techniques, like chromatography and NMR, very difficult.

Generally, in the copolymerization of two different monomers, the fraction of molecules entering the polymer chain at any instant (i.e the rate of polymerization of the individual monomers) is dependent on the relative reactivities of the monomers and the fraction of each component in the unreacted form [5]. The aim was to evolve a method which would give the fraction reacted, of each component (vinyl toluene and vinyl ester), at any stage of the reaction.

The work was undertaken from this perspective, but the investigation has resulted in a technique which can be applied in general to the IR analysis of binary polymer mixtures and which could give the required information in specific instances. A method has been reported for use with UV spectroscopy [9] for binary mixtures where the sum

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of the concentrations of the two components is a constant. Such a condition will hold for mixtures only if the mass or molar densities of the individual pure components are the same. The present technique does not place that restriction on the constituents of the mixture and can be applied to mixtures with components of different densities. This is therefore applicable to resin systems where typically one of the components has a lower molar and mass density relative to the other component.

2.2 Theory

The following is a presentation of the theoretical basis for the application of the method. This analysis is based on material balance on the system and Beer's law.

2.2.1 Development of the method

Consider two components 'a' and 'b' existing as a mixture. From a material balance consideration (assuming no volume change in mixing), we can write the following equation (2.1), where each term represents the volume fraction of the respective components.

$$\frac{C_a}{\rho_a} + \frac{C_b}{\rho_b} = 1 \qquad (2.1)$$

Let λ_i represent any wavelength in a region of the spectrum. We can write Beer's Law at that wavelength as:

$$A^{\lambda_i} = \varepsilon_a^{\lambda_i} l c_a + \varepsilon_b^{\lambda_i} l c_b \qquad (2.2)$$

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Similarly, at any other wavelength (say λ_1), we can write the same equation as

$$A^{\lambda_1} = \varepsilon_a^{\lambda_1} l c_a + \varepsilon_b^{\lambda_1} l c_b \qquad (2.3)$$

We can use equations (2.1), (2.2) and (2.3) to eliminate the concentrations C_a and C_b. If we assume that the path length l is the same for all the samples of different compositions and use $D_a^{\lambda i}$ and $D_b^{\lambda i}$ to represent the absorbencies of the respective pure components at the particular wavelengths λ_i, we get the following equation:

$$A^{\lambda_1} = A^{\lambda_i} \left(\frac{D_b^{\lambda_1} - D_a^{\lambda_1}}{D_b^{\lambda_i} - D_a^{\lambda_i}}\right) + \left(\frac{D_a^{\lambda_1} D_b^{\lambda_i} - D_b^{\lambda_1} D_a^{\lambda_i}}{D_b^{\lambda_i} - D_a^{\lambda_i}}\right) \qquad (2.4)$$

$$\textit{where} \quad D_x^{\lambda_i} = \varepsilon_x^{\lambda_i} l \rho_x \qquad (2.5)$$

The equation (2.4) shows that, for mixtures of different compositions, the absorbance at one wavelength will yield a straight line when plotted against the absorbance at any other wavelength. This is contingent on all the samples having the same path length.

For mixtures with different compositions, we can plot the absorbencies at a particular wavelength λ_1 against the absorbencies at different wavelengths λ_i. If λ_i is in a region where component 'a' has no absorbance, we can substitute $D_a^{\lambda i} = 0$ in equation (2.4) to get equation (2.6).

This equation shows that all of the above-mentioned plots will yield straight lines with a common intercept on the $A^{\lambda 1}$ axis that is independent of the wavelength λ_i. It also

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$$A^{\lambda_1} = A^{\lambda_i} \left(\frac{D_b^{\lambda_1} - D_a^{\lambda_1}}{D_b^{\lambda_i}}\right) + D_a^{\lambda_1} \qquad (2.6)$$

shows that the intercept will equal the pure component absorbance at wavelength λ_1, of the component which does not absorb in the region λ_i of the spectrum.

Similarly, plotting the absorbance of the mixture at wavelength λ_1 against another region λ_j where component 'b' does not absorb will yield another set of straight lines with a common intercept on the $A^{\lambda 1}$ axis. This intercept will be the absorbance of the pure component 'b' at the wavelength λ_1.

2.2.2 Quantitative analysis

Once the absorbencies of the pure components at the wavelength λ_1 are found using the above method, these values can then be used to calculate the composition of any mixture, given its absorbance $A^{\lambda 1}$, by using the following relation.

$$\frac{C_b}{\rho_b} = \frac{A^{\lambda_1} - D_a^{\lambda_1}}{D_b^{\lambda_1} - D_a^{\lambda_1}} \qquad (2.7)$$

This is obtained from equations (2.1) and (2.3) and represents the volume fraction of the component 'b' in the mixture. If we know the densities, we can find the actual concentration of each component in the mixture.

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2.2.3 Application to kinetic study

Different kinds of situations are encountered when working with different kinds of systems. The following paragraph identifies one such case and indicates how the above method may be applied to find the extent of reaction of each component of the system.

Consider the absorbencies at two wavelengths, where the total absorbance has contributions from both the reactive and nonreactive groups of both molecular species. If it is possible to draw a baseline to yield the absorbance of the mixture at those wavelengths, which includes only the contributions of the reactive groups in both molecules, then we can still apply the above method because the absorbance contributions due to these reactive groups will still be representative of the bulk concentration of the respective molecules and equation (2.1) holds if C_a and C_b are considered the concentrations of the respective reactive groups. It is then possible to estimate the absorbencies of the individual reactive groups in the pure state by using the method described above. When the reaction is in progress, equation (2.1) is no longer valid if C_a and C_b are considered the concentrations of the respective reactive groups, but at two different times, equation (2.2) can be written for the two different wavelengths to give four linear equations. These linear equations can then be solved to give an estimate of the extent of each component reacted.

2.3 Spectra recording

The spectra were collected on a Perkin-Elmer Model 1800 Fourier Transform Infrared Spectrophotometer with the following parameters: mode-double beam, range -

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4000 to 450 cm^{-1}, resolution - 2 cm^{-1}, jacquinot stop - 85 percent, apodization-medium, detector - DTGS, number of cycles - 4, scans per cycle - 4 sample and 2 reference scans.

2.4 Experimental

The manufacturer supplied resin mixture with 55% (w/w) methacrylic ester of DGEBA and 45% (w/w) vinyl toluene was diluted with different amounts of vinyl toluene. Four microliter samples of these mixtures were transferred using a micro-syringe, placed between two KBr disks, and scanned in the spectrophotometer. The spectra of the plain KBr disks scanned prior to this were then subtracted from the sample spectra in the absorbance mode. The resulting spectra were then shifted vertically to bring the point of least absorbance to zero value. To extend the range to higher concentrations of the vinyl ester, the resin mixture was placed on KBr disks and the vinyl toluene allowed to evaporate for different amounts of time before scanning.

Sample thicknesses were measured by mounting the KBr disks in acrylic holders, polishing and viewing them under an optical microscope. The sample thickness varied from 18 to 24 microns. The sample thicknesses showed a lot of variation and could not be more accurately reproduced even after using a micro-syringe to measure out the quantity of vinyl ester. It was observed that polishing removes the KBr in macroscopic crystals larger than the mesh size of the polisher, thereby leaving the interface very jagged, non-uniform and sometimes indiscernible. This suggests that the measurement of the sample thicknesses using this method is not very accurate.

2.5 Results

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2.5 Results

Fig. 2.1 shows the spectra of vinyl toluene, vinyl ester and a mixture of these. Four regions of the spectra have been identified where vinyl toluene exhibits very little absorbance. The absorbencies of a few of the peaks of the mixture have been plotted (y-axis) against the absorbencies at wavelengths in these regions (x-axis). The data points have been fitted using a linear regression. Table 2.1 shows the midpoint and the range within which the y-intercepts were obtained for each set of plots. Based on this, the average range of the intercepts was calculated to be 0.005 absorbance units on either side of the mid value. This can be considered the mean error in the calculated value of the absorbance at any wavelength.

Figure 2.1

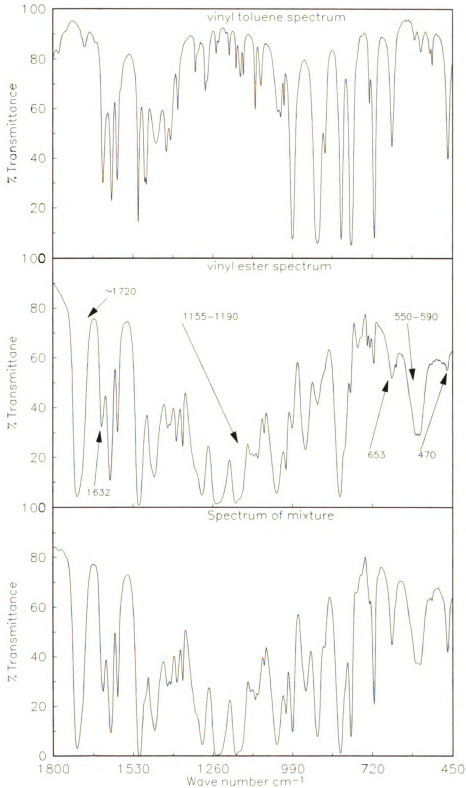

Figure 2.1 Spectra of the chemical systems

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Table 2.1

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Since the regions correspond only to absorption by vinyl ester (Figure 2.1), the common intercepts on the y-axis represent the absorbencies of pure vinyl toluene at the respective wavelengths. All sets of plots showed consistency in reporting the absorbance of pure vinyl toluene at the corresponding wavelengths with an accuracy of 0.005 absorbance units (each row in Table 2.1). This is proof of the applicability of this method.

Table 2.1 Absorbencies of vinyl toluene at different wave numbers (Column 1)

Regions → y axis ↓	1700 - 1730 cm^{-1}	1220 - 1260 cm^{-1}	1155 - 1190 cm^{-1}	550 - 590 cm^{-1}
470	0.182 ± 0.004	0.183 ± 0.003	0.179 ± 0.009	0.183 ± 0.005
653	0.229 ± 0.001	0.233 ± 0.001	0.226 ± 0.008	0.228 ± 0.004
1632	0.344 ± 0.005	0.346 ± 0.004	0.335 ± 0.015	0.341 ± 0.005
3088	0.358 ± 0.009	0.359 ± 0.004	0.359 ± 0.002	0.363 ± 0.002

More sets of plots were generated between the 1632 peak and a few more regions where both components have significant absorption. They resulted in lines with widely different y-intercepts. A few sets of plots are illustrated in Figures 2.2 - 2.5. It was also verified by this method that there were no regions of the spectra that correspond to strong absorbance by vinyl toluene and small absorbance by vinyl ester.

Figure 2.2

Figure 2.3

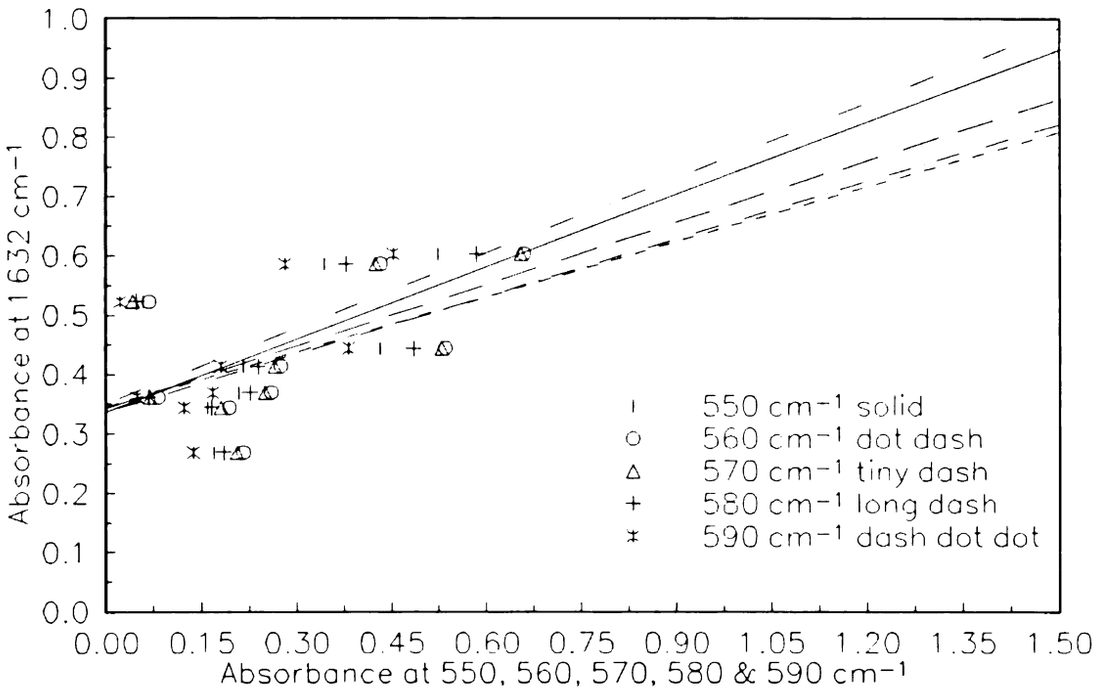


Figure 2.2 Absorbance at 1632 cm^{-1} vs. absorbencies in 550-590 cm^{-1} region

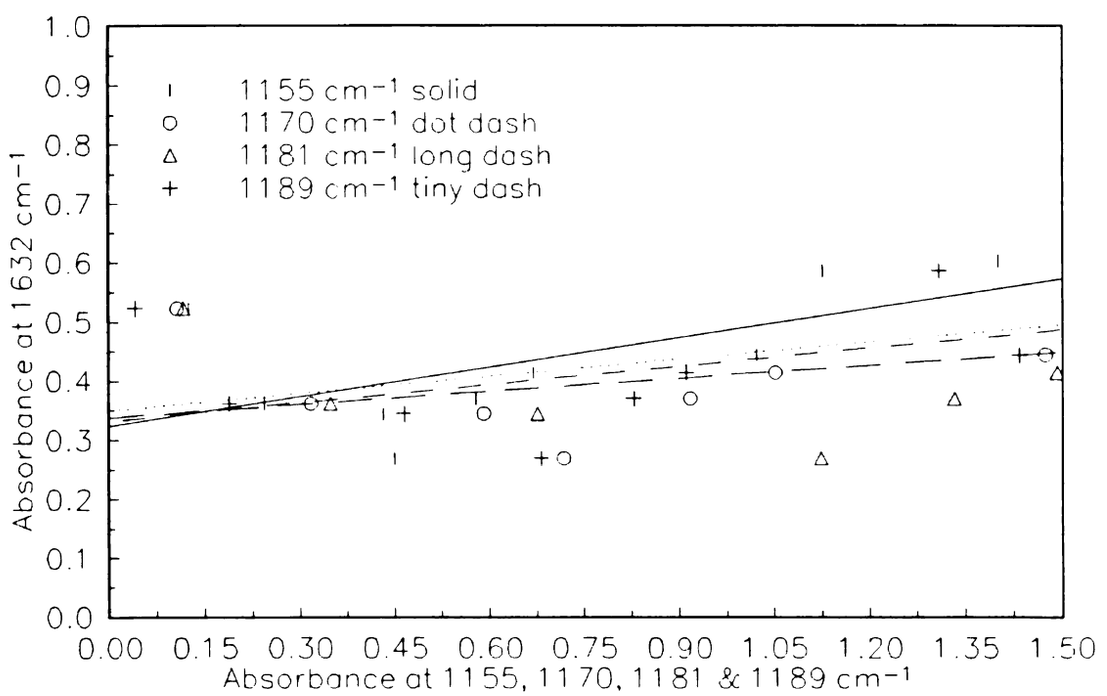


Figure 2.3 Absorbance at 1632 cm^{-1} vs. absorbencies in 1155-1189 cm^{-1} region

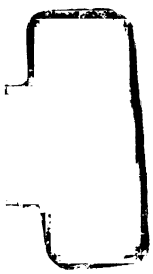


Figure 2.4

Figure 2.5

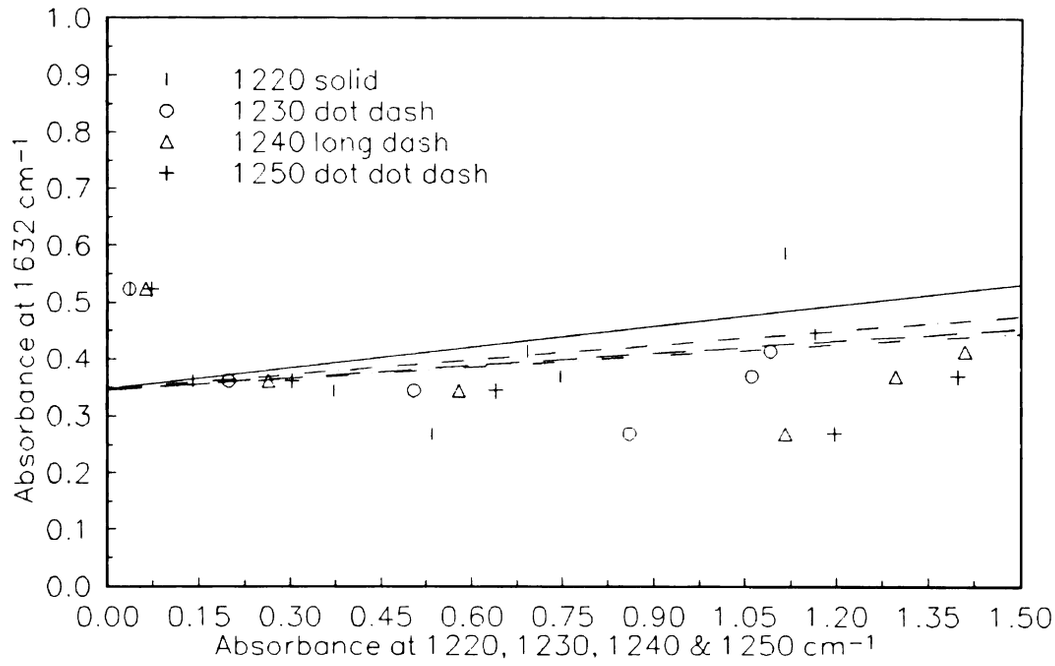


Figure 2.4 Absorbance at 1632 cm^{-1} vs. absorbencies in 1220-1250 cm^{-1} region

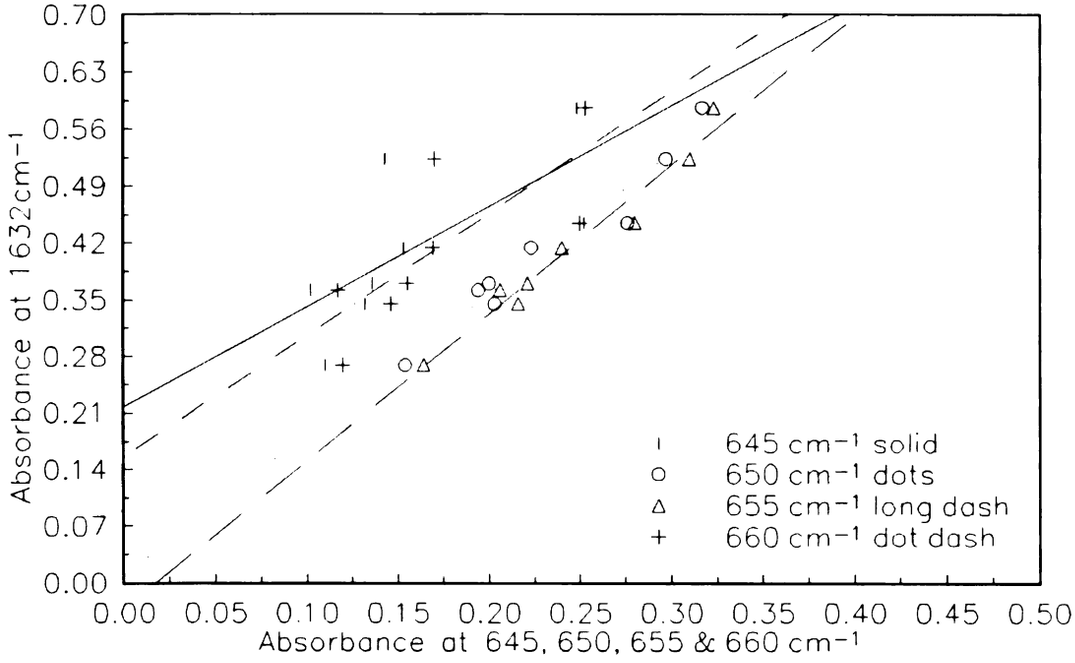
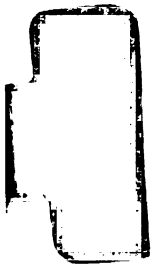


Figure 2.5 Absorbance at 1632 cm^{-1} vs. absorbencies in 645-660 cm^{-1} region



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2.6 Limitations and sources of error

The intercepts on the $A^{\lambda 1}$ axis will also coincide if the spectra of both the components are similar in the region considered [9]. Another limitation is the choice of the baseline considered. If the baseline used does not yield the net absorbance of the mixture, but instead yields the absorbance of the mixture offset by a value k^i, then this results in lines with different intercepts on the $A^{\lambda 1}$ axis even if only one component absorbs in the region λ_i. This can be verified by substituting the following relation in equation (2.4).

$$A^{\lambda i}_{observed} = A^{\lambda i}_{actual} + k^i \qquad (2.8)$$

It can however be observed that if k^i is small then the deviations in the intercepts on the $A^{\lambda i}$ axis will be small. The sample thickness for all the samples scanned should be the same. This is very difficult to maintain with thin films on KBr disks. The effect of this can be a scatter in the data as shown in the plots. The plots however, indicate that regression lines through the data points can accommodate these variations and still yield satisfactory results if a sufficiently large concentration range is taken for the two components. Error can also result if the components do not form an ideal mixture, in which case equation (2.1) does not apply. Some other sources of error that apply to this method have been mentioned in literature [6,10,11,12].

