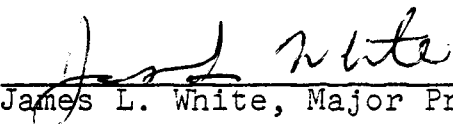
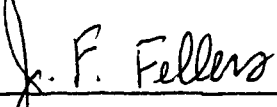


To the Graduate Council:

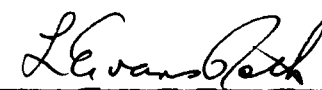
I am submitting herewith a thesis written by Yuh-Chen Shen entitled "Structure-Property and Residual Stress Characteristics in Epoxy Resin System." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Polymer Engineering.


James L. White, Major Professor

We have read this thesis and
recommend its acceptance:


Accepted for the Council:


Vice Chancellor
Graduate Studies and Research

STRUCTURE-PROPERTY AND RESIDUAL
STRESS CHARACTERISTICS IN
EPOXY RESIN SYSTEM

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Yuh-Chen Shen

June 1981

3051780

ACKNOWLEDGEMENTS

The author wishes to express his deepest and most sincere appreciation to Dr. J. L. White, the author's advisor, for his advice, guidance and inspirational source throughout this research study and for his help in the preparation of this manuscript.

Appreciation is also extended to Dr. D. C. Bogue for his interest and advice in the thermal stress and to Dr. H. Pih for his advice in the photoelastic measurement.

The author wishes to thank the Shell Chemical Company for providing resins for the research. Financial assistance provided by the Chemical, Metallurgical and Polymer Engineering Department is also gratefully acknowledged.

Thanks are extended to Mr. H. B. Thompson and his co-workers for making molds and for their assistance in carrying out the layer removal experiments.

Deepest gratitude is expressed to his family for their spiritual encouragement and support throughout graduate school. A special debt of gratitude is offered to his wife and parents for the years of understanding and encouragement.

ABSTRACT

The properties of crosslinked polymers are greatly dependent on their network structures. Knowledge of the relationships between characteristics, curing conditions, compositions, structural and mechanical properties is required to evaluate uses for critical and demanding applications. The characterization of properties of crosslinked polymers like epoxy resins has received great attention in past decades. However, due to their increasing important uses for engineering purposes such as composite matrices and adhesives in aerospace structural components, characterization of properties is becoming critical.

The effect of residual stresses on the properties of metals and glass has received extensive studies for a long time. The residual stress distribution in slabs of epoxies due to the cooling process was studied. In order to measure the residual stress, both layer removal and photo-elastic methods were used. A theoretical solution for the residual stresses, which is based on the assumption of a low modulus elastic rubbery state at temperatures above the softening point and a low temperature glassy state, was derived and compared to the results of the experiments. The agreement was good. The effect of the residual stress distribution on the impact strength of epoxies was also studied. It was found that residual stresses increase the impact strength.

The influence of the stoichiometric ratio (the curing agent, NMA to the epoxy resin, EPON 828) and the curing conditions such as cure temperature, postcure on the structure (as specified by swell index, density, T_g , etc.) and mechanical properties was studied. The kinetics of the curing reaction of epoxies was also examined by using the differential scanning calorimetry. The morphology of network structure was investigated in the scanning electron microscope and a globular structure was observed.

TABLE OF CONTENTS

CHAPTER	PAGE
1. INTRODUCTION	1
2. BACKGROUND AND REVIEW OF LITERATURE.	4
2.1 Synthesis and Characterization of Epoxy Resins	
2.2 Epoxy Resin Cure Mechanisms	
2.3 Methods to Characterize Kinetics of Curing Reaction	
2.4 Formation of Network Structure	
2.5 Effect of Characteristics of Constituents and Stoichiometry on Formation and Properties of Network Structure	
2.6 Effect of Cure History on Formation and Properties of Network Structure	
2.7 Characterization of Structural Properties of Cured Epoxies	
2.8 Methods to Characterize Structural Properties of Cured Epoxies	
2.9 Characterization of Mechanical Properties of Cured Epoxies	
2.10 Residual Stresses	
3. EXPERIMENTAL DETAILS	45
3.1 Materials	
3.2 Characterization of Kinetics of Curing Reaction by Differential Scanning Calorimetry	
3.3 Characterization of Cure Epoxies	
3.4 Measurement of Residual Stresses in Epoxy Specimen	
3.5 Mechanical Properties Measurement	
4. KINETICS OF POLYMERIZATION OF EPOXY RESIN DURING CURING REACTION	68
4.1 Characterization of Curing Reaction by Using DSC	
4.2 Discussion	
5. NETWORK STRUCTURAL PROPERTIES OF EPOXY RESINS	83
5.1 Swelling	
5.2 Glass Transition Temperature	
5.3 Density	

CHAPTER	PAGE
5. (Continued)	
5.4 Color	
5.5 SEM Studies of Etched Surfaces	
6. MECHANICAL PROPERTIES OF CURED EPOXIES	115
6.1 Small Strain Elastic Properties	
6.2 Ultimate Tensile Properties	
6.3 Impact Strength	
7. RESIDUAL STRESSES IN CURED EPOXY	125
7.1 Origins of Residual Stresses in Epoxy	
7.2 Theoretical Solution of Residual Stresses Distribution Due to Non- homogeneous Cooling	
7.3 Experimental Results of Residual Stress Distribution	
7.4 Discussion	
7.5 Effect of Residual Stresses on Impact Behavior of Epoxies	
8. SUMMARY AND CONCLUSIONS.	160
LIST OF REFERENCES	163
APPENDIX	171
VITA	190

LIST OF TABLES

TABLE		PAGE
3.1	Chemical structure of reactants.	46
3.2	Properties of epoxy resin and curing agent . .	48
3.3	Compositions and cure schedules of epoxy samples.	53
4.1	Total heat of reaction and glass transition temperature for dynamic scan	71
4.2	Total heat of reaction and glass transition temperature for isothermal scan.	72
4.3	Activation energy by peak temperature method	76
4.4	Activation energy by equation [3.4].	77
5.1	Glass transition temperature and density of epoxy resin series A	95
5.2	Glass transition temperature and density of epoxy resin series B and C	96
6.1	Effect of NMA to EPON 828 stoichiometry on tensile properties	117
6.2	Effect of cure temperature on tensile properties	118
7.1	Representative properties of epoxy in stress analysis	135
7.2	Data of measured curvature for a $\frac{1}{4}$ " thick slab under ice water quenching	136
7.3	Calculation of residual stresses for a $\frac{1}{4}$ " thick slab under ice water quenching	137
7.4	Data of measured curvature for a $\frac{1}{2}$ " thick slab under ice water quenching	138
7.5	Calculation of residual stresses for a $\frac{1}{2}$ " thick slab under ice water quenching	139

TABLE

PAGE

7.6	Data of measured curvature for a $\frac{1}{4}$ " thick slab under liquid nitrogen quenching	140
7.7	Calculation of residual stresses for a $\frac{1}{4}$ " thick slab under liquid nitrogen quenching . .	141

LIST OF FIGURES

FIGURE	PAGE
2.1 Schematic representation of development of network molecular.	17
2.2 (a) Proposed model for gelation process by Bobalek et al. (b) Proposed formation for a gel ball by Labana et al. (c) Proposed model for network formation by Misra et al.. . . .	21
2.3 Time-temperature-transformation diagram for the thermosetting process.	25
3.1 A typical DSC scan showing heat of reaction and peak temperature.	50
3.2 Photograph of molds for casting epoxy samples.	55
3.3 A typical DSC scan (2.5°C/min) of cured epoxy showing glass transition temperature . .	58
3.4 Schematic diagram for layer removal method to measure residual stress.	59
3.5 Schematic diagram of milling process for removing layers.	61
3.6 Schematic diagram for photoelastic method to measure residual stress	63
3.7 Schematic diagram for subslicing a slice of slab.	65
3.8 Test specimen geometrics: (a) tensile specimen, (b) Izod impact specimen	66
4.1 Isothermal DSC runs at various cure temperatures	70
4.2 Plots of DSC dynamic run (5°C/min) with various concentrations of catalyst BDMA. . . .	73
4.3 Plots of DSC dynamic run data with different scan rates	75
5.1 Swelling ratio and glass transition temperature of cured epoxies as a function of NMA/EPON 828 ratio.	84

FIGURE	PAGE
5.2 Swelling ratio and glass transition temperature of cured epoxies as a function of cure temperature	86
5.3 Swelling ratio and glass transition temperature of cured epoxies as a function of postcure time.	87
5.4 Glass transition temperature of cured epoxies as related to swelling ratio	92
5.5 Density of cured epoxies as related to glass transition temperature	97
5.6 Photograph showing colors of cured epoxies at various cure temperatures	99
5.7 Plots of exotherm profile at various cure temperatures	101
5.8 SEM micrographs showing globular structure of $\text{CrO}_3\text{-H}_2\text{SO}_4$ etched surface of cured epoxy samples having different stoichiometric ratio of NMA to EPON 828: (a) 0.5/1 (b) 0.7/1 (c) 0.8/1.	102
5.9 SEM micrographs showing globular structure of $\text{CrO}_3\text{-H}_2\text{SO}_4$ etched surface of cured epoxy samples having different stoichiometric ratio of NMA to EPON 828: (d) 0.9/1 (e) 1.0/1 (f) 1.2/1.	103
5.10 Globular size of cured epoxies as a function NMA/EPON 828 ratio.	104
5.11 SEM micrographs of etched epoxy samples with low magnification (500x): (a) 0.7/1 (b) 0.9/1.	106
5.12 SEM micrographs of etched epoxy samples cured at various temperatures: (a) 80°C (b) 93°C (c) 107°C	107
5.13 SEM micrographs of etched epoxy samples at various temperatures: (d) 121°C (e) 135°C (f) 150°C.	108