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2.7 Summary

A method has been developed which can be used to identify the regions of single component absorption in an IR spectra of a mixture of two chemical species with different densities. The applicability of the method has been demonstrated with the spectra of a mixture of a vinyl ester and vinyl toluene. The application of this method for the quantitative analysis of mixture compositions and for finding the extent of reaction of each component has been delineated. The limitations of the method and the sources of error have been discussed.

The above method was used to verify that there are no regions of the spectra with strong vinyl toluene absorbance and insignificant vinyl ester absorbance. This is because the vinyl ester molecule has all the fundamental chemical bonds present in vinyl toluene. It was therefore inferred that it is possible to extract information only on the fraction of the total vinyl groups that have reacted but not the fraction of each component of the resin that has reacted at any time. The fraction of total vinyl groups that have reacted can be used as a measure of the extent of reaction.

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3. THERMAL KINETICS OF POLYMERIZATION

3.1 Background

The study of polymerization kinetics offers a substantial incentive in the endeavor to manufacture polymer matrix composites at high speeds. The study of the kinetics of a resin makes it possible to specify the processing cycles for composites made with that resin. The study enables one to optimize the curing cycle based on the specific curing characteristics of the resin and also makes it possible to simulate the curing process. These considerations, coupled with the faster kinetics observed during previous experiments with different resin [13] provided the motivation to study the kinetics of polymerization of the vinyl ester resin and the differences between thermal and microwave curing.

The goal of this study was to develop a cure kinetics model for vinyl ester polymerization and estimate the parameters for the model during thermal as well as microwave curing of neat resin samples. This chapter reports the results of the modelling of thermal curing of the vinyl ester resin. The parameters for the proposed model have been calculated based on the conversion-vs-time data generated at various temperatures and benzoyl peroxide (initiator) concentrations. Isothermal curing runs were conducted on different samples for different time intervals to generate the conversion-vs-time data. The concentration of the initiator and the temperature of the run were the experimental parameters that were varied between runs. The conversion was calculated based on the

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disappearance of the total vinyl unsaturations. The extent of cure of the resin mixture was determined using Fourier Transform Infrared Spectroscopy (FTIR).

3.2 Theoretical development of the model

The polymerization of a mono-vinyl monomer and a di-vinyl monomer can be divided into four distinct phases. Phase I is characterized by low resin viscosity and therefore the polymerization follows conventional kinetics. Phase II is characterized by the gel effect during which the termination rate constant becomes diffusion limited due to the increasing difficulty of the growing free radicals to come in contact with each other. Therefore the termination rate constant falls and the reaction rate increases. During phase III, the termination rate constant stops falling and remains constant because the active chain ends still possess a certain degree of mobility due to the propagation reaction even though their translational motion is severely restricted due to their size. Therefore the reaction rate falls. During Phase IV, the propagation reaction also becomes diffusion limited and therefore the polymer vitrifies.

The following form the basis for the development of the cure kinetics model: (1) the curing reaction is isothermal (2) the vinyl groups of the mono-vinyl monomer, di-vinyl monomer and the intermediate oligomers have the same reactivity. (3) inhibition reaction is not considered and (4) a single initiator is used.

The cure kinetics for a reaction mixture containing mono-vinyl and di-vinyl monomers may be described by equations (3.1), (3.2) and (3.3) [14].

$$\frac{dX}{dt} = k_p \sqrt{\frac{2 f k_d [I]}{k_t}} \quad (1 - X) \tag{3.1}$$

$$[I] = \frac{[I]_0}{\left(1 - \frac{d_m}{d_p} sX\right)} \exp(-k_d t) \tag{3.2}$$

$$s = \left(\frac{d_p}{d_m}\right) - 1 \tag{3.3}$$

where X is the fractional conversion of the vinyl groups; t is the time of reaction; f is the initiator efficiency; k_d is the rate constant of initiator decomposition; k_p is the propagation rate constant and k_t is the termination rate constant. $[I]_0$ and $[I]$ are the initiator concentrations at time 0 and t respectively; s is the volume shrinkage factor; d_p is the density of the thermoset polymer formed; and d_m is the density of the monomer mixture. Polymerization of methyl methacrylate/ethylene glycol dimethacrylate system has been modelled using these equations with good predictions [14].

As the reaction proceeds and increasingly larger free radicals are formed, their translational diffusional motion becomes increasingly restricted and results in a decrease of the termination rate constant with increasing conversion. Even when the translational motion of the free radicals is severely restricted, the termination rate does not approach zero because the active chain ends still possess a degree of mobility due to the

propagation reaction [14]. So the termination rate constant was modelled as decreasing continuously with cure until a limiting value and then remaining constant. Based on this analysis the termination rate constant can be written as equation (3.4)

$$k_t = k_{t,t} + k_{t,p} \tag{3.4}$$

where $k_{t,t}$ is the translational diffusion-controlled termination rate constant and $k_{t,p}$ is the residual termination rate constant dependent on the propagation reaction. The rate constant $k_{t,t}$ can be correlated with conversion through free volume parameters as in equation (3.5) [14].

$$k_{t,t} = k_{t,t0} \exp\left(B_t \left[\frac{1}{V_{f0}} - \frac{1}{V_f} \right] \right) \tag{3.5}$$

$k_{t,t0}$ is the rate constant at zero conversion, B_t is an adjustable parameter and V_{f0} and V_f are the free volumes of the reaction mixture at zero conversion and conversion X respectively. The rate constant $k_{t,p}$ was correlated to be directly proportional to the propagation rate constant with the proportionality constant $B_{t,p}$ being an adjustable parameter as:

$$k_{t,p} = B_{t,p}\, k_p \tag{3.6}$$

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The following correlation (equations 3.7-3.10) between free volume and conversion was used [15]:

$$V_{f0} = (0.025 + 0.001*(T-T_{gm})) \tag{3.7}$$

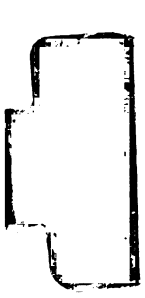
$$V_f = V_{f0} + [4.8e-4*(T-T_{gp}) - 0.001*(T-T_{gm})]*\phi_p \tag{3.8}$$

$$\epsilon = (d_m / d_p) - 1 \tag{3.9}$$

$$\phi_p = \frac{X(1 + \epsilon)}{1 + \epsilon X} \tag{3.10}$$

where T is the temperature of cure; T_{gm} and T_{gp} are the glass transition temperatures of the monomer and polymer respectively; ϕ_p is the volume fraction of the polymer being formed.

The propagation constant decreases with increasing conversion because of the increasing resistance to the diffusion of free radicals towards each other. The behavior of k_p with conversion is close to a step function with the value of k_p dropping to zero when the free volume of the polymer is zero [14]. The free volume of the polymer was calculated using equations (3.7-3.10) and it was found that the free volume does not go to zero even at complete conversion. Therefore, the propagation rate constant was modelled to be independent of conversion. Equations (3.1), (3.4), (3.5), and (3.6) can be combined to give equation (3.11).



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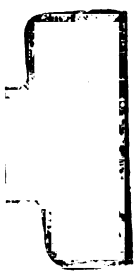
$$\frac{dX}{dt} = \frac{k_p \sqrt{f}\ \sqrt{2k_d[I]}}{\sqrt{k_{t,s0}}\sqrt{\exp\left(B_t\left[\frac{1}{V_{f0}} - \frac{1}{V_f}\right]\right) + \frac{B_{t,p}}{k_{t,s0}}\ k_p}}\ (1-X) \qquad \textbf{(3.11)}$$

The conversion-time data are sufficient to give only the value of the ratio $k_e = (k_p\sqrt{f}/\sqrt{k_{t,s0}})$. Molecular weight data are required to resolve the individual values. Therefore equation (3.6) can now be rewritten using k_e instead of k_p and a new adjustable parameter $B_{t,e}$ replacing $B_{t,p}$ as shown below in equation (3.12). k_e is the effective rate constant and B_t , $B_{t,e}$ are the model parameters.The expression for k_e as a function of temperature will still be in an Arrhenius form.

$$k_e = \frac{k_p\sqrt{f}}{\sqrt{k_{t,s0}}} \quad \textit{and} \quad B_{t,e} = \frac{B_{t,p}}{\sqrt{f\ k_{t,s0}}} \qquad \textbf{(3.12)}$$

Substituting equation (3.12) in (3.11) gives equation (3.13), which along with equations (3.2) and (3.3) forms the set of equations that describe the extent of reaction of the vinyl ester-vinyl toluene resin system.

$$\frac{dX}{dt} = \frac{k_e \sqrt{2k_d[I]}}{\sqrt{\exp\left[B_t\left(\frac{1}{V_{f0}} - \frac{1}{V_f}\right)\right] + B_{t,e}k_e}}\ (1-X) \qquad \textbf{(3.13)}$$



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The model therefore contains two parameters B_t , $B_{t,e}$ to be evaluated based on the experimental data, together with the Arrhenius expressions for the rate constants k_e and k_d.

3.3 Materials and methods

A methacrylic ester of Diglycidyl Ether of Bisphenol-A (DGEBA) vinyl ester resin with 45% (w/w) vinyl toluene as the monomer was used. Benzoyl peroxide (BPO) was used as the initiator.

3.3.1 Sample preparation and curing

A thin film technique based on IR spectroscopy was used to study the kinetics of polymerization of the resin. Samples were prepared by enclosing a thin film of the resin between two KBr disks 13 mm in diameter and 1 mm in thickness. KBr disks were used to support the resin because KBr is transparent to IR radiation. The KBr used to make the disks was stored in a desiccator to keep it dry and avoid interfering IR absorbance from water.

The samples were cured for different time intervals in a temperature controlled thermal oven. A set of samples constituting a run were loaded simultaneously into the oven. The temperature of the samples was measured by placing a fluoroptic temperature probe close to the samples. Individual samples were removed from the oven at appropriate time intervals and quenched in dry ice to freeze the reaction. The experiments were run at five different temperatures of 80°C, 90°C, 100°C, 110°C and

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120°C. Runs with 1%, 2%, 3%, 4% and 5% (w/w) benzoyl peroxide concentrations were made at each of these temperatures.

3.2.2 Analytical technique

FTIR analysis involves irradiation of samples with electromagnetic radiation of a range of frequencies in the infrared region. The fraction of light transmitted at each frequency is recorded and the output can be obtained as a plot of the transmittance vs the frequency of radiation. The specific nature of the interaction of the IR radiation with matter allows particular chemical groups to absorb strongly at only a few frequencies. This discrimination in absorption by different groups in a chemical system can be used to estimate the concentrations of the different chemical species in a given system.

The fundamental basis for quantitative FTIR analysis is Beer-Lambert's law:

$$-\log(T) = A = abc \tag{3.14}$$

where T is the transmittance, A is the absorbance or integrated absorbance, a is the molar absorptivity or the integrated molar absorptivity of the absorbing species, b is the path length and c is the molar concentration of the absorbing species.

The spectra of the samples were scanned using a PERKIN-ELMER model 1800 FTIR spectrophotometer. The spectra of the plain KBr disks, the resin samples (held between the KBr disks) before cure and the resin samples after cure were taken. The spectra of the plain KBr disks were subtracted in the absorbance mode from the spectra of the sample (held between KBr disks) to correct for the absorbance of KBr. The

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resulting spectra were then shifted vertically to bring the point of least absorbance to zero. This procedure was applied to the sample spectra before and after cure.

To eliminate the local background absorbance in the region of interest in a spectra, a baseline is usually drawn that closely matches the absorbance of this background in that region of the spectra. This usually is of the form of a straight line drawn between two appropriately chosen points on the spectra. The area enclosed by the baseline and the spectra between the wavelength limits imposed by the analyst is used to represent the integrated absorbance of the analyte as used in equation (3.14). The spectra should be in the absorbance mode for the area calculation. The calculation of the areas is illustrated in Figure 3.1 . The wave numbers b1 and b2 are the baseline limits and the wave numbers w1 and w2 are the limits on the wave numbers for the calculations of the area. The shaded region represents the area calculated.

The baseline limits and the area limits selected should be based on the identification of the peaks, the interference from neighboring peaks, and the requirement that the calculated area represent the concentration of the analyte as closely as possible. A consequence of this requirement is that the areas obtained from the selected baseline limits and the area limits should follow certain relations that are followed by the physical entities that they represent. These are delineated in the next section. Based on the spectra obtained in the initial runs and the criteria mentioned, a reference peak, a BPO peak and a reaction peak were chosen. The baseline limits and the area limits for the same were also selected. They are listed below in Table 3.1. The reaction peak measures the total vinyl unsaturation.

Absorbance

Figure 3.1

Table 3.1

Peak
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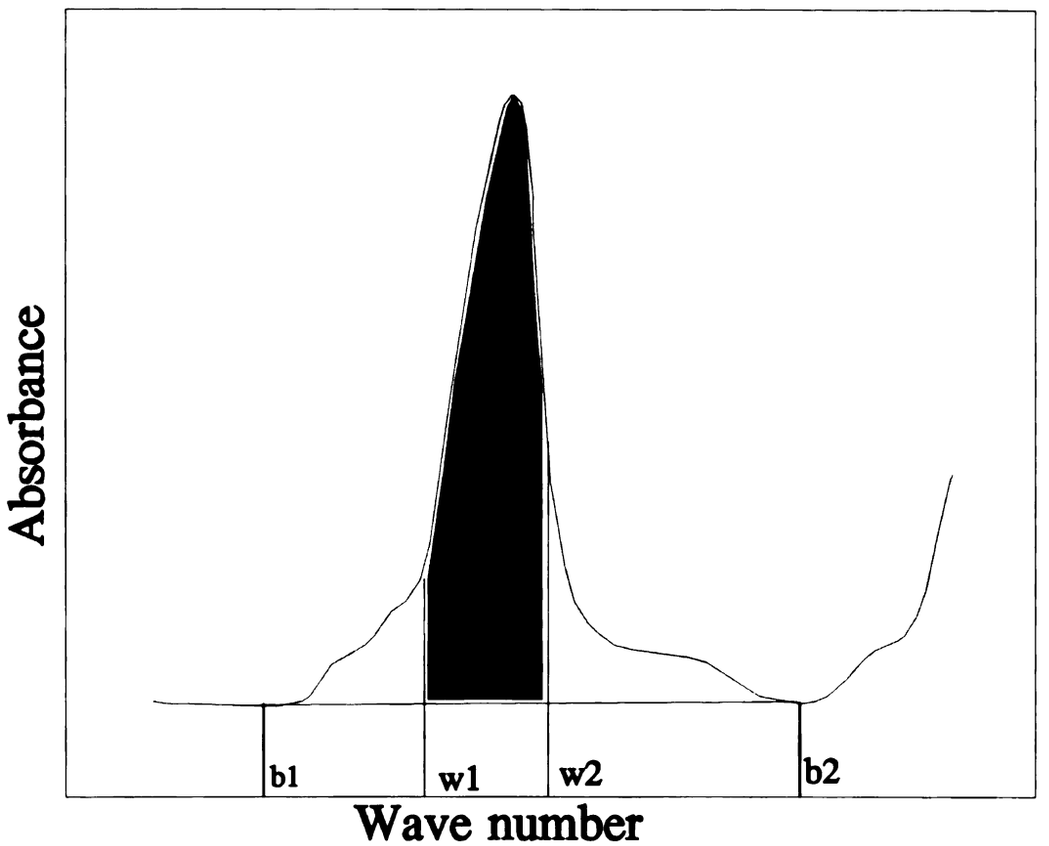

Figure 3.1 Area used for determining concentration of analyte

Table 3.1 The baselines and the limits for the areas under the different peaks

Peak	Baseline limits	Area Limits
Reference peak	1655-1560 cm^{-1}	1612-1602 cm^{-1}
BPO peak	1800-1662 cm^{-1}	1800-1765 cm^{-1}
Reaction peak	1655-1560 cm^{-1}	1645-1630 cm^{-1}

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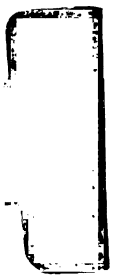
The extent of cure was calculated using equation (3.15)

$$X = 1 - \frac{[\, A_{Rxn} / A_{Ref} \,]_{after\ cure}}{[\, A_{Rxn} / A_{Ref} \,]_{before\ cure}} \qquad \textbf{(3.15)}$$

3.3.3 Data processing

Errors are introduced into some data points over the course of experimental and computational procedures. Plain KBr disks that are very smooth and parallel result in interference effects that result in the background being wavy. This cannot be eliminated by a straight line baseline. Foreign matter that gets into certain samples results in the distortion of the spectra and the quantitative data derived thereof. The application of heat during curing causes some resin flow that changes the sample geometry. These and other errors distort the quantitative information that is obtained from the spectra. Therefore the extent of cure calculated for these data point will be unreliable. To minimize the effects of these phenomena, different criteria were selected to verify that the areas under the different peaks were coherent with respect to their physical interpretation. This coherency was checked by verifying that the areas under the peaks satisfied relations, between themselves, that should be satisfied by the physical quantities they represent. This verification ensures that many of the errors induced into the data points through the experimental and computational procedures are eliminated. Some of the relations that should be satisfied by the values obtained from the spectra are listed below:

1. For any set of spectra of samples of the same composition, the area under any peak should be directly proportional to the thickness of the sample. Therefore, if



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the area under any peak (of the different samples), is divided by the area under the same peak of a reference sample, then these normalized areas represent the relative thickness of the samples with respect to the reference sample. These values should be the same if the reference peak, the BPO peak and the reaction peak are used.

2. For each sample, the ratio of the reaction peak area to the area of the reference peak (both before cure) is directly proportional to the concentration of the unreacted double bonds of the resin system. Since the concentration of the unreacted double bonds is the same in all the samples (before cure), the ratio of the reaction peak area to the reference peak area should be the same for all the samples. The same argument holds for the ratio, before cure, of the BPO peak area to the reference peak area for samples with the same BPO concentration.