FIGURE

PAGE

5.14	SEM micrographs of etched epoxy samples having postcure at 150°C: (a) 1 hr (b) 15 hr.	109
6.1	A typical force-elongation curve for cured epoxy sample	116
6.2	Impact strength and swelling ratio of cured epoxies as a function of NMA/EPON 828 ratio	121
6.3	Impact strength and swelling ratio of cured epoxies as a function of cure temperature.	122
6.4	Impact strength and swelling ratio of cured epoxies as a function of time of postcure.	123
7.1	Dimensionless temperature profile for different Nusselt number (a) 0.979 (b) 3.528.	131
7.2	Theoretical solution of residual stress distribution for various Nusselt numbers . . .	133
7.3	Theoretical solution of residual stress distribution for different thicknesses of slabs	134
7.4	Measured curvature and calculated residual stress for a $\frac{1}{4}$ " thick slab under ice water quenching.	142
7.5	Measured curvature and calculated residual stress for a $\frac{1}{4}$ " thick slab under liquid N ₂ quenching.	143
7.6	Measured curvature and calculated residual stress for a $\frac{1}{2}$ " thick slab under ice water quenching.	144
7.7	Photographs of fringe pattern of plates with thicknesses of $\frac{1}{4}$ ", $\frac{1}{2}$ ", $\frac{3}{4}$ " under (a) ice water quench and (b) liquid N ₂ quench	146

FIGURE

PAGE

7.8	Plots of measured total residual stress by photoelastic method for $\frac{1}{4}$ " slab under ice water quenching at various initial oven temperatures	147
7.9	Plots of measured residual stress: ● Total effect ● effect due to molecular orientation ● effect due to thermal stress ($\frac{1}{4}$ " slab, ice water quench)	150
7.10	Plots of measured residual stress: ● Total effect ● effect due to molecular orientation ● effect due to thermal stress ($\frac{1}{4}$ " slab, liquid N ₂ quench)	151
7.11	Plots of measured residual stress: ● Total effect ● effect due to molecular orientation ● effect due to thermal stress ($\frac{1}{2}$ " slab, ice water quench)	152
7.12	Calculated and measured residual stress for a $\frac{1}{4}$ " thick slab under ice water quenching.	153
7.13	Calculated and measured residual stress for a $\frac{1}{2}$ " thick slab under ice water quenching.	154
7.14	Measured residual stress for various thicknesses of slabs under slow cooling.	155
7.15	Effect of quenched epoxy sample on impact strength for various NMA/EPON 828 ratio.	159
A.1	Schematic diagram of coordinate system of a slab.	173

CHAPTER 1

INTRODUCTION

Epoxy resins contain the epoxide group which is a chemical group consisting of an oxygen atom bonded with two carbon atoms already formed in some other way. The simplest epoxide group is a three-membered ring (e.g., , to which the term α -epoxy or 1,2 epoxy is applied.

The credit for the synthesis of the material first designated as epoxy resins was shared by Pierre Castan of Switzerland in 1936 and S. O. Greenlee of the United States in 1939 (61). They synthesized these from epichlorohydrin and bisphenol A. The first commercial epoxy resins (e.g., DGEBA) were produced by the Devoe-Raynolds Company in 1947. After the late 1950's, a number of new epoxy resins different in kind from the earlier DGEBA were introduced and became commercially available such as glycidyl ethers of novolac resins, glycidyl ethers of aliphatic polyols and other glycidyl epoxy resin. The epoxies offer great versatility, low shrinkage, high mechanical strength, a good chemical resistance and outstanding adhesion. All these properties lead to their rapid growth and their use in a wide range of industries.

Polymeric materials are of two types: thermoplastics and thermosets. Unlike thermoplastics, thermosets (e.g.,

epoxy, unsaturated polyester) are generally polymerized and processed in a single operation, which transforms low molecular weight materials into a network polymer of infinite molecular weight in an irreversible process. The properties of thermosetting polymers depend on their network structure. The subject of structure-property relationship has long been a theoretical and practical interest of many previous workers (34, 64, 50, 73). In practice, common epoxy resin systems are cured under a variety of conditions where the optimum properties are not always achieved. This is probably due to the effect of constituents and compositions of uncured resins and the effect of curing cycle during the process. There are also many problems arising from the fabrication of epoxy resins which are greatly influenced by the curing conditions and fabrication processes. These problems will affect the structural and mechanical properties of products. It is well known that the curing reaction of thermosets are generally exothermic which may cause non-uniform polymerization rate throughout the material. This will give rise to both variations in distribution of crosslinking density and residual stresses. Several authors (11, 56, 72, 90) have indicated that a heterogeneous, two-phase network structure occurs during the curing reaction of thermosetting polymers which contains microgels with the size of 6 nm to 60 nm. Misra et al. (73) have claimed that the coherence of the network depends on the density strength of the connections between

the microgels formed in network structure which in turn governs its tensile strength.

All the previous mentioned factors or problems which if not realized and well-controlled will account for the poor performance properties in end use. Thus the study through the present research project is to investigate the influences of various curing conditions such as cure cycle, compositions of curing agent, postcure on the structural and mechanical properties of cured epoxies. Structural features such as degree of crosslinking, glass transition temperature and morphology will be characterized. These will be correlated with the mechanical properties such as tensile and impact strength to develop structure-property relationships. The kinetics of the curing reaction will also be investigated and compared to the results of previous workers. The second part of the research project involves the investigation of residual stresses produced during the cooling process and their influences on the mechanical properties.