These criteria were used to evaluate the data points obtained and eliminate those that failed to satisfy these criteria.

There is a latency associated with the heating of samples in a thermal oven. This is the time for the samples to heat up to the oven temperature. This heating time results in a shift in the conversion-time data along the time axis towards higher times. To eliminate this error in the conversion-time data, the data points at low times of cure were fitted with a straight line using linear regression and the intercept on the time axis was subtracted from all the data points of that run.

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3.4 Results and discussion

The initiation reaction was modelled separately as a first order reaction. The expression for k_d as a function of temperature was found using a least squares regression of the BPO reaction data. The reaction was monitored by the benzoyl peroxide peak mentioned earlier.

The glass transition temperature of the polymer was found using Differential Scanning Calorimetry (DSC) and the glass transition temperature of the monomer was evaluated using the equation by Soh [16]. The adjustable parameters of the model were found using a Simplex algorithm for minimizing the square of the error between the experimental data points and the model predictions. The values of the parameters obtained for this model are given in Table 3.2.

The predictions of the model and the experimental data at those conditions are illustrated for four different temperatures in Figures 3.2, 3.3, 3.4 and 3.5 respectively. The accuracy of the predictions is very good. The quality of the fit is comparable to that of other literature [14, 16]. The least error in the temperature measurement is 1°C, because this is the error in the measurement of the temperature using the fluoroptic temperature probe placed near the samples. The actual error would be more because of the temperature differences in the oven and also the fluctuations during the control of the oven temperature. The model predictions at 89°C and 91°C have been evaluated for different BPO concentrations and are illustrated in Figure 3.6, along with the model predictions and experimental values at 90°C. This gives a window of possible errors in the experimental values based on the estimated error in temperature alone. Most of the

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Table 3.2

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d_p	1.
T_{gm}	-1
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k_d	8
k_e	2

Note:

data points fall within this window indicating that the fit is very good. Other experimental errors exist and these cause some of the data points to fall slightly outside the window. The rate of reaction as a function of the extent of cure at 90°C, as predicted by the model has been illustrated in Figure 3.7. The reaction does not proceed to completion at low temperatures or low BPO concentrations. This is because of dead end polymerization whereby the short half-life of the initiator causes the reaction rate to fall as the initiator is consumed [17].

Table 3.2 Kinetic parameters for vinyl ester/vinyl toluene polymerization

d_m	1.04	gm/cm^3
d_p	1.11	gm/cm^3
T_{gm}	-160	^oC
T_{gp}	80	^oC
B_t	2.9885	
$B_{t,e}$	0.5068	
k_d	$8.02e7 \exp\left(\frac{-8795.4}{T+273}\right)$	s^{-1}
k_e	$2.051e6 \exp\left(\frac{-6760.4}{T+273}\right)\left[\frac{L}{mole-s}\right]^{\frac{1}{2}}$	

Note: T is the temperature in ^oC

Figure 3.2

Figure 3.3

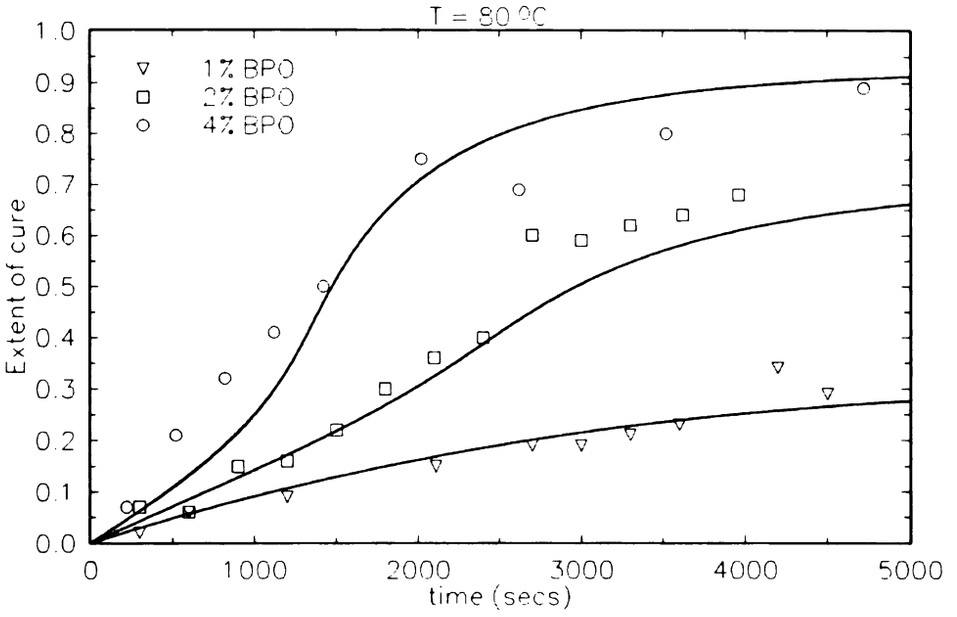

Figure 3.2 Model predictions and experimental data of extent of cure at 80°C

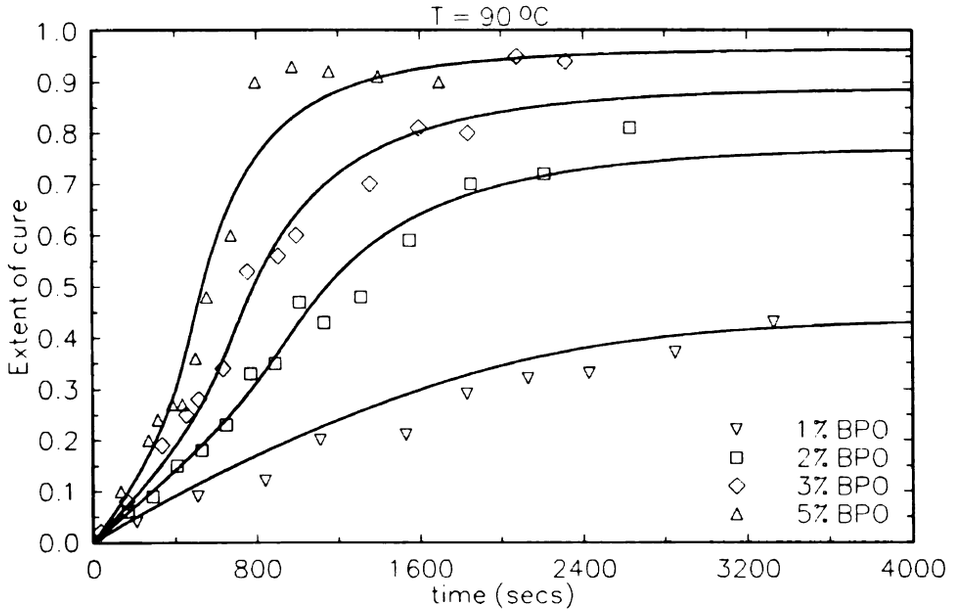

Figure 3.3 Model predictions and experimental data of extent of cure at 90°C

Figure 3.4

Figure 3.5

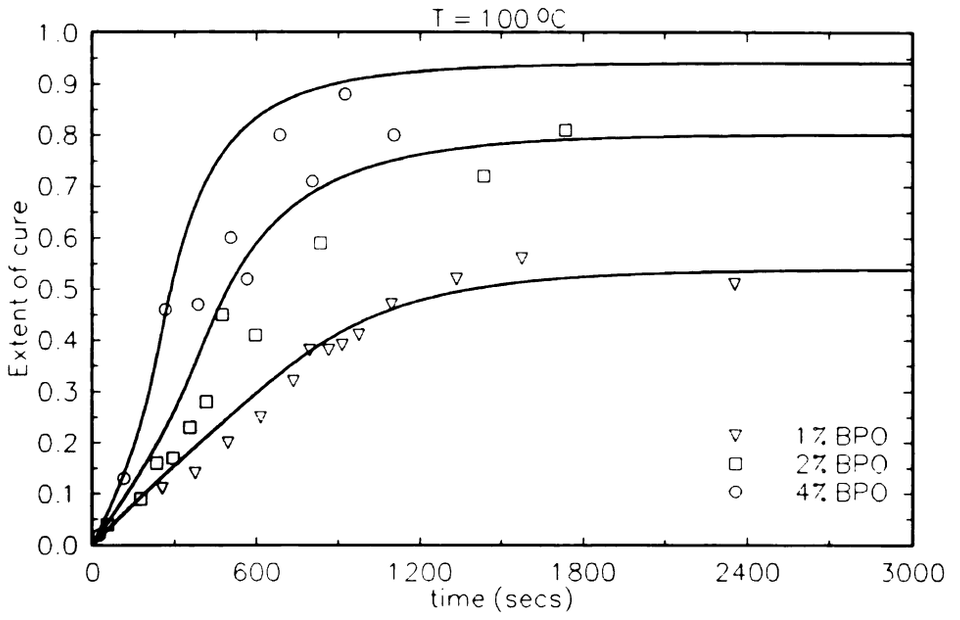

Figure 3.4 Model predictions and experimental data of extent of cure at 100°C

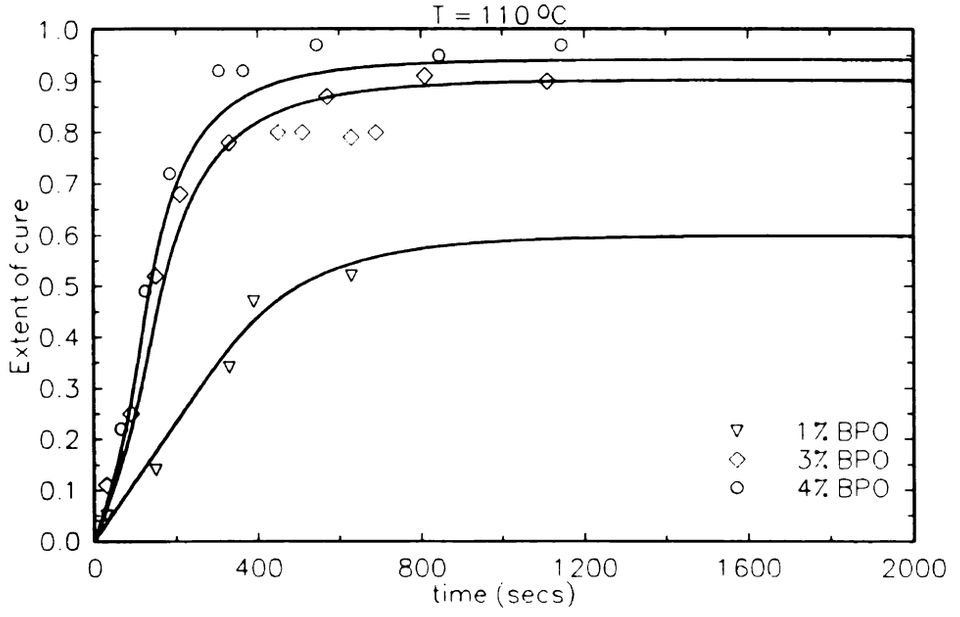

Figure 3.5 Model predictions and experimental data of extent of cure at 110°C

Figure 3.6

Figure 3.7

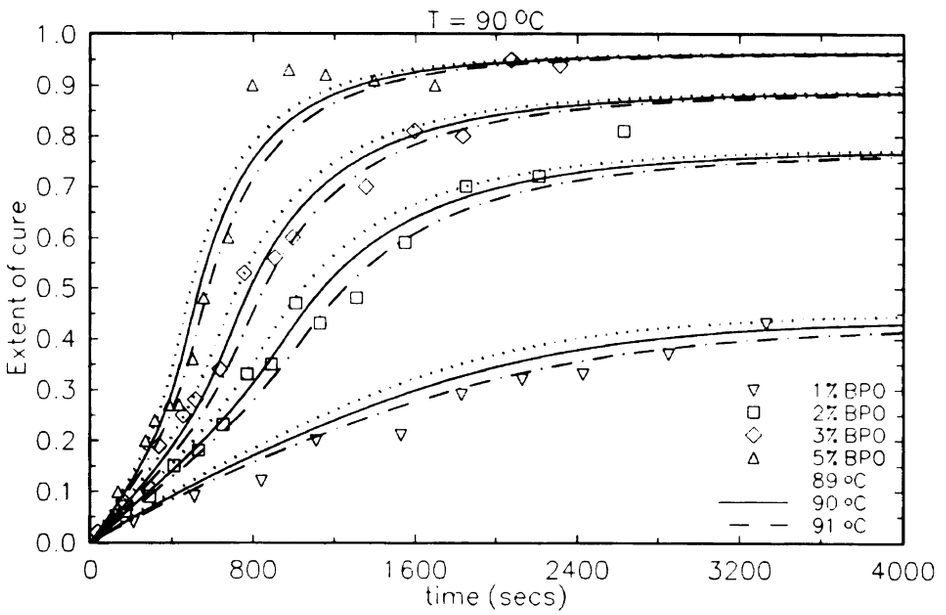

Figure 3.6 Error windows based on error in temperature measurement

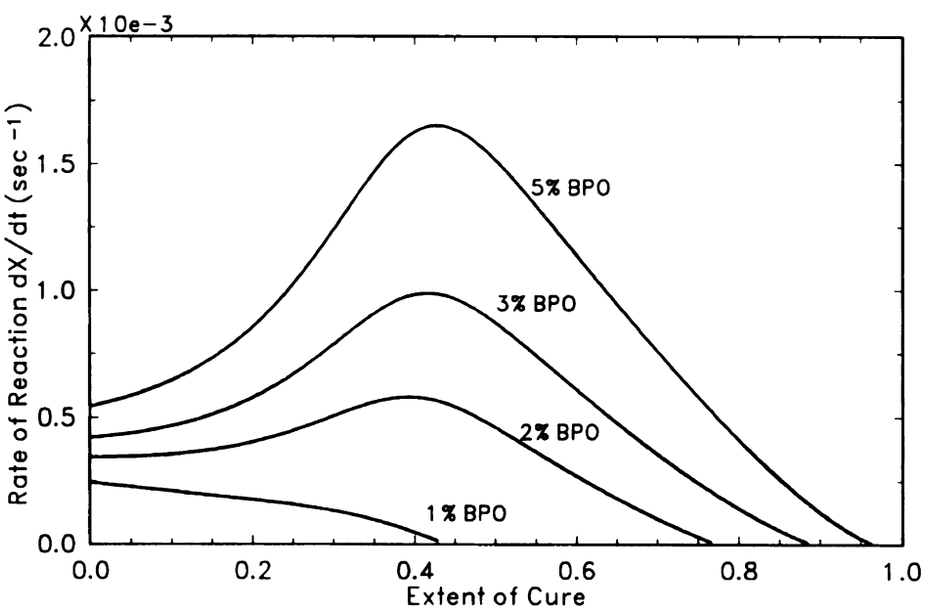

Figure 3.7 Model predictions of rate of reaction vs. extent of cure at 90°C

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3.5 Summary

The polymerization reaction of a vinyl ester resin during thermal curing was modelled. The initiation reaction was modelled separately using a first order rate expression. The BPO reaction peak was monitored to obtain the conversion of the initiator with time and the initiation rate constant k_d was obtained based on a regression of this data. The propagation rate constant was modelled to be independent of the extent of reaction. The termination rate constant was considered to fall with the extent of cure until a limiting value is reached. The limiting value is directly proportional to the propagation rate constant. The model parameters were evaluated using a simplex algorithm to minimize the sum of the squares of the error between the model predictions and the experimental values. A good agreement was observed between the model predictions and the experimental data generated at different temperatures and initiator concentrations.

4. MICROWAVE KINETICS OF POLYMERIZATION

4.1 Background

To better understand the effect of microwaves on the cure kinetics process, different materials have to be studied. This chapter reports the results of the study of microwave cure kinetics of a vinyl ester resin.

4.2 Experimental

A thin film technique similar to the one used in the thermal curing experiments was used to cure the microwave samples. The same materials used for the thermal kinetics study were used. In the preparation of the thin film samples, about 4 mg of the resin was evenly distributed on KBr disks 13 mm in diameter and 1 mm in thickness. The resin was covered with another disk with a fine hole in the center for placing the temperature probe.

Microwave curing experiments were conducted at temperatures of 80°C, 90°C, and 100°C respectively. At each of these temperatures runs were made with 1%, 2%, 3%, 4% and 5% BPO. Higher temperatures were not used because the reaction rate at those temperatures is very fast compared to the time for loading the sample in the cavity and removing them to quench the reaction. The runs were made in a cylindrical, single mode microwave tunable cavity at 2.45 Ghz, as described in Chapter 1. The samples were held horizontally in a cylindrical teflon holder with a hole in the center,

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corresponding to the hole in the top KBr disk. The samples were individually cured for different time intervals at constant temperatures.

The temperature of the sample was monitored using a fluoroptic temperature probe placed in contact with the sample through the hole in the top KBr disk. A typical temperature profile during the curing process is shown in Figures 4.1 and 4.2. These illustrate the heat-up time as well as the steadiness of the sample temperature. The sample temperature was controlled by appropriately tuning and detuning the cavity to bring the cavity into or out of resonance. The samples were removed from the microwave cavity at appropriate times and quenched in dry ice.

The spectra were obtained using an FTIR spectrophotometer and were processed to yield the extent of cure of each sample. The same scan parameters and procedures were used for the microwave cured samples as the thermal samples (refer Chapter 3). The resin samples were scanned to obtain the before-cure and after-cure spectra. The spectra of the plain KBr disks (with one disk having the hole in the center) was taken prior to placing the resin between them so that the absorbance of the KBr disks can be corrected from the sample spectra before and after cure. The corrected spectra were used to find the extent of reaction of the samples at different times.

The data points were checked to eliminate erroneous values as detailed in the previous chapter. The times of cure of the sample as recorded, were modified to correct for the heat-up time for the samples. The heat-up time for each sample was calculated from the temperature profile data of the curing run as the time taken to reach the reaction temperature.