CHAPTER 2

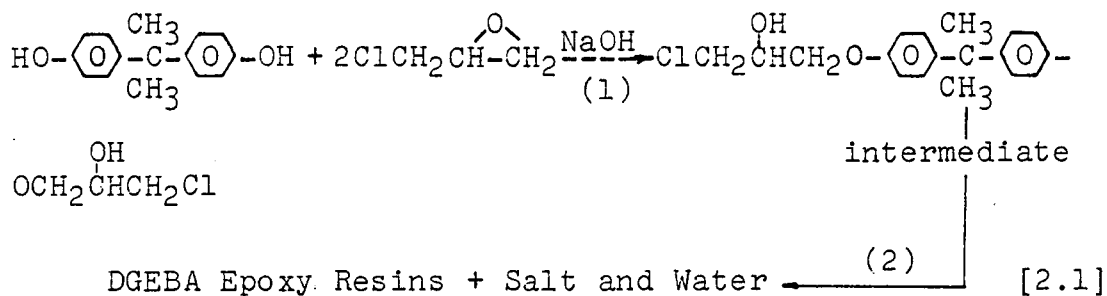
BACKGROUND AND REVIEW OF LITERATURE

2.1 Synthesis and Characterization of Epoxy Resins

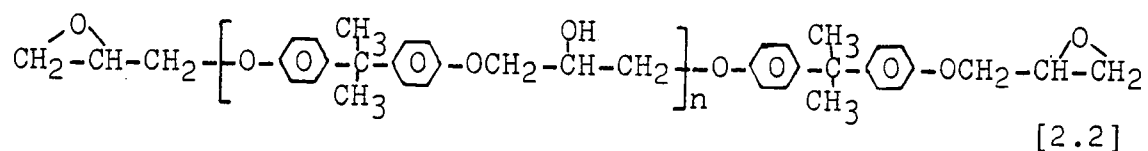
Synthesis of Epoxy Resins

There are many kinds of commercially available epoxy resins. They are synthesized by various procedures. The details of their synthesis have been reviewed by Lee and Neville (61), Potter (88), May and Tanaka (68). The most common epoxy resins (i.e., DGEBA type) which were the first developed and now still dominate the world-wide market are those based on bisphenol A and epichlorohydrin. These are also the materials of interest in this thesis.

The synthesis of DGEBA type epoxy resins involves the condensation of bisphenol A and epichlorohydrin in the presence of aqueous caustic soda. These are described by Castan (17) to occur in two steps: 1. the formation of a chlorohydrin intermediate and 2. the dehydrohalogenation of the intermediate to the glycidyl ethers which as shown:



The resulting resins can be represented by the general formula:



The number of repeated units, n , is dependent essentially on the molar ratio of epichlorohydrin/bisphenol A used during the polymerization. A series of resins may therefore be obtained, each grade consisting of a mixture of molecules differing in chain length and molecular weight. Resins of short chain length and low molecular weight (i.e., M.W. $\approx$ 370-400) are syrupy viscous liquids whereas resins of longer chain length and higher molecular weight (i.e., M.W. $\approx$ 1000) are hard, brittle and amber-colored solids at room temperature (109).

Characterization of Epoxy Resins

The characteristics of primary importance of uncured epoxy resins are the epoxide equivalent, viscosity, average molecular weight, molecular weight distribution, and chemical structure which determine both the applications of resins and the performance in their cured states.

The epoxide equivalent indicates the number of grams of resin containing 1 gram-mole of α -epoxy groups. Once the epoxide equivalent is known, the optimum amounts of curing agents and modifier required for the resin can be

calculated. Several methods have been used to determine the α -epoxy group content such as infrared absorption (20, 43) and chemical titration (22, 100). One of the chemical methods based on the reaction of a hydrogen halide with the epoxy group was widely used (22).

The viscosity of the resin is a particularly important variable in determining its processibility. Low viscosity resins are useful in casting, potting and encapsulating, whereas high viscosity or solid resins are useful in hot melt systems such as molding and fluidized bed coating systems. It has been noted that the viscosity of resins is dependent on the chain length of molecules (61). Increasing chain length results in a corresponding increase in viscosity. The viscosity is also greatly affected by the chemical structure of the epoxy resin (49). For instance, epoxies based on saturated-ring structures (i.e., cycloaliphatics) give lower viscosities than comparable resins based on aromatic-ring, and linear aliphatic epoxies give lower viscosities than comparable cycloaliphatic epoxy resins.

The average molecular weight and the molecular weight distribution are factors which determine the network structure of the cured epoxy, which accordingly governs the performance of engineering behaviors.

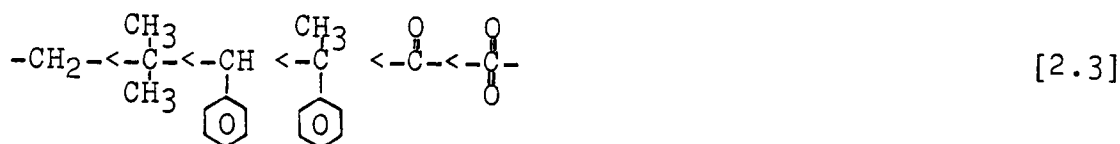
In commercial low molecular weight resins, the epoxy groups are usually separated by short spacings (3 to 10 units) which give rigidity in the network. High molecular

weight commercial resins are separated by long spacings (over 30 units). These result in more flexibility in the network (61).

The molecular weight distribution of a series of epoxy resins has been examined by Miles (71), using gel permeation chromatography (GPC), which shows broad molecular weight distribution in most commercial grades of epoxies. The broad distribution of molecular weight will result in a distribution of crosslink density in the final network. Nielsen (82) has reported that the broadening of the transition region can be attributed to this distribution effect. A study of correlation of the engineering behavior of epoxy networks and the distribution of crosslink density has been reported by Misa, Manson and Sperbing (73).