Figure 4.1

Figure 4.2

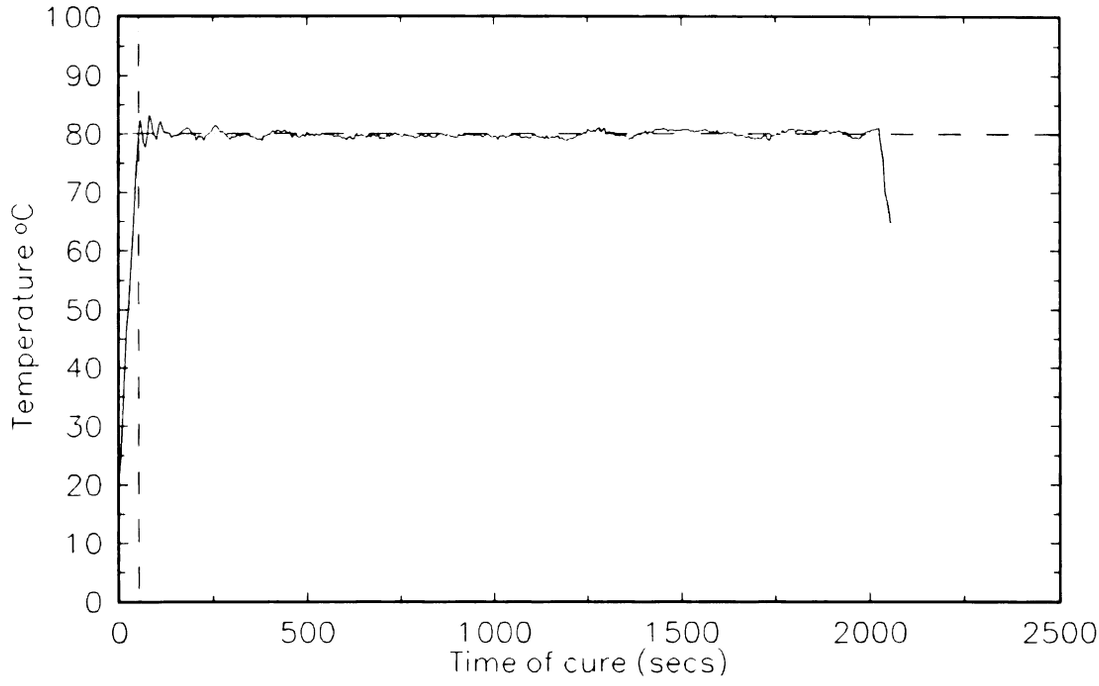

Figure 4.1 Temperature profile of microwave curing of a neat resin sample

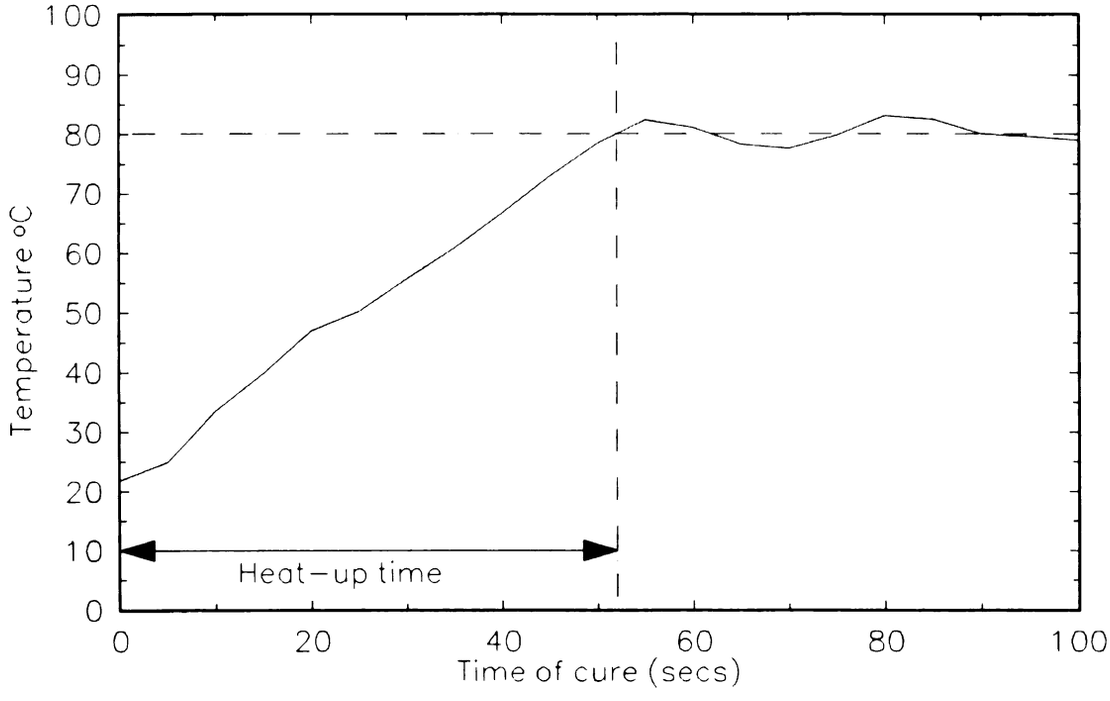

Figure 4.2 Temperature profile during microwave curing (close up)

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4.3 Results and discussion

The extent of reaction vs. time data was used to model the reaction using the same model as that used for the thermal curing. The BPO reaction was modelled separately and it was found that the initiation rate constant k_d was close to the value evaluated for thermal curing. The progression of the BPO dissociation as predicted with this k_d was close to the values predicted using the k_d evaluated for thermal curing. Therefore the k_d evaluated for thermal curing was used as the k_d for microwave curing.

The different model parameters including the effective rate constant k_e, were calculated using a Simplex procedure to minimize the square of the error between the extent of cure predicted by the model and the experimental value at the same time of cure. The initial guess for the procedure was taken to be the parameters estimated for the thermal curing. The model parameters for thermal and microwave curing are given in Table 4.1. The model predictions and the experimental data at three temperatures are illustrated in Figures 4.3, 4.4 and 4.5.

Table 4.1 Comparison of kinetic parameters for thermal and microwave curing

Parameters	Thermal	Microwave
B_t	2.9885	4.367
$B_{t,e}$	0.5068	0.9440
k_e $[L/(mole\text{-}sec)]^{0.5}$	2.051e6 * exp[-6760.4/(T+273)]	3.336e7 * exp[-7818.6/(T+273)]

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The microwave samples were cured individually, in contrast to thermal curing where the samples were cured as a set. Therefore their temperature profiles, along with other experimental factors like heat-up time etc., vary from sample to sample in the same run. Therefore the microwave data are more scattered, than the corresponding thermal data. The model predictions match well with the experimental data at low extent of cure. At high extent of cure, the model under-predicts the conversion. This suggests that the model has limitations when used to predict microwave curing at high extent of cure (possibly, after gelation).

One of the assumptions used in the development of the model is that the reactivities of the vinyl groups in the mono-vinyl monomer and di-vinyl monomer are the same. This might not be valid, resulting in the predicted extent of cure being less than the experimental values. The reason could be that, during microwave curing, the microwaves can preferentially couple with the dipole carbonyl group close to the vinyl group of vinyl ester, resulting in the kinetic energy of the vinyl group in vinyl ester being greater than that of the vinyl group from vinyl toluene. This could also lead to an increase in its reactivity over the corresponding thermal curing values. The reactivities of the vinyl toluene and vinyl ester can be considered to be different to improve the model. A complete quantitative analysis would require further data on the fraction of each monomer reacted at different times, but a qualitative analysis under simplifying assumptions is given in part IV of Appendix-A. The simplifying assumptions are the consideration of the radical reactivity to be independent of the radical chain end-monomer.

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The model can also be refined by introducing more parameters in the model. This can be done by obtaining molecular weight data and separating the propagation rate constant from the effective rate constant as used in this model. More detail on this is available in literature [15, 16, 17]. An adjustable parameter can then be introduced into the propagation reaction based on the expected interaction of microwaves with the resin. However, obtaining molecular weight data could be a problem after gelation takes place. Special techniques have to be investigated for this purpose. The experimental procedure could also be improved by taking the IR spectra while the sample is curing in the cavity. This would eliminate a lot of scatter and also make it possible to collect data at higher temperatures because there would be no quenching of the reaction.

The comparisons of the model predictions using parameters estimated from the microwave and thermal data are shown in Figure 4.6. The model predictions at low extent of cure are almost the same, when predicted using either of these parameters. Therefore the parameters estimated for the thermal curing can be used to predict the conversions at low extent of cure.

Figure 4.3

Figure 4.4

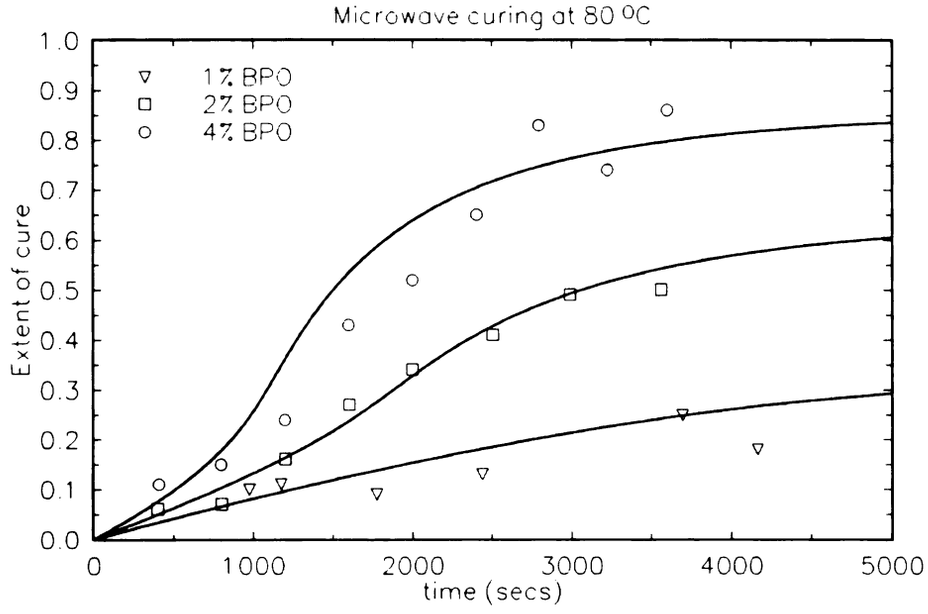


Figure 4.3 Model predictions and experimental data during microwave curing

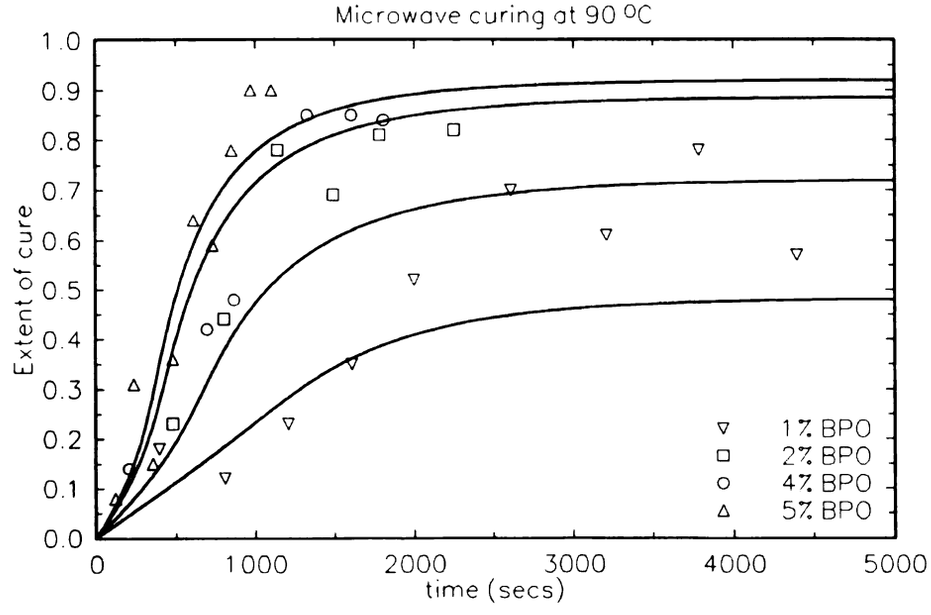


Figure 4.4 Model predictions and experimental data during microwave curing

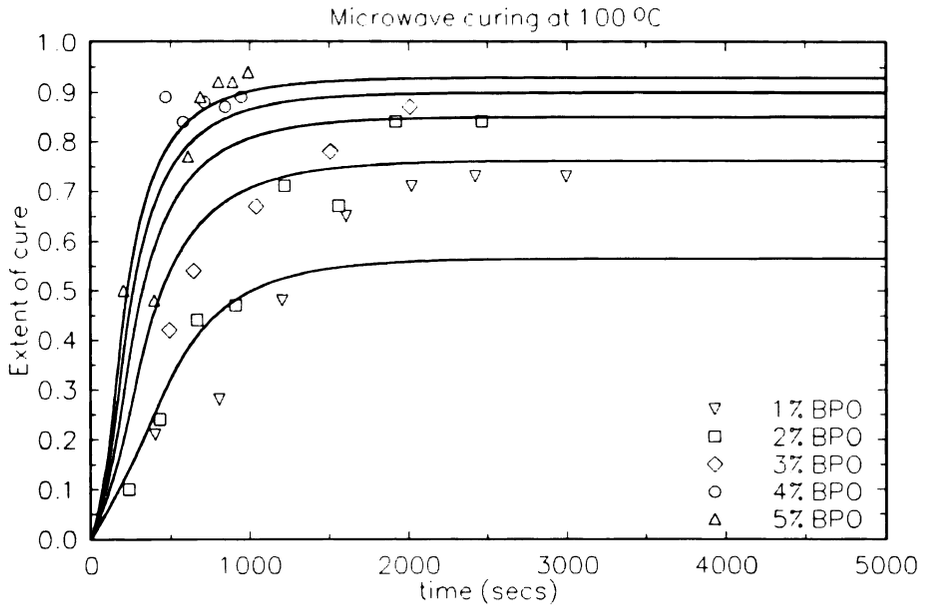


Figure 4.5 Model predictions and experimental data during microwave curing

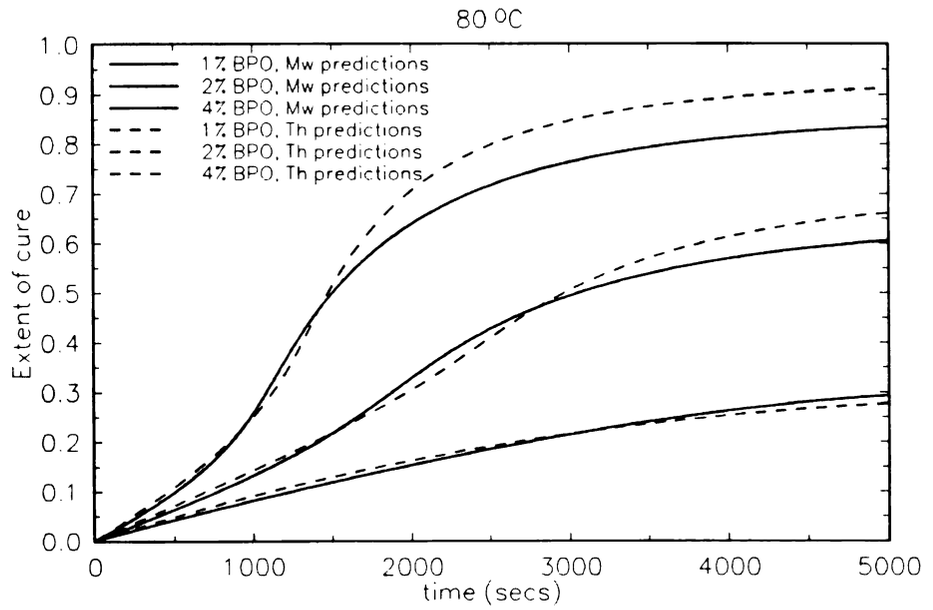


Figure 4.6 Model predictions with microwave and thermal parameters at 80°C

4.4 Summary

The polymerization reaction of a vinyl ester resin during microwave curing was modelled. A thin film technique based on FTIR analysis was used to obtain the extent of cure data. The initiation reaction was modelled separately to obtain the initiation rate constant. It was found that the initiator decomposition rate is the same during both thermal and microwave curing. The propagation rate constant was modelled to be independent of the extent of reaction. The termination rate constant was modelled to fall with reaction until a limiting value is reached. The model parameters for microwave curing were evaluated using a simplex procedure to minimize the error between the experimental and predicted values.

A good agreement between model predictions and experimental data was found at low extent of cure. The model under-predicts the conversion at higher extent of cure. This indicates that the model needs to be refined based on the expected interaction of microwaves and the resin. This could be done by obtaining the propagation constant separately using molecular weight data, and then introducing a parameter based on the effect of microwaves on the propagation reaction. The model predictions at low conversions are close to the model predictions calculated using the parameters estimated with thermal cure kinetics data. Therefore the microwave cure kinetics at low extent of reaction can be modelled using the same parameters and improvements are required to make good predictions at higher extent of cure.

5. THERMAL PROCESSING OF LAMINATES

5.1 Introduction

Consolidation is a very important step in the manufacture of polymer matrix composites. Usually, consolidation is accomplished by the application of mechanical pressure on the composite boundary, accompanied by the application of vacuum and suitably high temperatures. While curing thermosetting matrix composites, pressure and vacuum are maintained at least as long as the gelation time for the resin. This process squeezes air and other sources of voids (including volatiles) out of the composite and also increases the fiber volume fraction.

The present setup of the microwave cavity does not allow the application of pressure during the curing process and this results in large volume fractions of voids in the laminates cured in the microwave cavity. The effect of voids on the mechanical properties of the laminates is more of a statistical nature rather than a deterministic nature. To make a proper comparison of the microwave and thermal curing processes, the void fractions must be very low so that the inherent differences, if any, are not masked by the statistical noise in the mechanical properties of high void fraction composites.

This chapter presents the development of a pre-consolidation technique which can be used to produce low void fraction laminates without the application of pressure during curing. This study was conducted to produce good laminates in a thermal oven under conditions similar to those that can be applied, at present, in the microwave cavity. The

technique was demonstrated by reproducibly producing laminates in the thermal oven with very low void fractions and mechanical properties comparable to autoclave cured laminates. This study also forms a part of the effort to demonstrate that laminates can be manufactured in a microwave cavity with properties equivalent to thermally cured laminates.

5.2 Development of the method

Recent studies have characterized the behavior of laminates during the consolidation process [18-22]. Gutowski [19-22] has shown that the fibers act as elastic springs during the consolidation process, and also that the load carried by the fibers increases with increasing fiber volume fraction.

It was initially attempted to reduce the void content by just subjecting the laminates to mechanical pressure and vacuum prior to the application of temperature for curing the laminate. This method was unsuccessful in reducing the void content of the laminates. This is attributed to the following. The initial application of pressure squeezes out the voids and some resin. The removal of pressure results in the relaxation of fibers to their original state with the surrounding air occupying the volume thus formed. This phenomenon is analogous to the deconsolidation of thermoplastic composites on heating above their melt temperature [19].

Based on the above mentioned aspects, a pre-consolidation technique has been developed, that can be used to produce low void fraction composites. In this method the uncured laminate is enclosed in a resin-rich environment. The enclosure is suitably

prepared to control the flow of resin during pre-consolidation, while allowing the evacuated air (voids) to leave the surroundings of the laminate. Pressure and vacuum are simultaneously applied for specific times during the pre-consolidation. The resin-rich environment ensures that the resin takes most of the load during the initial stage of the pre-consolidation. The accompanying high hydrostatic pressure aids in forcing the voids out of the laminate. The enclosure ensures that during the fiber relaxation process accompanying the release of pressure after pre-consolidation, the resin surrounding the laminate occupies the volume between the fibers. This results in an overall decrease in the void volume fraction.

5.3 Experimental

5.3.1 Preparation of the laminates and laminate molds

Prepreg was made in-house from glass fiber and a vinyl ester resin (containing 45% vinyl toluene by wt. and 1% benzoyl peroxide). It was cut to 3" X 3" pieces and stacked to make twelve-ply, unidirectional laminates. Individual laminates were then placed on nonporous teflon sheets cut to about 9" X 9" in size. Fifteen milliliters of the vinyl ester resin containing 1% benzoyl peroxide as the catalyst was then spread on the laminate to make it resin-rich for pre-consolidation. The nonporous teflon sheet was then folded closely over the laminate and was held in place by tape near the edges of the laminate and running around the laminate. The laminate coupon in this stage of the pre-consolidation is shown in Figure 5.1.

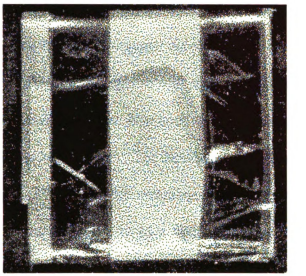


Figure 5.1 Laminate coupon

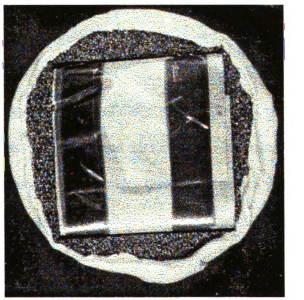


Figure 5.2 Laminate coupon in the teflon mold.

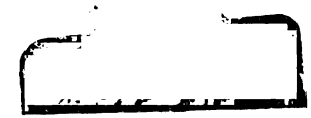
A mold was prepared by covering a circular teflon block (12.6 cm in diameter) with release film. A cork dam was prepared on this to the exact dimensions of the laminate coupon. The cork dam was prepared such that the height of the dam was greater than the height of the laminate coupon. The cork dam was then sealed on the outside with tacky tape (a vacuum bag sealant). The laminate coupon was then placed in this mold as shown in Figure 5.2. The whole assembly was then covered with three layers of bleeder cloth and sealed hermetically in a vacuum bag, with a tube attached for connection to a vacuum pump.