The chemical structure of epoxies is also an important parameter which determines the reactivity and functionality of epoxies (61). This in turn significantly affects the crosslink density and thermal stability of the cured epoxy. It is well known that steric factors will influence reactivity. Compact molecules containing a number of epoxy groups (such as Novalac epoxy) or bulky side chains will block reactive sites. This prevents the completion of the reaction. The effect of backbond structure and the effect of introducing substitution on the backbone have been reported by Reinking et al. (92). They showed that as the backbone became more highly substituted or less compact, the permeability to water vapor or oxygen

would increase. This was presumably because the chains are less closely spaced. Thermal stability of the cured epoxy will depend in part on the crosslink density of the resin, as well as on the chemical structure. Aromatic ether or ester links provide better thermal stability in epoxy formulations than those of the aliphatic ethers or ester links. The following order has been reported (107):



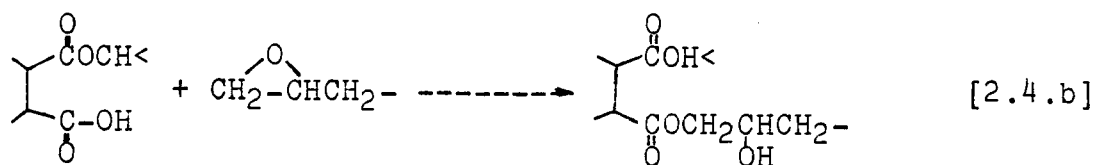
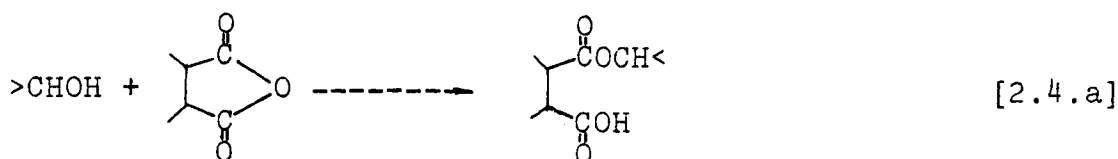
2.2 Epoxy Resin Cure Mechanisms

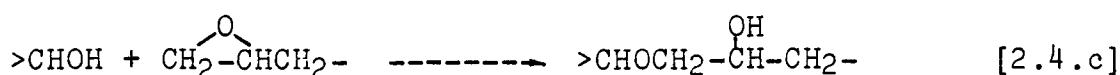
The term "curing" or "hardening" is usually used in the processing of thermosets which refer to the conversion from liquid epoxy resins and curing agents or catalysts into a three-dimensional infusible network structure through their particular chemical reactions. Cure normally proceeds through several transformations from the liquid state to gelation, rubbery state, and finally to a vitrified solid (or glassy state). Gillham (34) has examined the phenomena encountered in the thermosetting process by torsional braid analysis and proposed a generalized time-temperature-transformation phase diagram. The details of these phenomena will be discussed in the later section.

In epoxy curing systems, the curing agents fall into two types, catalytic and polyfunctional (88). The catalytic

curing agents serve as initiators for resin homopolymerization, whereas the polyfunctional curing agents are used as reactants or comonomers in the polymerization. Lewis bases such as tertiary amines, inorganic bases such as sodium or potassium hydroxide and Lewis acid such as boron-trifluoride are all in the former classification, whereas aliphatic polyamines and polyamides, aromatic polyamines and polyamides, polymercaptans, polyphenols, and polybasic acids, acid anhydrides and their derivatives are all in the latter classification. For each curing agent-epoxy systems, the cure mechanism is very complicated, and hence never be conclusively described. For details of various systems, we refer to the previous workers (57, 78, 95).

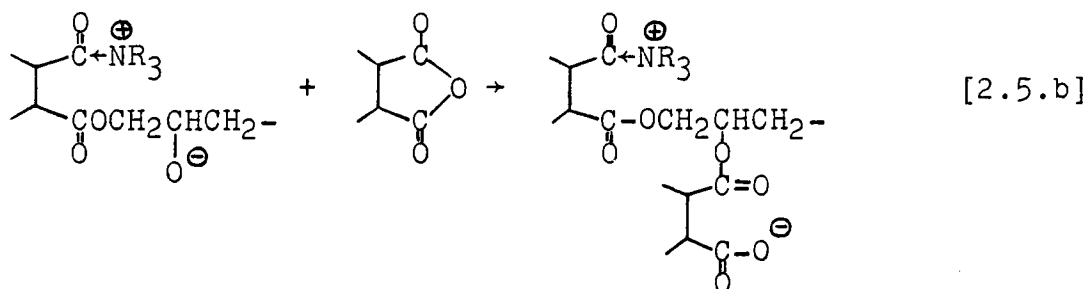
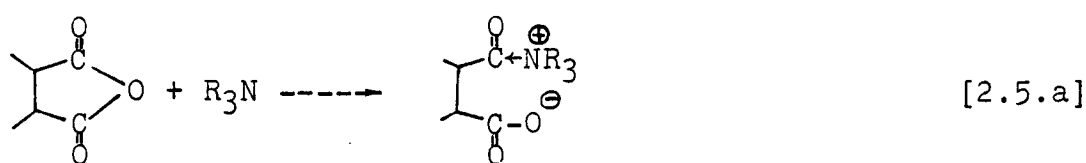
Since acid anhydride-epoxy system will be examined throughout this research, more attention will therefore be paid to this system. In the absence of catalysts, epoxide and anhydride interact only sluggishly at 200°C. Fisch et al. (29) proposed the following series of reactions:

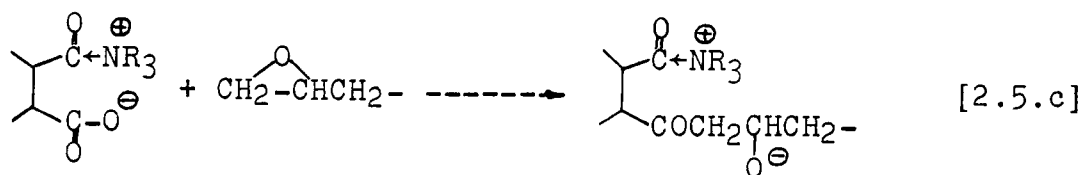




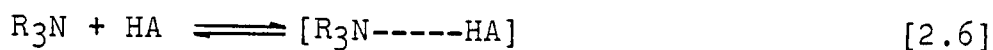
The anhydride ring is opened by a hydroxyl group (e.g., a secondary hydroxyl found on the higher molecular weight resins), forming a half-ester (2.4.a). This half-ester then reacts through its acid group with the epoxy ring forming a hydroxyl diesters (2.4.b). However, it was also found that the epoxy groups were consumed at a greater rate than could be accounted for by reaction (2.4.b) alone, so they presumed that possibly an epoxide-hydroxyl etherification reaction (2.4.c) occurs.

With the base-catalyzed system, tertiary amines are used to open anhydride rings and then act as catalysts for epoxy-anhydride reactions. Fisch (29) also proposed the cure mechanism as shown below:

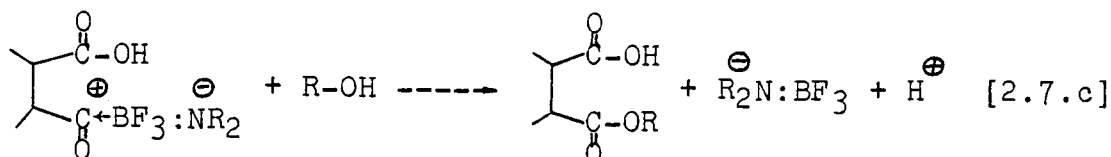
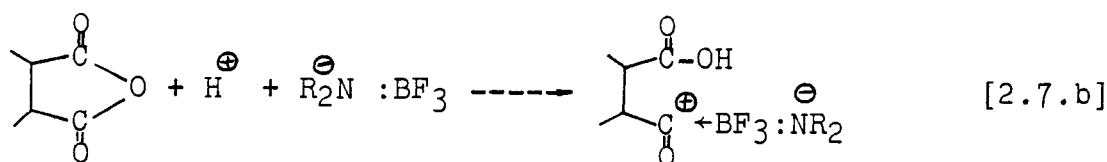
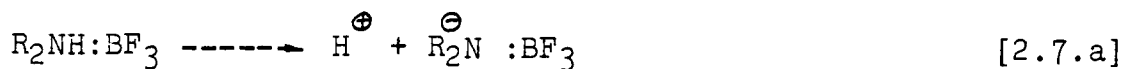




The tertiary amine opens the anhydride ring, forming the carboxylate ion (2.5.a) which in turn reacts with an epoxy group yielding the alkoxide ester (2.5.b), this anion undergoes reaction with an anhydride, resulting in the formation of the polyester (2.5.c). Following the reaction by analytical methods, Tanaka and Kakiuchi (100) concluded that with the base-catalyzed systems, etherification did not occur. Tanaka et al. (106) also proposed a catalyst activation step



in the epoxy-anhydride polymerization system to form an initiator which followed by the reaction with either the epoxy or anhydride. A first-order kinetics of the DGEBA/NMA/BDMA system has been proposed by Feltzin et al. (27). The reaction rate is first order with respect to epoxy concentration. However, Tanaka and Kakiuchi (101) claimed a second order kinetics for a variety of epoxy-anhydride systems. With the acid-catalyzed system, borontrifluoride or other Lewis acids, are acted as accelerators for the epoxy-anhydride reaction. The following mechanism has been proposed (6).



The reaction is accelerated by opening the anhydride ring, and continues with the regeneration of active groups. However, a parallel reaction of etherification also proceeds resulting from the reaction of Lewis acid catalysts alone.

In summary, the anhydride ring must be opened before reaction can occur with the epoxy group. However, the preference of reactions which occur is essentially dependent on the catalyzed effect as mentioned above. In case (1) when no catalyst is added, both esterification and etherification occur. When base catalysts are used (case 2), esterification is favored. When acid catalysts are added (case 3), etherification is promoted. However, in the anhydride epoxy system, usually etherification is undesirable since it results in unreacted anhydrides or acid monoesters being left in the crosslinked network. It is therefore the base-catalyzed system which represents the most favorable mechanism in the anhydride-epoxy reaction.

2.3 Methods to Characterize Kinetics of Curing Reaction

There are numerous methods to follow the process of cure in thermosetting materials. They include measurement of volume electrical resistivity (21), refractive index (19), infrared absorption (20, 46), dynamic mechanical properties (50, 64), heat of reaction (25, 87, 89), and gel times (39, 100). Some of these methods are not a quantitative mode of characterization due to their limitations of sensitivity and ability to discriminate between small differences in degree of cure. However, several techniques have been successfully applied in this area.

Analytical Evaluation of Epoxy Content

Analytical methods allow functional groups analysis which can be used to keep track of the extent of reaction. In the infrared analytical method (20), epoxy groups can be determined from the absorption band at 10.92 μm which is assigned to a fundamental vibration of the oxirane ring

 $(-\text{C}-\text{C}-)$. The change in the absorption spectrum at various time intervals due to the consumption of epoxy group can be related to the extent of curing reaction. By chemical analysis, the functional groups are titrated at time intervals to keep following the extent of reaction. Tanaka and Kakiuchi (100) have reported the determination of the consumption of α -epoxy groups and acid anhydride groups by

using the pyridine-pyridinium chloride and esterification method respectively.

Thermoanalytical Techniques

Differential Scanning Calorimetry (DSC) was first proposed by Fava (25) to apply to the study of the cure of epoxies with acid anhydride. Peyser and Bascom (86, 87), by the use of DSC, have also established the kinetics of polymerization of the epoxy-anhydride system. The DSC measures the rate of the exothermic evolution of the heat of reaction as a function of time and temperature. These are directly related to the kinetics of the curing reactions. There are some other methods, such as Thermogravimetric Analysis (TGA) (62), Thermomechanical Analysis (TMA) (18), which have also been applied to study the cure of epoxies, but they are only indirectly related to the kinetics of cure.

Dynamic Mechanical Techniques

There are several techniques available which allow the dynamic mechanical properties of epoxy resins to be determined during the actual curing process.

Torsional Braid Analysis (TBA) has been shown by Gillham (34, 42) to be a useful method for characterizing the curing behavior of epoxy through both the gelation and the vitrification stages of reactions. Two mechanical properties, rigidity and mechanical damping which associated with dynamic shear modulus (G') and loss tangent (G''/G'),

respectively, are obtained from the frequency and decay constant which characterize each wave. These results were used to determine the gelation time and the vitrification time as a function of temperature. The apparent activation energy can then be evaluated.

The method of Dynamic Spring Analysis (DSA) was proposed by Naganuma et al. (76). They employed a Rheovibron Dynamic Viscoelastometer with the sample coated on the small metal spring, and allowed both storage and loss modulus to be obtained as a function of time for the curing reaction. The technique is said to be well suited to the determination of the onset of gelation under isothermal curing conditions but is not useful for monitoring later stages of reaction when the resin becomes more rigid (93).

Another technique which has been reported by Mussatti and Macosko (77) is a continuous monitoring of dynamic viscosity and storage modulus in the curing reaction using the Rheometrics Mechanical Spectrometer. They indicated that a change in dynamic viscosity and dynamic storage modulus vs. cure time at various temperatures can be directly related to the apparent activation energy of the polymerization.

All the techniques mentioned previously have been successfully applied to characterize the curing reaction of thermosetting materials. In a sense each is incapable of giving the whole picture of the reaction if used alone. For instance, Differential Scanning Calorimetry provides a

measure of the heat output as a function of time which represents directly the rate of reaction, and Torsional Braid Analysis (TBA) allows determination of the gel time and vitrification time which are the two key physical parameters of the curing processes. However, the parameters determined by DSC and TBA only provide little insight into the chemical mechanism of cure.

2.4 Formation of Network Structure

Molecules of thermoplastic materials, as well known, are linear. These are generally polymerized from bifunctional reactants (i.e., A-A or A-B) through either polyaddition or polycondensation reactions. However, a three-dimensional network polymers can only be synthesized from systems containing multifunctional (>2) reactants, such as $\begin{smallmatrix} A \\ \diagup \diagdown \end{smallmatrix} A + B-B$. During the reaction, the low molecular weight prepolymers firstly react with monomer molecules such as curing agents to form numerous branched molecules. As noted by Flory (30) through further reaction, a critically branched state is reached, which is the so called gel point. This corresponds to the incipient formation of branched molecules of theoretical infinite molecular weight. Finally a network is developed by the intramolecular reactions of branched molecules and becomes one giant molecule. The development of the network is schematically represented as in Figure 2.1 (34).