5.3.2 Pre-consolidation cycle

The laminate mold prepared as mentioned above was placed in a Carver press and subjected to a force equivalent to approximately 250 psi. Vacuum was simultaneously applied. At the end of the pre-consolidation period of 10 minutes, the vacuum was released slowly, followed by the release of the force.

5.3.3 Thermal curing

The laminate coupon, pre-consolidated as described above, was cured in a thermal oven at 90°C for 1 hour and post-cured at 125°C for 2 hours. This curing cycle was chosen because there is no exotherm under these conditions and therefore it is easier to control the cure conditions and more importantly study the microwave and thermal curing under similar conditions.



5.3.4 Mechanical testing of cured laminates

The thermal and microwave cured laminates were conditioned at the standard lab conditions of 23°C and 50% relative humidity for over 48 hours. The laminates were cut parallel to the fiber direction into approximately 3" X 0.4" specimens. These specimens were polished to make the top and bottom surfaces flat and parallel and were subjected to a three point bending test in accordance with the ASTM standard D790M. The test data were used to evaluate the flexural strength and the tangent modulus of elasticity in bending of each sample [23].

5.3.5 Void fraction analysis of the laminates

10 x 10 mm sections were cut from each laminate. These were set in acrylic mounts and polished to 0.05 micron grit. These finely polished surfaces were viewed under an optical microscope at a linear magnification of 50. The images observed were digitized and stored into a computer. An image processing program was used to evaluate the fractions of the different degrees of gray scales present in the image [24]. The void volume fraction was calculated based on the degree of gray scales constituting the voids.

5.3.6 Fiber volume fraction analysis

The polished surfaces of the acrylic mounts were treated with a mixture of chromic acid and sulfuric acid to etch the matrix material of the laminate. The surfaces were viewed under an optical microscope at a linear magnification of 400. The unetched glass fibers appear as bright circles in a dark background of the acid-etched matrix of the

laminate. The fiber volume fraction of the laminate was found as before, based on the degree of white scales constituting the glass fibers.

5.4 Results and discussion

Table 5.1 lists the properties of the thermally cured laminates. The pre-consolidation technique developed here has been very successful in reducing the void fractions of the laminates to very low values. The mechanical properties of the thermal cured laminates are comparable to the autoclave cured laminate which further prove the success of the pre-consolidation technique in eliminating most of the voids.

Table 5.1 Properties of thermally cured laminates

Sample #	S (Flex. Strength, MPa)	E_b (Flex. modulus, GPa)	Void fraction (%)	Fiber fraction (%)
Th #1	1066	47.0	0.96	67.6
Th #2	1150	65.9	1.14	63.4
Th #3	1135	68.9	1.88	57.0
Th #4	1036	85.0	5.90	66.6
Th #5	1110	93.5	1.34	53.0

S = Flexural Strength, E_b = Initial Tangent Modulus in Bending

There are certain drawbacks of this method. This method results in laminates that have very poor surface appearance. The laminates made using this method also have higher resin content than the laminates made with the application of pressure during curing. This method however, is useful in giving a common basis for the comparison of the thermal and microwave curing processes.

5.5 Summary

A pre-consolidation method was developed to make very low void fraction laminates without the application of pressure during curing. This method was used to process twelve-ply unidirectional laminates made from glass fiber and vinyl ester/vinyl toluene resin mixture in a thermal oven. The mechanical properties of the thermally cured laminates were evaluated and it was found that the properties were comparable to the properties of autoclave cured sample.

6. MICROWAVE PROCESSING OF LAMINATES

6.1 Introduction

Microwave processing has been investigated as an alternative to the conventional processing of polymers and polymer matrix composites. Different studies have demonstrated its viability and advantages [1, 2, 25-27], but various aspects related to its industrial applicability are still being investigated.

Different resonant modes of the microwave cavity have been found to transfer energy non-uniformly across the volume of the composite. Processing of composites in single modes therefore results in large temperature gradients in the material. Different modes have different energy distribution patterns. Temperature probes can be placed at different positions on the sample to measure the temperatures as the material is heated in different single modes. From a knowledge of such single mode heating patterns, it is possible to switch between appropriate modes to reduce the temperature gradients and obtain relatively uniform temperature profiles in the material being processed. Automation of such processing using knowledge based control systems is presently being investigated [28].

In this chapter, the results of the study of two aspects related to the industrial applicability of this process are presented. A qualitative evaluation was done to determine the reproducibility of heating patterns of these laminates in different resonant modes of a cylindrical microwave cavity under the following conditions: (1) the same sample is

heated in slightly different orientations in the cavity and (2) different samples prepared to similar physical and chemical specifications are heated in the cavity.

Another evaluation was done to compare the mechanical properties of microwave and thermally cured laminates subjected to flexural load. The samples were processed using similar cure cycles. The microwave samples were cured using a mode-switching technique and the thermal samples were cured in a temperature controlled oven. A pre-consolidation technique was used, that allows the production of very low void fraction composites in the cavity without the application of pressure during the curing process. These studies are necessary to determine the amenability of microwave processing to automation and its suitability for industrial production of composites.

6.2 Experimental

The laminates were prepared and pre-consolidated as described in the previous chapter. The pre-consolidated laminate, along with the mold, was placed in a 7" microwave cavity. The microwave processing circuit has been described elsewhere [3]. The position of the temperature probes on the laminate and the position of the sample in the cavity are shown in Figures 6.1 and 6.2. The different resonant modes available were found using a sweep oscillator. The heating patterns for each mode were determined by heating the laminate to about 65°C at 60 Watts of microwave power input to the cavity. A mode-switching technique was used to heat the laminate as uniformly as possible during curing [29]. The curing cycle was the same as that of the thermal cured samples.

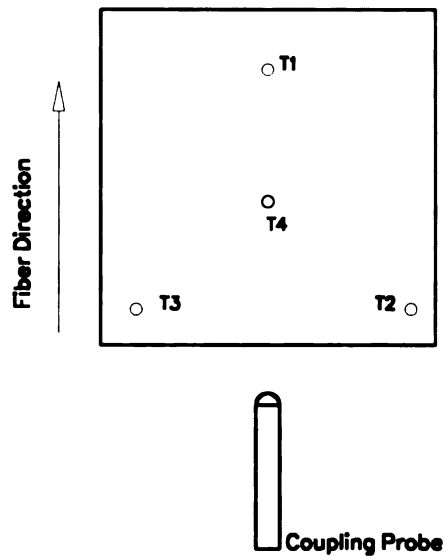


Figure 6.1 Position of temperature probes on the sample

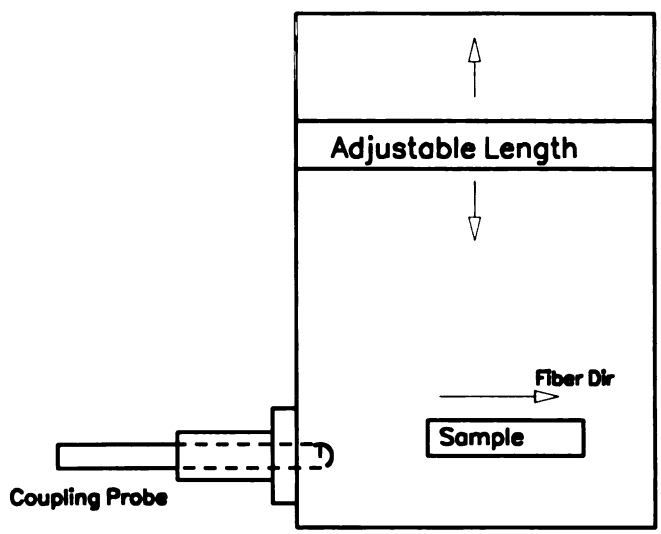


Figure 6.2 Position of the sample in the cavity

The cured laminates were conditioned and tested for their mechanical properties as described in the previous chapter. The void fractions and the fiber volume fractions were also evaluated as described in the previous chapter.

6.3 Results and discussion

Figures 6.3 and 6.4 illustrate the heating patterns of the same sample in two slightly different orientations (fiber orientations within 5° of the coupling probe) in the same resonant mode. The heating patterns are very similar, indicating that the cavity is not very sensitive to small variations in the orientation of the sample in the cavity. Figures 6.5 and 6.6 show the heating patterns in the same mode of two different samples. The heating patterns obtained were very different from each other, as illustrated by these plots. This is attributed to the manual lay-up of the molds which results in significant differences in the amount and shape of the accompanying material used for each mold. These differences give rise to very different heating patterns. Further experiments are needed to establish the sensitivity of the cavity to small differences in the physical specifications of the material being processed in the cavity. Finding the heating patterns of the laminates without any mold lay-up would be a good beginning.

Table 6.1 lists the properties of the microwave cured laminates and compares them to thermally cured laminates. The low void fractions achieved using the pre-consolidation technique demonstrate the success of the method. The mechanical properties of both the thermal and microwave cured laminates are equivalent, which

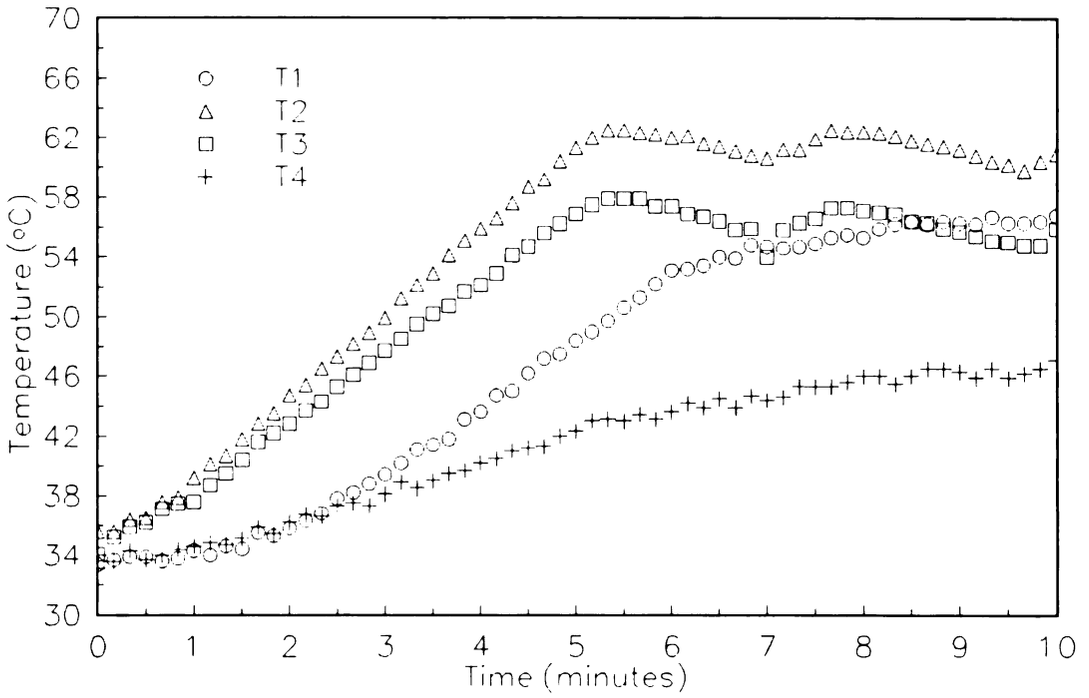


Figure 6.3 Single mode heating pattern of sample RP1244 in one orientation

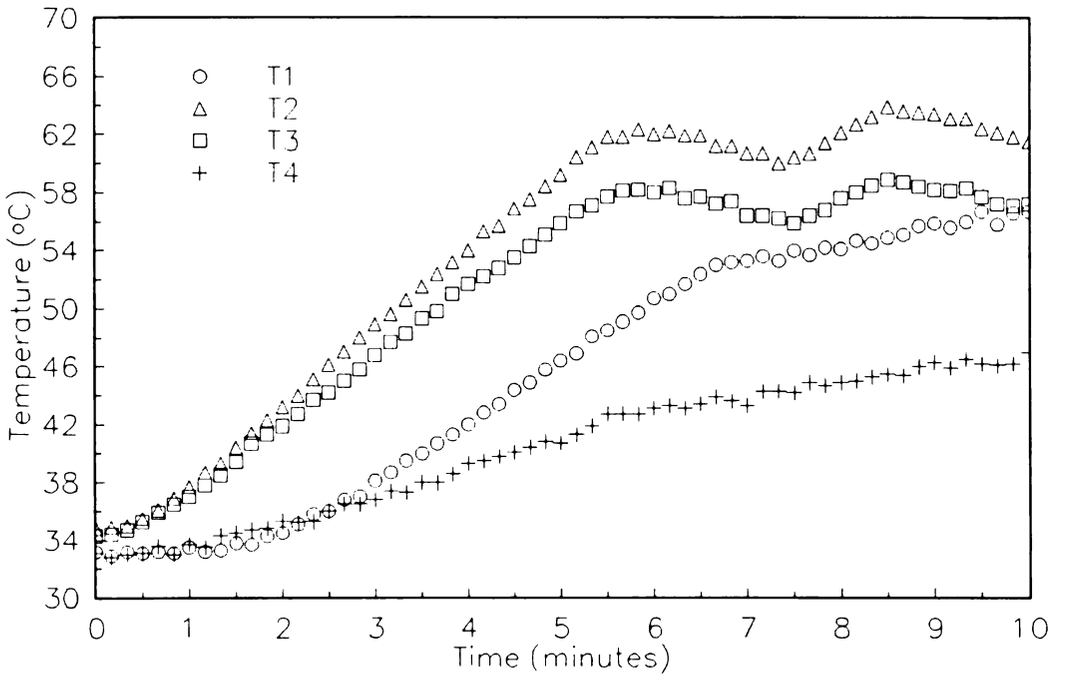


Figure 6.4 Single mode heating pattern of sample RP1244 in different orientation

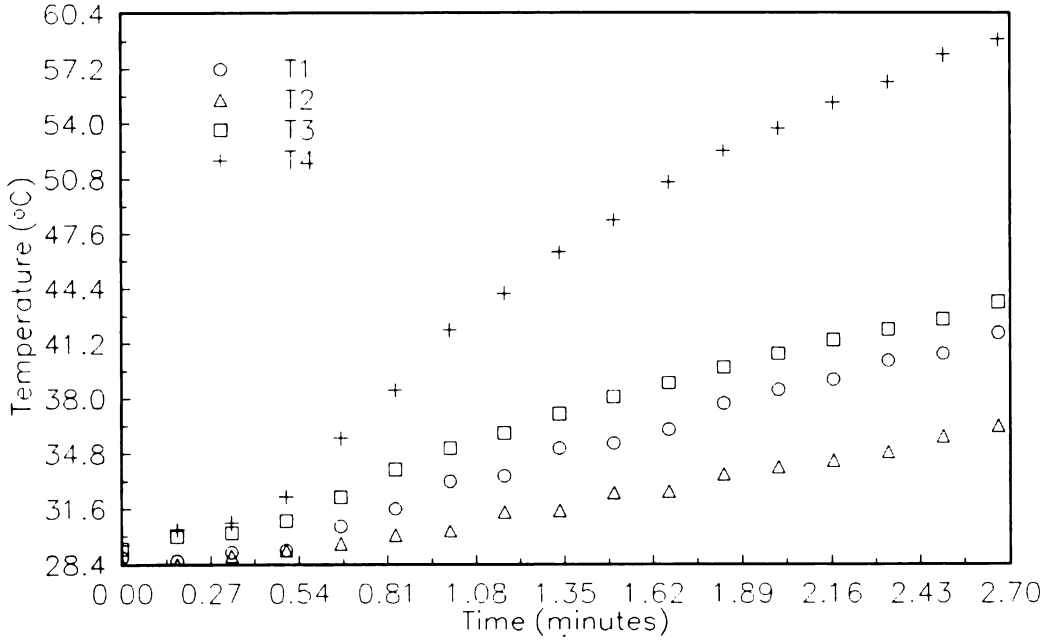


Figure 6.5 Single mode heating pattern of sample MwB7

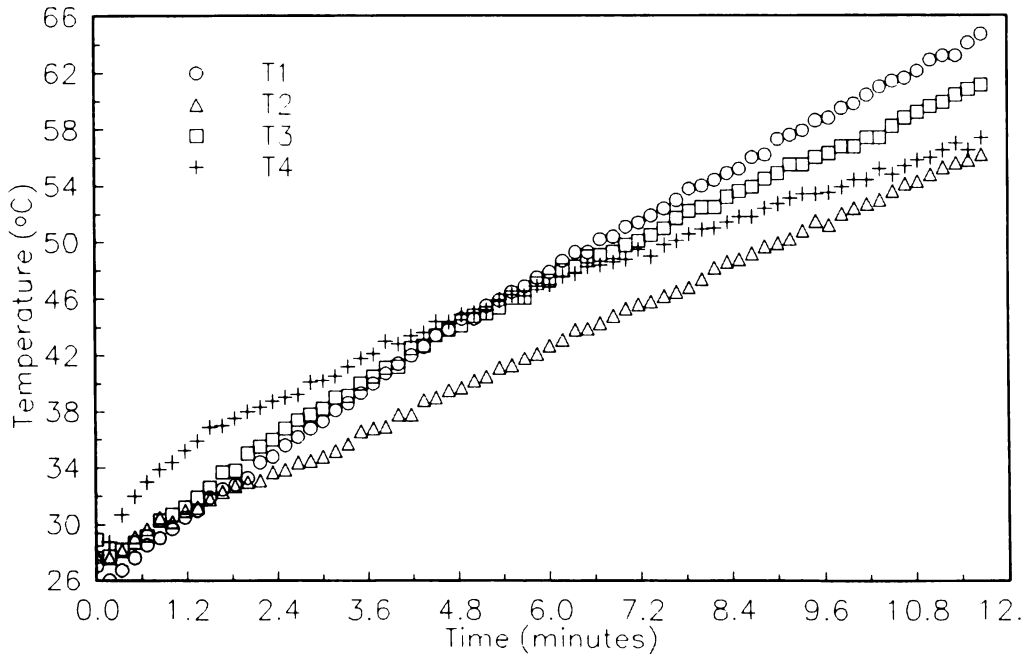


Figure 6.6 Single mode heating pattern of sample MwB8

demonstrates conclusively that microwave curing can be used to produce laminates with properties equivalent to a thermally cured laminate. Modification of the microwave cavity to apply pressure during curing is however necessary because the lack of pressure during curing results in a poor finish. The pre-consolidation technique has however, helped establish that microwave processing is inherently capable of producing laminates with very good mechanical properties. The greater variation in the flexural modulus values is possibly due to the differences in the curing between samples and also the differences in the fiber and void volume fractions. Figures 6.7 and 6.8 illustrate the comparison of the average mechanical properties of microwave and thermally cured laminates with the mechanical properties of the autoclave sample.

Table 6.1 Properties of microwave and thermally cured laminates

Sample #	S (Flex. Strength, MPa)	E_b (Flex. modulus, GPa)	Void fraction (%)	Fiber fraction (%)
Th #1	1066	47.0	0.96	67.6
Th #2	1150	65.9	1.14	63.4
Th #3	1135	68.9	1.88	57.0
Th #4	1036	85.0	5.90	66.6
Th #5	1110	93.5	1.34	53.0
Mw #1	1060	52.2	0.9	65.8
Mw #2	1082	70.9	2.81	54.0
Mw #3	1158	84.0	0.46	58.9
Mw #4	1255	94.3	0.11	59.3
Mw #5	1170	107.2	0.41	63.9

S = Flexural Strength, E_b = Initial Tangent Modulus in Bending

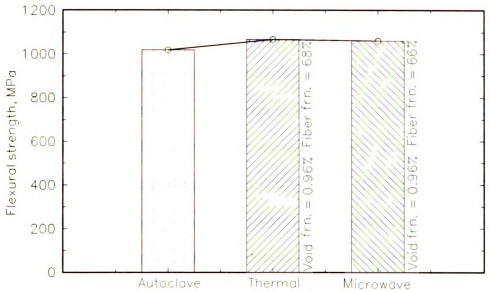


Figure 6.7 Comparison of flexural strength of Autoclave, Oven and Microwave cured laminates

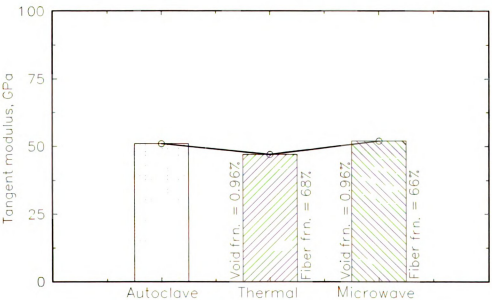


Figure 6.8 Comparison of Tangent modulus of Autoclave, Oven and Microwave cured laminates

6.4 Summary

Twelve-ply unidirectional laminates were made from glass fiber and vinyl ester/vinyl toluene resin mixture. The heating patterns for these laminates in individual resonant modes were evaluated. It was found that the microwave cavity is not very sensitive to small variations in the orientation of the same sample in the cavity. The heating patterns in the different individual modes were also evaluated for different samples prepared as similarly as possible in their physical and chemical specification. Large differences were found in the heating patterns between these samples. This is due to the manual lay-up of the mold, which introduces significant differences in the amount of material used for the mold and the physical specifications of the mold. Further experiments are necessary to evaluate the sensitivity of the cavity to small and controlled changes in the physical specifications of the sample and the mold. A pre-consolidation method, to make very low void fraction laminates without the application of pressure during curing, was used to process laminates in a microwave cavity using mode-switching. The mechanical properties of the microwave cured laminates were compared with those of the thermal cured laminates. It was shown that vinyl ester/ glass fiber laminates can be cured in a microwave cavity with properties equivalent to those of thermally cured laminates.

7. GLASS TRANSITION TEMPERATURE DATA

7.1 Experimental method

The Glass Transition Temperatures (Tg) were determined using TMA for different samples cured in the thermal oven and microwave cavity for different extents of cure . A small section of the sample used to study the cure kinetics was used to measure the Tg at different extents of cure. The section was obtained by cutting the sample used for kinetic study into four parts. A load of 1 gram was placed on the specimens and a heating rate of 10°C per minute was used. At low extents of cure, liquid nitrogen was used to cool the specimens to below -125°C before the heating was started. This method was followed because at low extent of cure the Tg is close to zero and therefore there needs to be sufficient time for the system to stabilize to a constant heating rate of 10°C per minute. The Tg was measured as the point of slope change in the graph of dimension change vs. temperature. If the slope change was gradual instead of being sharp, then the Tg value was taken to be the intersecting point of the linear portions of the graph.

7.2 Results

The Tg values for the microwave and thermal cured samples are given in Table 7.1 and are illustrated in Figure 7.1.

Table 7.1 Tg of thermal and microwave cured samples

Thermal Samples		Microwave samples	
Extent of cure	Tg (°C)	Extent of cure	Tg (°C)
0.00	7	0.00	7
0.02	6	0.08	22
0.10	-13	0.13	25
0.20	-12	0.20	12
0.26	17	0.23	33
0.36	45	0.36	28
0.41	38	0.37	44
0.48	37	0.42	50
0.60	58	0.58	40
0.72	120	0.83	104
0.81	119	0.90	141
0.90	117		
0.93	143		
1.00	180		

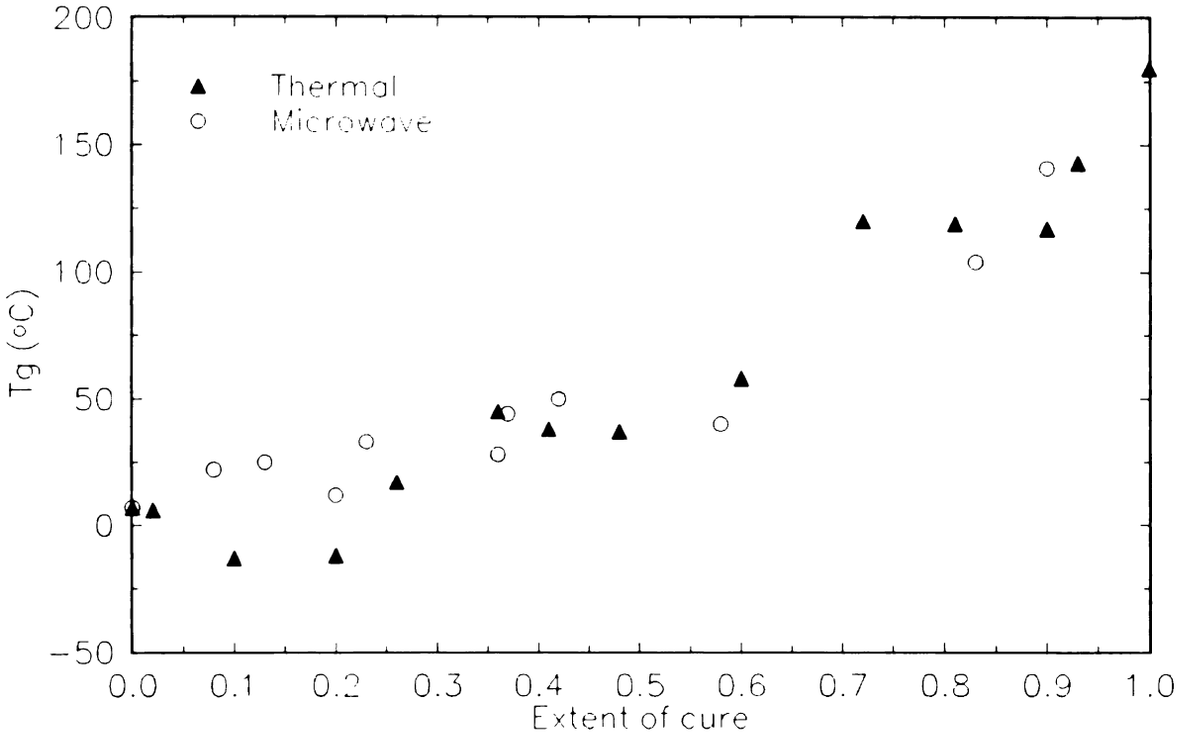


Figure 7-1 Tg vs Extent of cure of thermal and microwave cured samples

8. CONCLUSIONS

8.1 Summary of results

Studies have been conducted to enhance the understanding of the interaction of microwaves with polymer resins. A vinyl ester resin with vinyl toluene as the crosslinking monomer was used to study the differences between thermal and microwave polymerization. Benzoyl peroxide was used as the initiator for the polymerization reaction. Composite processing studies were also conducted to demonstrate the applicability of microwave curing to the industrial production of polymer matrix composites.

A method has been developed which can be used to identify the regions of single component absorption in an IR spectra of a mixture of two chemical species with different densities. The applicability of the method has been demonstrated with the spectra of a mixture of a vinyl ester resin and vinyl toluene. Based on this method, an experimental protocol was developed for the kinetic analysis of the vinyl ester resin.

The polymerization reaction of a vinyl ester resin during thermal curing and microwave curing was modelled. The initiation reaction was modelled separately using a first order rate expression. The Benzoyl peroxide reaction peak was monitored to obtain the conversion of the initiator with time. The initiation rate constant k_d was obtained on a regression of this data. The initiation rate constant was evaluated for both microwave and thermal curing and was found to be the same. The Benzoyl peroxide decomposition rate constants for different solutions are reported in literature [30]. The decomposition

rate constants at the same temperature vary a lot between solutions. There are also different values reported by different sources, for the same solutions at the same temperature. The decomposition rate constants for the current mixture were evaluated for different temperatures and were found to be comparable to the range of values found in literature [30].

The propagation rate constant was modelled to be independent of the extent of reaction. The termination rate constant was considered to fall with the extent of cure until a limiting value is reached. The limiting value is directly proportional to the propagation rate constant. The model parameters were evaluated, for both the thermal and microwave curing, using a simplex algorithm to minimize the sum of the squares of the error between the model predictions and the experimental values. A good agreement was observed between the model predictions and the experimental data generated at different temperatures and initiator concentrations during thermal curing. During microwave curing, the model predictions were accurate at low extent of cure but under-predict the conversion at high extent of cure. The difference could be the coupling of microwaves to one of the vinyl groups, thereby increasing its reactivity over the corresponding thermal case. The increase would result in a corresponding increase in the total extent of cure as measured here. This is shown in part IV of Appendix-A.

A pre-consolidation method was developed to make very low void fraction laminates without the application of pressure during curing. This method was used to process twelve-ply unidirectional laminates, made from glass fiber and vinyl ester/vinyl toluene resin mixture, in a thermal oven. The mechanical properties of the thermally

cured laminates were evaluated and it was found that the properties were comparable to the properties of the autoclave cured sample. The autoclave cured sample was processed under similar temperature cycles but with the simultaneous application of pressure and vacuum during the curing process.

Twelve-ply unidirectional laminates were prepared from glass fiber and vinyl ester/vinyl toluene resin mixture. The heating patterns for these laminates in individual resonant modes were evaluated. It was found that the microwave cavity is not very sensitive to small variations in the orientation of the same sample in the cavity. The heating patterns in the different individual modes were also evaluated for different samples prepared as similarly as possible in their physical and chemical specification. Large differences were found in the heating patterns between these samples. This is due to the manual lay-up of the mold, which introduces significant differences in the amount of material used for the mold and the physical specifications of the mold.

A pre-consolidation method, to make very low void fraction laminates without the application of pressure during curing, was used to process laminates in a microwave cavity using mode-switching. The mechanical properties of the microwave cured laminates were compared with those of the thermally cured laminates. Laminates were reproducibly produced in the microwave cavity with mechanical properties equivalent to the thermal and autoclave cured samples. Coupled with the advantages of faster and more controllable heating, this demonstrates that microwave processing is a viable and attractive alternative to the conventional thermal processing of polymer matrix composites.

8.2 Scope for future work

Various possibilities exist for further studies in the area of microwave processing. A broad range of issues have to be studied to obtain a comprehensive knowledge of the microwave processing aspects before the application can be used on a large scale in the industry. Some of the important issues are listed below.

The model can be refined by obtaining the molecular weight data and separating the propagation rate constant from the effective rate constant. A parameter can then be added to the propagation rate constant to reflect the possible interaction between the resin and microwaves. Molecular weight distribution is difficult to determine and special techniques have to be utilized for this purpose. The experimental procedure for microwave curing can be modified to obtain spectra while the sample is curing in the cavity. This would greatly reduce the experimental error involved in the measurement of the time of cure and therefore improve the results. Fiber optics may be used to optically connect the sample to the spectrophotometer.

The model can be also improved by considering the vinyl ester and vinyl toluene to have different reactivities [5]. This would require the ability to obtain the change in concentrations of each component in the reacting system. NMR can be used for this purpose. An analysis of such a consideration is given in Part IV of Appendix-A. Different model monovinyl compounds (such as styrene) and their homopolymerization rate constants obtained from literature can be used instead of vinyl toluene. The transient reaction can also be monitored which can give the ratio of k_p to k_t using the rotating sector method.

Studying the mechanical properties of laminates of non-planar shapes will give an insight into the amenability of microwave processing of products of industrial value. Such a study is also likely to generate a database of information on the heating patterns during the curing of different shaped materials. This database can later be used to model the behavior of complex shaped materials in the cavity.

Application of pressure and vacuum are vital in the processing of polymer matrix composites, to eliminate a lot of voids and give a proper finish to the products. Presently the microwave curing processes suffer from the inability to apply pressure during the curing process. This could mean the loss of otherwise easily achievable and desirable properties. Future work can be directed towards achieving this goal in a systematic and phased manner.

Automation using computers will greatly enhance the quality of the product obtained through microwave processing. Algorithms can be developed that utilize a database and appropriately control the cavity to produce composites efficiently and also incorporate versatility, to cure different kinds of materials, into the system.

APPENDICES

Appendix A: Derivation of kinetic equations

Part I Derivation of equation considering equal reactivity for the vinyl groups

The derivation of equation (3.1) from first principles is presented below. Some of the nomenclature is in common with chapter 3.

Chain polymerization occurs in three stages. During the *initiation* stage an "active" center is formed that initiates the chain polymerization. *Propagation* is the addition of more monomer to the growing chain end. *Termination* is the disappearance of "active" centers. The schematic notation for these stages is given in Figure 1.4. The kinetic model based on this mechanism assumes the following.

1. The reactivity of all the intermediate free radicals is the same. Therefore all the free radicals formed can be considered as one chemical constituent for kinetics purpose. They can be represented by [R.].
2. The reaction proceeds slowly enough that a steady state is reached, where the radical population does not change rapidly with time. Therefore we have

$$\frac{d[R.]}{dt} = 0 \qquad \text{(A-1)}$$

Hence, a material balance on the components gives the following equation:

$$2\, k_d\, [I] - k_t\, [R.]^2 = \frac{d\,\{[R.]\}}{dt} = 0 \qquad \text{(A-2)}$$

3. Therefore from equation (A-2) we get

$$[R.] = \sqrt{\frac{2\ k_d\ [I]}{k_t}} \qquad \textbf{(A-3)}$$

4. The reaction is considered to be based on the disappearance of the monomer molecules. The propagation reaction occurs so much more often than the others that it is effectively the only consumer of the monomer. The rate of polymerization therefore becomes:

$$\textit{Rate of polymerization} = R_p = k_p[R.]\ [M] \qquad \textbf{(A-4)}$$

5. The design equation for the variable volume reactor is

$$R_p = -\frac{1}{V}\frac{d\ \{V.[M]\}}{dt} \qquad \textbf{(A-5)}$$

6. Combining equations (A-4) and (A-5), we get

$$-\frac{d\ \{V.[M]\}}{dt} = k_p[R.]\ (V\ .\ [M]) \qquad \textbf{(A-6)}$$

7. The conversion of the monomer is defined as

$$X = \frac{V_0\ .\ [M]_0\ -\ V\ .\ [M]}{V_0\ .\ [M]_0} \qquad \textbf{(A-7)}$$

from which we get

$$V\ .\ [M] = V_0.[M]_0\ \ (1\ -\ X) \qquad \textbf{(A-8)}$$

8. Substituting equation (A-8) in equation (A-6), we get

$$- V_0.[M]_0 \frac{d\{(1 - X)\}}{dt} = k_p[R.]\{V_0.[M]_0 (1 - X)\} \quad \textbf{(A-9)}$$

Therefore

$$\frac{dX}{dt} = k_p [R.] (1 - X) \quad \textbf{(A-10)}$$

9. Substituting equation (A-3) in (A-10) we get

$$\frac{dX}{dt} = k_p \sqrt{\frac{2 k_d [I]}{k_t}} (1 - X) \quad \textbf{(A-11)}$$

10. If only a certain fraction 'f' of the initiator fragments can successfully react then the concentration of the initiator should be multiplied by 'f'.

$$\frac{dX}{dt} = k_p \sqrt{\frac{2 f k_d [I]}{k_t}} (1 - X) \quad \textbf{(A-12)}$$

Part II Decomposition of Benzoyl peroxide

The derivation of Equation (3.2) from first principles is presented below.

$$[I] = \frac{[I]_0}{\left(1 - \frac{d_m}{d_p} sX\right)} \exp(-k_d\, t) \qquad \textbf{(3.2)}$$

1. The design equation for the conversion of the initiator is

$$R_i = - \frac{1}{V} \frac{d\,\{V.[I]\}}{dt} \qquad \textbf{(A-13)}$$

2. The first order rate expression for the decomposition of the initiator is

$$R_i = k_d \,.\, [I] \qquad \textbf{(A-14)}$$

3. Combining equations (A-13) and (A-14) and integrating, we get

$$\int_{\{V_0.[I_0]\}}^{\{V.[I]\}} \frac{d\{V.[I]\}}{\{V.I\}} = \int_0^t - k_d \,.\, dt \qquad \textbf{(A-15)}$$

Therefore

$$V.[I] = V_0.[I_0] \exp(-k_d\, t) \qquad \textbf{(A-16)}$$

4. The total volume 'V' of the polymerizing mixture is the sum of the volume of the unreacted monomer and the volume of the polymer formed

$$V = V_m + V_p \qquad \text{(A-17)}$$

5. The total number of moles of monomer left in the polymerizing mixture after a conversion 'X' is

$$V_0.[M_0]\ (1 - X) \qquad \text{(A-18)}$$

where $[M_0]$ is the monomer concentration and V_0 is the volume, both at zero conversion.

6. Therefore the volume of the monomer in the polymerizing mixture is given by

$$V_m = V_0.\ (1 - X) \qquad \text{(A-19)}$$

7. The weight of polymer formed is equal to the weight of monomer reacted

$$(\textit{mol. of monomer reacted})(\textit{mol. wt. of monomer}) = M_0.V_0.X\ .M_w \qquad \text{(A-20)}$$

where M_w is the monomer molecular weight.

8. Volume of polymer formed is then given by

$$V_p = V_0\ .\ X\ .\left(\frac{M_0.M_w}{d_p}\right) \qquad \text{(A-21)}$$

where d_p is the polymer density.

9. Substituting equations (A-19) and (A-21) in equation (A-17) gives

$$V = V_0(1 - X) + V_0.X\left(\frac{M_0.M_w}{d_p}\right) \qquad \textbf{(A-22)}$$

$$V = V_0\left(1 - \frac{d_m}{d_p}\, sX\right) \qquad \textbf{(A-23)}$$

where (M_0M_w) is the monomer density and s is given by equation (3.3). Substituting equation (A-23) in (A-16), we get

$$[I] = \frac{[I]_0}{\left(1 - \frac{d_m}{d_p}\, sX\right)} \exp(-k_d\, t) \qquad \textbf{(A-24)}$$

Part III Comparison with Poehlein's model

The following section gives the differences between the model used by Poehlein [14] and the model used in this work. These simplifications were used because, in their case the propagation rate constant was available a priori and also because it was felt that the error involved in the experiments was high enough that the fine differences in the predictions as made by their model are masked anyway. The rate constant $k_{t,p}$ in their case was correlated to jump length and jump frequency as follows:

$$k_{t,p} = \left\{ \pi \, j_c^{0.5} \, a^3 \, N_{AV} \, k_p \frac{([m] + [d])}{1500} \right\} \ln \left\{ \frac{\left(\frac{150}{\pi \, j_c \, a^2 N_{AV}^{2/3}} \right)^{3/2}}{[R*]} \right\}$$

where j_c is the average number of monomer units in a dangling chain, a is the average root-mean-square end-to-end distance per square root of the number of monomer units in the dangling chain, N_{AV} is the Avogadro's constant, [m] is the concentration of the monovinyl monomer, [d] is the concentration of unreacted vinyl group in the divinyl monomer, and $[R^*]$ is the concentration of the free radicals.

The propagation rate constant was considered to vary as follows

$$\frac{1}{k_p} = \frac{1}{k_{p0}} + \frac{1}{k_{pvf}}$$

where k_{p0} is chemical reaction controlled propagation rate constant and k_{pvf} is the translational diffusion controlled propagation rate constant. k_{pvf} was described by the following equation.

$$k_{pvf} = \left(\frac{N_{AV}}{1000}\right) 4\pi \left\{ \frac{[m]_0}{([m]_0 + [d]_0)} + \frac{[d]_0}{([m]_0 + [d]_0)} (1 - X)^2 \right\} D_{AB} R_{AB}$$

where $[m]_0$ and $[d]_0$ are the vinyl group concentrations of the monovinyl and divinyl monomers at zero conversion, respectively. D_{AB} is the mutual diffusivity and R_{AB} is the collision radius for the encounter between spheres A and B.

The propagation reaction involves the reaction between a macroradical and monomer molecule. Since the mobility of a macroradical is much smaller than that of a monovinyl or divinyl monomer molecule, D_{AB} was represented as the average diffusion coefficient for the monovinyl and divinyl monomers. The free volume concept was used to correlate change in D_{AB} with conversion as given below.

$$D_{AB} = D_{AB0} \exp\left(B_p \left[\frac{1}{v_{f0}} - \frac{1}{v_f} \right] \right)$$

where D_{AB0} is the mutual diffusivity at zero conversion and B_p is an adjustable parameter. V_{f0} and V_f are the fractional free volumes of the reaction mixture at zero conversion and conversion X, respectively.

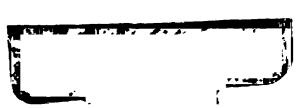
Part IV Consideration of unequal reactivities for the vinyl groups

The following section considers the analysis based on considering the reactivities of vinyl ester and vinyl toluene as different. This analysis is provided to show that the consideration of different reactivities for the vinyl groups from both the vinyl ester and vinyl toluene could possibly explain the higher extents of cure observed in the microwave case compared to the model predictions. The analysis in this case involves more kinetic constants than the case where the reactivities are assumed to be same. Therefore proper quantitative analysis would require the information on the fraction of each component reacted at different times. Therefore some simplifying assumptions have been made to illustrate the possibility that this form of analysis could better explain the data. The equations have been derived based on the mechanism shown in Figure 1.4. The assumptions still remain the same as those used in part I.

The net change in concentrations of the vinyl groups is measured by the disappearance of the monomers M1 and M2.

$$-\frac{d[M1]}{dt} = k_{11}\,[M1][R1.] + k_{21}\,[M1][R2.] \qquad \textbf{(A-25)}$$

$$-\frac{d[M2]}{dt} = k_{12}\,[M2][R1.] + k_{22}\,[M2][R2.]$$



We can assume that the reactivity for a free radical is independent of the end group in the radical, but is dependant only on the monomer with which it reacts. Therefore we have the following relations

$$k_{11} = k_{21} = k_1$$

$$k_{22} = k_{12} = k_2 \qquad \textbf{(A-26)}$$

Since we are assuming that the radical reactivity is independent of the end group, we can substitute **[R.]** in place of **[R1.]** and **[R2.]**. Substituting this and equation (A-26) in equation (A-25) we get the following

$$-\frac{d[M1]}{dt} = 2\, k_1\, [M1][R.]$$

$$-\frac{d[M2]}{dt} = 2\, k_2\, [M2][R.] \qquad \textbf{(A-27)}$$

Since the total radical concentration is assumed constant, equation (A-3) can be used to substitute for **[R.]**. If we include the effect of the volume change, the equations become very difficult to integrate because of the dependance of **[I]** on the volume change. If we neglect the volume change, the concentration of **[I]** is given as follows:

$$[I] = [I]_0 \exp(-k_d\, t) \qquad \textbf{(A-28)}$$

Substituting equations (A-3) and (A-28) in (A-27) we get the following equation for monomer **M1**:

$$-\frac{d[M1]}{dt} = 2\,k_1\,[M1]\sqrt{\frac{2\,k_d\,[I]_0\,\exp(-k_d\,t)}{k_t}} \qquad \textbf{(A-29)}$$

This can be rearranged as:

$$-\frac{d[M1]}{[M1]} = 2\,k_1\sqrt{\frac{2\,k_d\,[I]_0}{k_t}}\,\exp\left(\frac{-k_d\,t}{2}\right)dt \qquad \textbf{(A-30)}$$

We will have a similar equation for **[M2]**. The equations can now be integrated to give the change in the individual concentrations with time. The addition of the integrated equations gives the change in the total vinyl concentration with time which can be related to the extent of reaction data that has been acquired here. Now if one of the rate constants is higher than the corresponding value in the thermal case because of the interaction of the microwaves with that vinyl compound, then the net rate of reaction as measured in this work would be higher and this could therefore explain the microwave data where the current model under-predicts the conversion.

Appendix B: OBEY programs

Given below are the OBEY Programs written for the idris operating system running on the PERKIN-ELMER model 1800 Fourier Transform Infrared Spectrophotometer. The programs can be used for similar future work without any modifications. The lines that begin with a "*" are the comment statements for the programs and do not affect the running of the programs.

```
*************************************************************************
*                                  RamKBr1.oy                           *
*************************************************************************
gclear
do sclear
* This obey program was used to scan the spectra of the plain KBr disks
*
* Enter a file name to save into ( File will be saved into drive f0: )
&enter a1
scan x 4 4000 450 1.00
do display off
&def a2 = clk
&def a3 = date
&def a5 = "1992"
ident x &a3
&def a4 = ident x 1 7
ident x Plain KBr disks for correction. &a4&a5, &a2 (24 hr clock)
do display on
save x /usr/user/Dhulipal/Spectra/&a1
save x f0:&a1
```

```
*************************************************************************
*                                RamBcure1.oy                           *
*************************************************************************
gclear
do sclear
* Enter a file name to save into ( File will be saved in drive f0: )
*
*
&def a1 = ""
&enter a1
scan x 4 4000 450 1.00
do display off
&def a2 = ""
&def a3 = ""
&def a4 = ""
&def a5 = ""
&def a2 = clk
&def a3 = date
&def a5 = "1992"
ident x &a3
&def a4 = ident x 1 7
ident x &a1
&def a8 = ""
&def a8 = ident x 1 2
ident x &a8 samples before cure &a4&a5, &a2 (24 hr clock)
do display on
save x /usr/user/Dhulipal/Spectra/&a1
save x f0:&a1

*************************************************************************
*                                RamAcure1.oy                           *
*************************************************************************
gclear
do sclear
* This FTIR obey program was used to scan the spectra of samples after cure
*
* Enter a file name to save into. (File will be saved in drive f0:)
&def a1 = ""
&enter a1
*
*Enter the time of cure in mins. If seconds exist enter after decimal point.
* e.g : 10 min and 45 secs should be entered as 10.45
*If no secs exist enter .0 after the time in mins
* e.g : 10 mins as 10.0
```

```
*
*
&def a9 = ""
&enter a9
*
*Enter the BPO concentration in wt% used
&def a10 = ""
&enter a10
*
* Enter the Temperature of curing in deg C
&def a11 = ""
&enter a11
scan x 4 4000 450 1.00
do display off
&def a2 = ""
&def a3 = ""
&def a4 = ""
&def a5 = ""
&def a2 = clk
&def a3 = date
&def a5 = "1992"
ident x &a3
&def a4 = ident x 1 7
ident x &a1
&def a8 = ""
&def a8 = ident x 1 2
ident x T=&a11C,BPO=&a10%,&a9 min &a8 cure(num aft pt is sec)&a4&a5,@ &a2
do display on
save x /usr/user/Dhulipal/Spectra/&a1
do display on
save x f0:&a1

*****************************************************************************
*                                    Proc2.oy                                 *
*****************************************************************************
gclear
do sclear
* THIS PROGRAM WAS WRITTEN BY DHULIPALA RAMAKRISHNA ON 10 July
1992
* WHILE DOING HIS MASTERS PROGRAM IN CHEMICAL ENGINEERING
*
*
* This program takes a series of spectra and then subtracts these from a series
* of other spectra ; The subtraction being done in the absorbance mode
```

```
* Then it shifts the resultant spectra to bring the least absorbance value to
* zero value. It then converts the spectra into transmittance mode and saves
* it as another series. This can be used to subtract the spectra of plain
* KBr disks from the fresh and cured sample spectra.
*
* The series is assumed to be of the form BB(A1-A2)CC
* Where              BB is the string in the name before the numeric series
*                    CC is the string in the name after  the numeric series
*                    A1 is the beginning number of the series and
*                    A2 is the ending number of the series.
*
* You can stop the program anytime by pressing the break key.
* THIS PROGRAM TAKES ONLY THE RANGE 4000 - 450 WAVE NUMBER OF
THE SPECTRA
* Press enter when ready
&enter a1
do sclear
* The input spectra files are to be placed in the directory
*          /usr/user/Dhulipal/Spectra
*
*
* NOTE CAREFULLY
* WARNING! WARNING! WARNING! WARNING! WARNING! WARNING!
*************************************************************************
*
* THESE INPUT FILES WILL AUTOMATICALLY BE DELETED AFTER
* THE PROCESSING IF YOU WISH TO,  PRESS y if you want this to happen
*
*
*
* Enter (y/n)
&enter a7
do sclear
&def a3 = ""
&def a12= ""
&def a14= ""
&def a16= ""
* do you want the numeric series (1-9) to be of the form (01-09) enter (y/n)
&enter a2
&if a2 = "n" then L90 *
&def a3 ="0"
do display off
&L90 do display on
*
```

```
* Enter the beginning value of the numeric series
&enter a5
*
* Enter the end value of the numeric series
&enter a6
* calc v1 = &a5
* calc v2 = &a6
do sclear
* For the Spectra to be subtracted
* Enter the general name of the files before the numeric series
&enter a11
*
* Enter the general name of the files after the numeric series
&enter a12
do sclear
* For the spectra from which to subtract
* Enter the general name of the files before the numeric series
&enter a13
*
* Enter the general name of the files after the numeric series
&enter a14
do sclear
* For the resulting spectra to be stored
* Enter the general name of the files before the numeric series
&enter a15
*
* Enter the general name of the files after the numeric series
&enter a16
do sclear
&for v3 = a5,a6,1
&if v3 > 9 then L110 *
do display off
retrieve x /usr/user/Dhulipal/Spectra/&a11&a3&v3&a12
&error L150
retrieve y /usr/user/Dhulipal/Spectra/&a13&a3&v3&a14
&error L150
copy x x 4000 450
copy y y 4000 450
diff y x z
abex z z 1
taat z z
ident z &a13&a3&v3&a14 corrected using &a11&a3&v3&a12
&L100 *
save z f0:&a15&a3&v3&a16
```

```
&error L200
&if a7 <> "y" then L105 *
idris rm /usr/user/Dhulipal/Spectra/&a11&a3&v3&a12.sp
idris rm /usr/user/Dhulipal/Spectra/&a13&a3&v3&a14.sp
&L105 do display on
* &a11&a3&v3&a12 and &a13&a3&v3&a14 processed and stored in F0:
&a15&a3&v3&a16
&goto L120
&L110 do display off
retrieve x /usr/user/Dhulipal/Spectra/&a11&v3&a12
&error L150
retrieve y /usr/user/Dhulipal/Spectra/&a13&v3&a14
&error L150
copy x x 4000 450
copy y y 4000 450
diff y x z
abex z z 1
taat z z
ident z &a13&v3&a14 corrected using &a11&v3&a12
&L115 *
save z f0:&a15&v3&a16
&error L210
&if a7 <> "y" then L117 *
idris rm /usr/user/Dhulipal/Spectra/&a11&v3&a12.sp
idris rm /usr/user/Dhulipal/Spectra/&a13&v3&a14.sp
&L117 do display on
* &a11&v3&a12 and &a13&v3&a14 processed and stored in F0: &a15&v3&a16
&L120 do display off
&next v3
&goto L800
&L150 do display on
* File Not Found (This is at line 150)
&goto L120
&L200 do display on
&gosub L250
&goto L100
&L210 do display on
&gosub L250
&goto L115
&L250 do display on
*
* The floppy in F0 seems to be full.
* Either replace it and press return or press return to re-try to save
* in the same floppy
```

```
*
&enter a1
do display off
&return
*
&L800 do display on
* end of program

*************************************************************************
*                                RamAreaRxn1.oy                         *
*************************************************************************
gclear
do sclear
do display on
* This is for finding the areas under different peaks in the spectrum.
* This program finds the areas under four different peaks using a user
* defined baseline. The areas under the zero base line and  user defined
* base line are output for all the four peaks. The screen is printed to the
* plotter at the end of the program. This limits the number of files to
* 15 if all the areas are to be printed on the plotter. If the series has more
* than 15 files then it has to be done by running this program more than once
*
*
* For each peak the area under the zero baseline is reported first followed by
* a comma and the area under the user defined baseline. Each line contains the
* areas pertaining to each spectra.

* Press enter when ready
&enter a1
do display off
* The variables a11 to a26 are used to store the peaks under which the areas
* are to be found out.
* Each set of four variables (a11-a14), (a15-a18), ... determine a peak and
* in each set the first two values determine the baseline higher and lower
* wave number and the next two values determine the limits within which the
* area has to be found out.  If no user baseline is required just give
* the same values for the baseline definition as are given to the limits of
* integration. Then just ignore the minus baseline areas.
*
* e.g :- a15 has the higher wavenumber of the user defined baseline and the
*  value a16 has the lower  wavenumber of the user defined baseline
*        a17 has the higher wavenumber of the limits of integration
*   and  a18 has the lower  wavenumber of the limits of integration
*
```

```
*****************************
&def a11 = "3150"
&def a12 = "2650"
*--------------
&def a13 = "2972"
&def a14 = "2965"
*****************************
&def a15 = "1655"
&def a16 = "1560"
*---------------
&def a17 = "1612"
&def a18 = "1602"
*****************************
&def a19 = "1800"
&def a20 = "1662"
*---------------
&def a21 = "1800"
&def a22 = "1765"
*****************************
&def a23 = "1655"
&def a24 = "1560"
*---------------
&def a25 = "1645"
&def a26 = "1630"
*****************************
*
do sclear
do display on
* THIS PROGRAM WAS WRITTEN BY DHULIPALA RAMAKRISHNA ON 15 July
1992
* WHILE DOING HIS MASTERS PROGRAM IN CHEMICAL ENGINEERING.
*
*
* This program takes a series of spectra and then finds the areas under certain
* peaks of the spectra with a user defined baseline. It will do that for four
* peaks and output the results to the plotter. Make sure it is switched on and
* is working properly. The areas under the zero baseline as well as the area
* under the user defined baseline will be output.
*
* The spectra are taken from the directory /usr/user/Dhulipal/Spectra
* Make sure that the spectra are in that directory
*
* The series is assumed to be of the form BB(A1-A2)CC
```

```
* Where          BB is the string in the name before the numeric series
*                CC is the string in the name after  the numeric series
*                A1 is the beginning number of the series and
*                A2 is the ending number of the series.
*
* You can stop the program anytime by pressing the break key.
* Press enter when ready
&enter a1
do sclear
&def a3 = ""
&def a1 = "y"
* do you want the numeric series (1-9) to be of the form (01-09) enter (y/n)
&enter a1
&if a1 = "n" then L90 *
&def a3 ="0"
&L90 do display on
*
* Enter the beginning value of the numeric series
&enter a5
*
* Enter the end value of the numeric series
&enter a6
do sclear
* For the series of spectra for which the areas are to be calculated
* Enter the general name of the files before the numeric series
&enter a4
*
* Enter the general name of the files after the numeric series
&enter a7
do sclear
do display on
*Base line limits->&a11-&a12!  &a15 - &a16   !  &a19 - &a20   !  &a23 - &a24 !
*Area limits -> &a13 - &a14 !  &a17 - &a18   !  &a21 - &a22   !  &a25 - &a26 !
&for v3 = a5,a6,1
&if v3 <10 then L95 *
&def a3 = ""
&L95 do display off
&def a2 = a4 + a3 + v3 + a7
do display off
retrieve x /usr/user/Dhulipal/Spectra/&a2
&error L150
* This is where the area have to be found out and output
area x &a11 &a13 &a14 &a12
calc v11 = v58
```

```
calc v12 = v57
area x &a15 &a17 &a18 &a16
calc v13 = v58
calc v14 = v57
area x &a19 &a21 &a22 &a20
calc v15 = v58
calc v16 = v57
area x &a23 &a25 &a26 &a24
calc v17 = v58
calc v18 = v57
do display on
*&a2->&v11.4,&v12.4<>&v13.4,&v14.4<>&v15.4,&v16.4<>&v17.4,&v18.4#
&L120 do display off
&next v3
&goto L800
&L150 do display on
*&a2        File NOT found
&goto L120
&L800 do display on
rprint
* End of program

*****************************************************************************
*                                    RamTrans2.oy                           *
*****************************************************************************
do sclear
* THIS PROGRAM WAS WRITTEN BY DHULIPALA RAMAKRISHNA ON 29th
OCT
* 1991 WHILE DOING HIS MASTERS PROGRAM IN CHEMICAL ENGINEERING.
*
*
*
*
* THIS PROGRAM CALCULATES THE ABSORBANCE AT ANY POINT IN A
* SEQUENCE OF FILES AND OUTPUTS THE VALUES ON TO THE SCREEN.
*
*
*
*
*
* You can stop the program anytime by pressing the break key.
* Press enter when you are ready
&enter a4
&L100 *
```

```
do sclear
* Enter the general name of the files before the start of the numeric sequence
* i.e The file names are assumed to be name1(1-number of files)name2
* So enter the name before the number sequence
&enter a6
do sclear
* Enter the total number of files.
&enter a7
&L105 *
do sclear
* Enter the wave number where you want to calculate the absorbance values.
&enter a4
do sclear
* Place the floppy containing all these files in the drive 0 (left drive)
* Press enter after you are ready.
&enter a25
do sclear
* Filename              Wave number          Absorbance
&for v1 = 1,a7,1
do display off
retrieve x f0:&a6&v1
calc v10=absr(x(&a4))
do display on
* &a6&v1                &a4                  &v10
do display off
&next v1
do display on
&goto L800
&L500
do display on
* &a6&v1&a15            File not found
&if a1 = "n" then L115
&goto L107
&L800 *
* Do you want to calculate for another wave length (y/n)
&enter a22
&if  a22 = "y" then L105
* End of program
```

Appendix C: MATLAB script files

Given below are the script files used in MATLAB. Some of the files were used to perform the Simplex minimization of the total error between the experimental and predicted values of the extent of cure. Other files were used to plot the predicted extent of cure data along with the experimental values. The lines that begin with a "%" are the comment statements for the files and do not affect the running of these script files. The three lines identifying the file names must however be deleted before execution.

```
**************************************************************************
*                                  Total_Reg3.m                          *
**************************************************************************
% This is a matlab script file.
% This program starts the simplex procedure and stores the results in the
% file Total_Reg_Data3. The lines that start with a % are comment lines.
%
diary Total_Reg_Data3;
diary on;
options(18) = 0;
options(1) = 1;
options(2) = 1e-4;
options(3) = 1e-4;
options(14) = 500;
fmins('Total_Error3_New',[6437 18.2420 2.7446 0.5787], options)
diary off;
quit;

**************************************************************************
*                              Total_Error3_New.m                        *
**************************************************************************
function f = Total_Error3_New(X_In)
```

```
Kpm = X_In(1);
Kpc = X_In(2);
Btc = X_In(3);
Ktp_Factor = X_In(4);
Btm = 0;

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%  REMEMBER TO CHANGE THE RHS OF THE FIRST LINE TO THIS FILE
%  NAME IF THE NAME OF THIS FILE IS CHANGED
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

Error = 0;
T = 080;

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% The files tc080b11.m etc. contain the extent of cure vs time
% data for the corresponding temperatures and BPO concentrations.
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

tc080b11;
tc080b21;
tc080b31;
tc080b41;

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% For each of the temperatures and each BPO concentrations the following lines
% find the sum of the square of the error between the predicted and experimental
% values of the extent of cure and then add this to the total error. That value
% is then returned to the matlab function 'fmins' that does a simplex
% minimization of the error.
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

    clear t_Actual;
    clear X_Actual;
    wt_Percent_I = 1;
    Size_of_Exp_Data = size(TC080B11,1);
    for Junk = 1:1:Size_of_Exp_Data
       t_Actual(Junk) = TC080B11(Junk,2);
       X_Actual(Junk) = TC080B11(Junk,1);
    end;
    Max_Time = t_Actual(Size_of_Exp_Data);
    Total_EFinder_New;
%   ________________________________________
```

```
clear t_Actual;
clear X_Actual;
wt_Percent_I = 2;
Size_of_Exp_Data = size(TC080B21,1);
for Junk = 1:1:Size_of_Exp_Data
  t_Actual(Junk) = TC080B21(Junk,2);
  X_Actual(Junk) = TC080B21(Junk,1);
end;
Max_Time = t_Actual(Size_of_Exp_Data);
Total_EFinder_New;
%  ---------------------------------------------------------

%clear t_Actual;
%clear X_Actual;
%wt_Percent_I = 3;
%Size_of_Exp_Data = size(TC080B31,1);
%for Junk = 1:1:Size_of_Exp_Data
%  t_Actual(Junk) = TC080B31(Junk,2);
%  X_Actual(Junk) = TC080B31(Junk,1);
%end;
%Max_Time = t_Actual(Size_of_Exp_Data);
%Total_EFinder_New;
%  ---------------------------------------------------------

clear t_Actual;
clear X_Actual;
wt_Percent_I = 4;
Size_of_Exp_Data = size(TC080B41,1);
for Junk = 1:1:Size_of_Exp_Data
  t_Actual(Junk) = TC080B41(Junk,2);
  X_Actual(Junk) = TC080B41(Junk,1);
end;
Max_Time = t_Actual(Size_of_Exp_Data);
Total_EFinder_New;
%  ---------------------------------------------------------

%clear t_Actual;
%clear X_Actual;
%wt_Percent_I = 5;
%Size_of_Exp_Data = size(TC080B51,1);
%for Junk = 1:1:Size_of_Exp_Data
%  t_Actual(Junk) = TC080B51(Junk,2);
%  X_Actual(Junk) = TC080B51(Junk,1);
%end;
```

```
    %Max_Time = t_Actual(Size_of_Exp_Data);
    %Total_EFinder_New;
%   ____________________________________________

% ***************************************************************************
% ^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^

T = 090;
tc090b11;
tc090b21;
tc090b31;
tc090b41;
tc090b51;

    clear t_Actual;
    clear X_Actual;
    wt_Percent_I = 1;
    Size_of_Exp_Data = 10;
    for Junk = 1:1:Size_of_Exp_Data
      t_Actual(Junk) = TC090B11(Junk,2);
      X_Actual(Junk) = TC090B11(Junk,1);
    end;
    Max_Time = t_Actual(Size_of_Exp_Data);
    Total_EFinder_New;
%   ____________________________________________

    clear t_Actual;
    clear X_Actual;
    wt_Percent_I = 2;
    Size_of_Exp_Data = 14;
    for Junk = 1:1:Size_of_Exp_Data
     t_Actual(Junk) = TC090B21(Junk,2);
     X_Actual(Junk) = TC090B21(Junk,1);
    end;
    Max_Time = t_Actual(Size_of_Exp_Data);
    Total_EFinder_New;
%   ____________________________________________

    clear t_Actual;
    clear X_Actual;
    wt_Percent_I = 3;
    Size_of_Exp_Data = 14;
    for Junk = 1:1:Size_of_Exp_Data
     t_Actual(Junk) = TC090B31(Junk,2);
```

```
  X_Actual(Junk) = TC090B31(Junk,1);
end;
Max_Time = t_Actual(Size_of_Exp_Data);
Total_EFinder_New;
%  ____________________________________________

%clear t_Actual;
%clear X_Actual;
%wt_Percent_I = 4;
%Size_of_Exp_Data = 11;
%for Junk = 1:1:Size_of_Exp_Data
%  t_Actual(Junk) = TC090B41(Junk,2);
%  X_Actual(Junk) = TC090B41(Junk,1);
%end;
%Max_Time = t_Actual(Size_of_Exp_Data);
%Total_EFinder_New;
%  ____________________________________________

clear t_Actual;
clear X_Actual;
wt_Percent_I = 5;
Size_of_Exp_Data = 13;
for Junk = 1:1:Size_of_Exp_Data
  t_Actual(Junk) = TC090B51(Junk,2);
  X_Actual(Junk) = TC090B51(Junk,1);
end;
Max_Time = t_Actual(Size_of_Exp_Data);
Total_EFinder_New;
%  ____________________________________________

% ************************************************************************
% ^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^

T = 100;
tc100b11;
tc100b21;
tc100b31;
tc100b41;
tc100b51;

clear t_Actual;
clear X_Actual;
wt_Percent_I = 1;
Size_of_Exp_Data = 13;
```

```
for Junk = 1:1:Size_of_Exp_Data
   t_Actual(Junk) = TC100B11(Junk,2);
   X_Actual(Junk) = TC100B11(Junk,1);
end;
Max_Time = t_Actual(Size_of_Exp_Data);
Total_EFinder_New;
%  ------------------------------------------------

clear t_Actual;
clear X_Actual;
wt_Percent_I = 2;
Size_of_Exp_Data = 11;
for Junk = 1:1:Size_of_Exp_Data
  t_Actual(Junk) = TC100B21(Junk,2);
  X_Actual(Junk) = TC100B21(Junk,1);
end;
Max_Time = t_Actual(Size_of_Exp_Data);
Total_EFinder_New;
%  ------------------------------------------------

%clear t_Actual;
%clear X_Actual;
%wt_Percent_I = 3;
%Size_of_Exp_Data = 14;
%for Junk = 1:1:Size_of_Exp_Data
%  t_Actual(Junk) = TC100B31(Junk,2);
%  X_Actual(Junk) = TC100B31(Junk,1);
%end;
%Max_Time = t_Actual(Size_of_Exp_Data);
%Total_EFinder_New;
%  ------------------------------------------------

clear t_Actual;
clear X_Actual;
wt_Percent_I = 4;
Size_of_Exp_Data = 10;
for Junk = 1:1:Size_of_Exp_Data
  t_Actual(Junk) = TC100B41(Junk,2);
  X_Actual(Junk) = TC100B41(Junk,1);
end;
Max_Time = t_Actual(Size_of_Exp_Data);
Total_EFinder_New;
%  ------------------------------------------------
```

```
%clear t_Actual;
%clear X_Actual;
%wt_Percent_I = 5;
%Size_of_Exp_Data = 10;
%for Junk = 1:1:Size_of_Exp_Data
%  t_Actual(Junk) = TC100B51(Junk,2);
%  X_Actual(Junk) = TC100B51(Junk,1);
%end;
%Max_Time = t_Actual(Size_of_Exp_Data);
%Total_EFinder_New;
%  ____________________________________________

% ***********************************************************************
% ^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^

T = 110;
tc1 10b11;
tc1 10b21;
tc1 10b31;
tc1 10b41;
tc1 10b51;

clear t_Actual;
clear X_Actual;
wt_Percent_I = 1;
Size_of_Exp_Data = 05;
for Junk = 1:1:Size_of_Exp_Data
  t_Actual(Junk) = TC110B11(Junk,2);
  X_Actual(Junk) = TC110B11(Junk,1);
end;
Max_Time = t_Actual(Size_of_Exp_Data);
Total_EFinder_New;
%  ____________________________________________

%clear t_Actual;
%clear X_Actual;
%wt_Percent_I = 2;
%Size_of_Exp_Data = 10;
%for Junk = 1:1:Size_of_Exp_Data
%  t_Actual(Junk) = TC110B21(Junk,2);
%  X_Actual(Junk) = TC110B21(Junk,1);
%end;
%Max_Time = t_Actual(Size_of_Exp_Data);
%Total_EFinder_New;
```

```
%  ____________________________________________

    clear t_Actual;
    clear X_Actual;
    wt_Percent_I = 3;
    Size_of_Exp_Data = 12;
    for Junk = 1:1:Size_of_Exp_Data
      t_Actual(Junk) = TC110B31(Junk,2);
      X_Actual(Junk) = TC110B31(Junk,1);
    end;
    Max_Time = t_Actual(Size_of_Exp_Data);
    Total_EFinder_New;
%  ____________________________________________

    clear t_Actual;
    clear X_Actual;
    wt_Percent_I = 4;
    Size_of_Exp_Data = 09;
    for Junk = 1:1:Size_of_Exp_Data
      t_Actual(Junk) = TC110B41(Junk,2);
      X_Actual(Junk) = TC110B41(Junk,1);
    end;
    Max_Time = t_Actual(Size_of_Exp_Data);
    Total_EFinder_New;
%  ____________________________________________

    %clear t_Actual;
    %clear X_Actual;
    %wt_Percent_I = 5;
    %Size_of_Exp_Data = 09;
    %for Junk = 1:1:Size_of_Exp_Data
    %  t_Actual(Junk) = TC110B51(Junk,2);
    %  X_Actual(Junk) = TC110B51(Junk,1);
    %end;
    %Max_Time = t_Actual(Size_of_Exp_Data);
    %Total_EFinder_New;
%  ____________________________________________

% ***************************************************************
% ^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^

T = 120;
tc120b11;
tc120b21;
```

```
tc120b31;
tc120b41;
tc120b51;

    clear t_Actual;
    clear X_Actual;
    wt_Percent_I = 1;
    Size_of_Exp_Data = 07;
    for Junk = 1:1:Size_of_Exp_Data
      t_Actual(Junk) = TC120B11(Junk,2);
      X_Actual(Junk) = TC120B11(Junk,1);
    end;
    Max_Time = t_Actual(Size_of_Exp_Data);
    Total_EFinder_New;
%   ------------------------------------------------

    clear t_Actual;
    clear X_Actual;
    wt_Percent_I = 2;
    Size_of_Exp_Data = 08;
    for Junk = 1:1:Size_of_Exp_Data
     t_Actual(Junk) = TC120B21(Junk,2);
     X_Actual(Junk) = TC120B21(Junk,1);
    end;
    Max_Time = t_Actual(Size_of_Exp_Data);
    Total_EFinder_New;
%   ------------------------------------------------

    %clear t_Actual;
    %clear X_Actual;
    %wt_Percent_I = 3;
    %Size_of_Exp_Data = 11;
    %for Junk = 1:1:Size_of_Exp_Data
    %  t_Actual(Junk) = TC120B31(Junk,2);
    %  X_Actual(Junk) = TC120B31(Junk,1);
    %end;
    %Max_Time = t_Actual(Size_of_Exp_Data);
    %Total_EFinder_New;
%   ------------------------------------------------

    clear t_Actual;
    clear X_Actual;
    wt_Percent_I = 4;
    Size_of_Exp_Data = 12;
```

```
    for Junk = 1:1:Size_of_Exp_Data
      t_Actual(Junk) = TC120B41(Junk,2);
      X_Actual(Junk) = TC120B41(Junk,1);
    end;
    Max_Time = t_Actual(Size_of_Exp_Data);
    Total_EFinder_New;
%   ____________________________________________

    clear t_Actual;
    clear X_Actual;
    wt_Percent_I = 5;
    Size_of_Exp_Data = 07;
    for Junk = 1:1:Size_of_Exp_Data
      t_Actual(Junk) = TC120B51(Junk,2);
      X_Actual(Junk) = TC120B51(Junk,1);
    end;
    Max_Time = t_Actual(Size_of_Exp_Data);
    Total_EFinder_New;
%   ____________________________________________

% ***************************************************************************
% ^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^
f = Error;

*****************************************************************************
*                                Total_EFinder_New.m                        *
*****************************************************************************
% This script file actually calculates the predicted values of extent of cure
% for each unit time at a particular cure temperature and benzoyl peroxide
% concentration. It then calculates the square of the error for each
% experimental data point and then adds that to the total error.

Step_Time = 1;
No_of_Steps = Max_Time/ Step_Time;
f = 1;
Ktt0 = 1;
Tgm = -160;
Tgp = 080;

VF0 = (0.025 + 0.001 * (T-Tgm));
Kp = 1e-2 * exp((-Kpm/(T+273)) + Kpc);
Bt = (Btm * T) + Btc;
Ktp = Ktp_Factor * Kp;
```

```
dm = 1.04;
CI0 = (wt_Percent_I/242.2)/(0.1/dm);
s = 0.07;
Kd = 8.02e7 * exp(-8795.4/(T+273));

time = [0:Step_Time:Max_Time];
clear Extent;
Extent(1) = 0;
Kt_Array(2) = 0;

for N = 2:1:No_of_Steps+1
X = Extent(N-1);
t = time(N);

PhyP = X / (1+s - s*X);
Vf = VF0 + PhyP * (0.00048*(T-Tgp) - 0.001*(T-Tgm));
Ktt = Ktt0 * exp(Bt*((1/VF0) - (1/Vf)));
Kt = Ktt + Ktp;

R = s / (s + 1);
CI = ( CI0 * exp (-Kd * t) )/(1 - R*X);
Dx_by_dt_Temp1 = Kp * sqrt(2*f*Kd*CI/Kt);
Dx_by_dt = Dx_by_dt_Temp1 * (1-X);
X_New = X + ( Dx_by_dt * Step_Time) ;
if X_New > 1
        X_New = 1;
end;

Extent(N) = X_New;
Kt_Array(N) = Kt;

end;

for jj = 1:1:Size_of_Exp_Data
  t_Data = t_Actual(jj);
  X_Data = X_Actual(jj);
  X_Calc = Extent(t_Data + 1);
  Error = Error + ((X_Calc - X_Data)^2);
end;

*************************************************************************
*                                Total_Draw090.m                        *
*************************************************************************
% This program generates the predicted cure curves and plots it along with the
```

```
% cure data generated at 90 C and different BPO concentrations.
% The same script file with minor modifications can be used to plot
% similar curves for reaction at other temperatures.
%

clear;
!rm T090;
diary T090;
diary off;

% Uncomment the following if the plot of rate of reaction vs. extent of cure is also
required.
%subplot(2,1,1), hold off;
%subplot(2,1,2), hold off;

% DDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDD
tc090b11;
tc090b21;
tc090b31;
tc090b41;
tc090b51;
% DDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDD

% ************************************************
T = 090;
Max_Time = 4000;

%_____________________________________________________
wt_Percent_I = 5;
subplot(1,1,1); plot(TC090B51(:,2),TC090B51(:,1),'b+');
diary on;
TC090B51(:,2)
TC090B51(:,1)
diary off;
% The following script file generates the extent of cure data for the conditions above.
Total_Extent_New;
hold on;
plot(time,Extent,'b');
% Uncomment the following if the plot of rate of reaction vs. extent of cure is also
required.
%subplot(2,1,2); plot(Extent,Dxdt_Array,'b');
hold on;
diary on;
% The following lines output data to a file.
```

```
time'
Extent'
diary off;
%Dxdt_Array' * 1000
diary off;
%^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^

% The following sets of code are similar except that some of the lines are commented
because
% the corresponding plots are not needed.
%_____________________________________________________________
wt_Percent_I = 4;
subplot(1,1,1);
%diary on;
%TC090B41(:,2)
%TC090B41(:,1)
%diary off;
Total_Extent_New;
hold on;
%plot(time,Extent,'c');
%subplot(2,1,2); plot(Extent,Dxdt_Array,'c');
hold on;
diary on;
%time'
Extent'
diary off;
%%Dxdt_Array' * 1000
%diary off;
%^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^

%_____________________________________________________________
wt_Percent_I = 3;
subplot(1,1,1); plot(TC090B31(:,2),TC090B31(:,1),'gx');
diary on;
TC090B31(:,2)
TC090B31(:,1)
diary off;
Total_Extent_New;
hold on;
plot(time,Extent,'g');
%subplot(2,1,2); plot(Extent,Dxdt_Array,'g');
hold on;
diary on;
%time'
```

```
Extent'
diary off;
%Dxdt_Array' * 1000
diary off;
%^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^

%_____________________________________________________________________
wt_Percent_I = 2;
subplot(1,1,1); plot(TC090B21(:,2),TC090B21(:,1),'m*');
diary on;
TC090B21(:,2)
TC090B21(:,1)
diary off;
Total_Extent_New;
hold on;
plot(time,Extent,'m');
%subplot(2,1,2); plot(Extent,Dxdt_Array,'m');
hold on;
diary on;
%time'
Extent'
diary off;
%Dxdt_Array' * 1000
diary off;
%^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^

%_____________________________________________________________________
wt_Percent_I = 1;
subplot(1,1,1); plot(TC090B11(:,2),TC090B11(:,1),'r+');
diary on;
TC090B11(:,2)
TC090B11(:,1)
diary off;
Total_Extent_New;
hold on;
plot(time,Extent,'r');
%subplot(2,1,2); plot(Extent,Dxdt_Array,'r');
hold on;
diary on;
%time'
Extent'
diary off;
%Dxdt_Array' * 1000
diary off;
```

```
%^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^

% ********************************************************

subplot(1,1,1); axis([0 Max_Time 0 1]);
ylabel('Extent of cure ');
xlabel('time');
title(['Extent of cure vs time at T = ',num2str(T),' C']);
text(200,-0.1,['Kpm = ',num2str(Kpm),' Kpc = ',num2str(Kpc),' Bt = ',num2str(Bt) ,'
Ktp_factor = ',num2str(Ktp_Factor)]);
print -append junk;

*************************************************************************
*                                Total_Extent_New.m                     *
*************************************************************************
% Given a set of parameters this will automatically calculate the X vs
% t for the current set of conditions. The set of conditions are the
% Temperature T (C), Wt percent of BPO, and the Maximum time of the reaction
% This script file is called from different places in other files like Total_Draw090.m
% A finite difference approach is used here to calculate the rate of reaction and extent of
cure
% as a function of time.

Kpm = 6760.4;
Kpc = 19.1390;
Btm = 0.0;
Btc = +2.9885;
Ktp_Factor = 0.50682;

%-----------------------------------------------------------
% The actual Kp is calculated from the simulation parameters Kpm and Kpc.
Kp = 1e-2 * exp((-Kpm/(T+273)) + Kpc);
Bt = (Btm * T) + Btc;
Ktp = Ktp_Factor * Kp;
%************************************************************

if T == 80
        Max_Time = 5000;
        Step_Time = 2;
end;
if T > 85
  if T < 95
        Max_Time = 4000;
        Step_Time = 2;
```

```
  end;
end;
if T == 100
        Max_Time = 3000;
        Step_Time = 2;
end;
if T == 110
        Max_Time = 2000;
        Step_Time = 1;
end;
if T == 120
        Max_Time = 1000;
        Step_Time = 1;
end;

No_of_Steps = Max_Time/ Step_Time;
f = 1;
Ktt0 = 1;
Tgm = -160;
Tgp = 080;

VF0 = (0.025 + 0.001 * (T-Tgm));
dm = 1.04;
CI0 = (wt_Percent_I/242.2)/(0.1/dm);
s = 0.07;
Kd = 8.02e7 * exp(-8795.4/(T+273));

time = [0:Step_Time:Max_Time];

clear Kp_Array;
clear Vf_Array;
clear Phyp_Array;
clear Extent;
clear Dxdt_Array;
clear Ktp_Array;

Extent(1) = 0;
Kt_Array(2) = 0;

for N = 2:1:No_of_Steps+1
X = Extent(N-1);
t = time(N);

PhyP = X / (1+s - s*X);
```

```
Vf = VF0 + PhyP * (0.00048*(T-Tgp) - 0.001*(T-Tgm));

Ktt = Ktt0 * exp(Bt*((1/VF0) - (1/Vf)));
Kt = Ktt + Ktp;
R = s/(s+1);
CI = (CI0 * exp (-Kd * t) / (1 - R*X) );
Dx_by_dt_Temp1 = Kp * sqrt(2*f*Kd*CI/Kt);
Dx_by_dt = Dx_by_dt_Temp1 * (1-X);
X_New = X + ( Dx_by_dt * Step_Time) ;
if X_New > 1
        X_New = 1;
end;

Extent(N) = X_New;
Kp_Array(N) = Kp;
Kt_Array(N) = Kt;
Vf_Array(N) = Vf;
Phyp_Array(N) = PhyP;
Ktp_Array(N) = Ktp;
Dxdt_Array(N) = Dx_by_dt;
end;

Kp_Array(1) = Kp_Array(2);
Kt_Array(1) = Kt_Array(2);
Vf_Array(1) = Vf_Array(2);
Dxdt_Array(1) = Dxdt_Array(2);
Ktp_Array(1) = Ktp_Array(2);
```

LIST OF REFERENCES

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