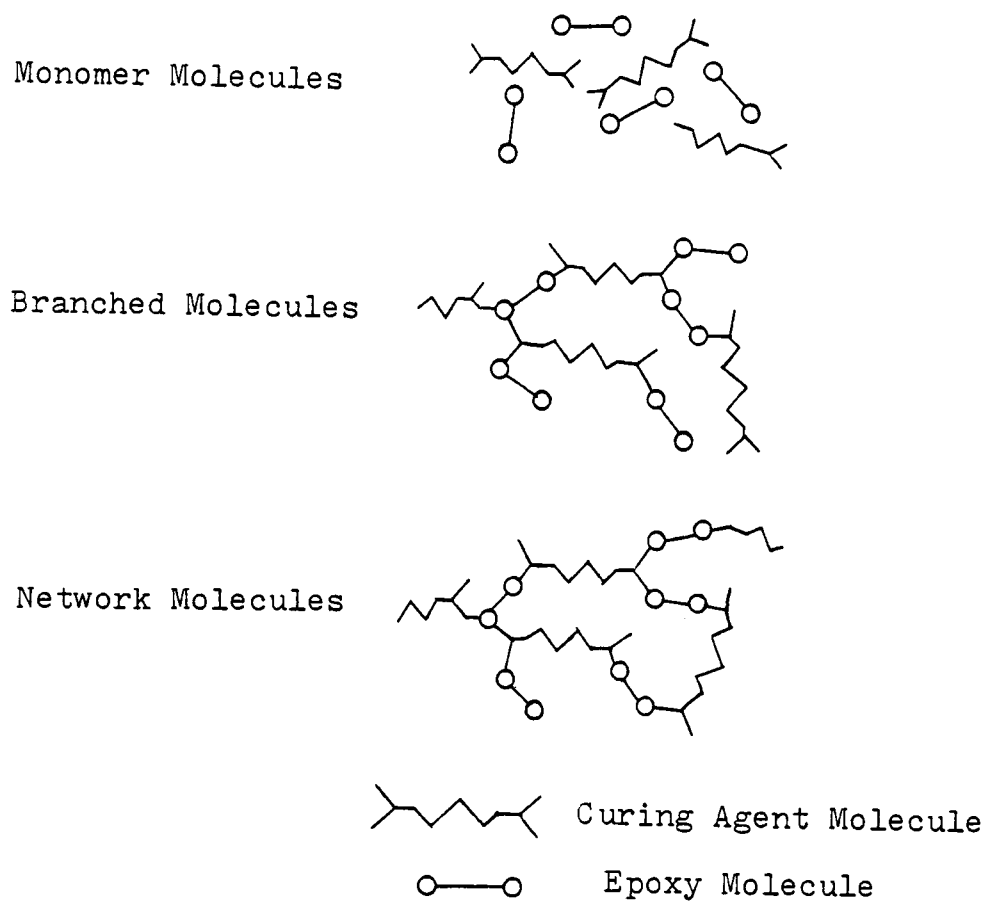


Figure 2.1. Schematic representation of development of network molecular.

A network structure can be made like rubber if the segments between linked points of network are flexible, or it can be formed like a glassy solid if the network is highly crosslinked. In a highly crosslinked network structure, when the segments of network are immobilized due to further crosslinking reaction, the network will then become vitrified. This vitrification can retard further reactions, therefore further reaction can take place only if the cure temperature is increased.

Gordon, Ward and Whitney (38) have noted that the network forming processes can generally be divided into three stages: 1. reaction rate control, 2. selective diffusion control of some component steps, and 3. complete diffusion control of all steps. In the early stage of polymerization, the reaction occurs completely through chemistry without diffusion control. The second stage of network formation, when the gel point is reached, is governed partly by diffusion control and partly by chemistry which assumes that some small molecules free from crosslinks to another primary chain can diffuse sufficiently freely through the gel network. In the third stage of the network forming process, when crosslink formation has raised the glass transition temperature up to the vicinity of the cure temperature, all component chemical steps of further reaction are controlled by segmental diffusion rather than by chemistry.

Crosslinked polymer networks are generally considered as homogeneous three-dimensional structures. However, this has been quite controversial for many years, because if the network were regarded as a continuum, its strength should theoretically be about one hundred times higher than that presently being observed (66). Many investigators have argued that polymer networks consist of inhomogeneous network structures. They have suggested either inhomogeneities of crosslinking density in the polymer network (18, 23) or the presence of two phases in the network structure (50, 54). These inhomogeneities have been attributed to incompatibility or to non-optimum curing conditions (47), but have also been proposed to be an inherent feature of all thermosetting systems (56).

In considering inhomogeneities of network structure, several previous investigators have proposed models to represent the mechanism of network formation. Bobalek et al. (11) firstly suggested that there were some molecules with infinite networks formed prior to physical gelation and dispersed in a continuous phase of low molecular weight in the early stage of polymerization. These dispersed molecules are termed as microgels. Solomen et al. (97) also showed that the functional groups in the microgel particles exhibited greatly reduced reactivity, since they are no longer in the same phase as the other reacting entities. From studies of chemical effects on the ultimate properties of polymer network in the glassy state, Labana et al. (56)

pointed out that ultimate properties were remarkably sensitive to slight variations in chemical composition and network topology. They developed a statistical theory based on configurational restrictions which provides a general mechanism of formation of crosslink density inhomogeneities. The mechanism predicted formation of spherical entities, "gel balls," formed long before the gel point of the mixture was reached. They also indicated that the excessive intramolecular reactions within the gel balls exhausted the amount of available crosslinking agent and causes a deficiency in crosslink density in the region between the gel balls which will affect the coherence of the network and ultimate properties of polymers. The resulting network can be represented schematically as in Figure 2.2. A similar model has also been suggested by Kuhn (55). Recently, Misra et al. (73) have proposed a mechanism which comprises a synthesis of the mechanisms proposed by Bobalek et al., Solomon, and Labana et al. They considered that the formation of network took place in three sequential steps: formation of the primary microgels, formation of the secondary microgels and formation of the macrogels. They also indicated that the secondary microgels and the macrogels were not completely coherent. The proposed model is represented as in Figure 2.2.

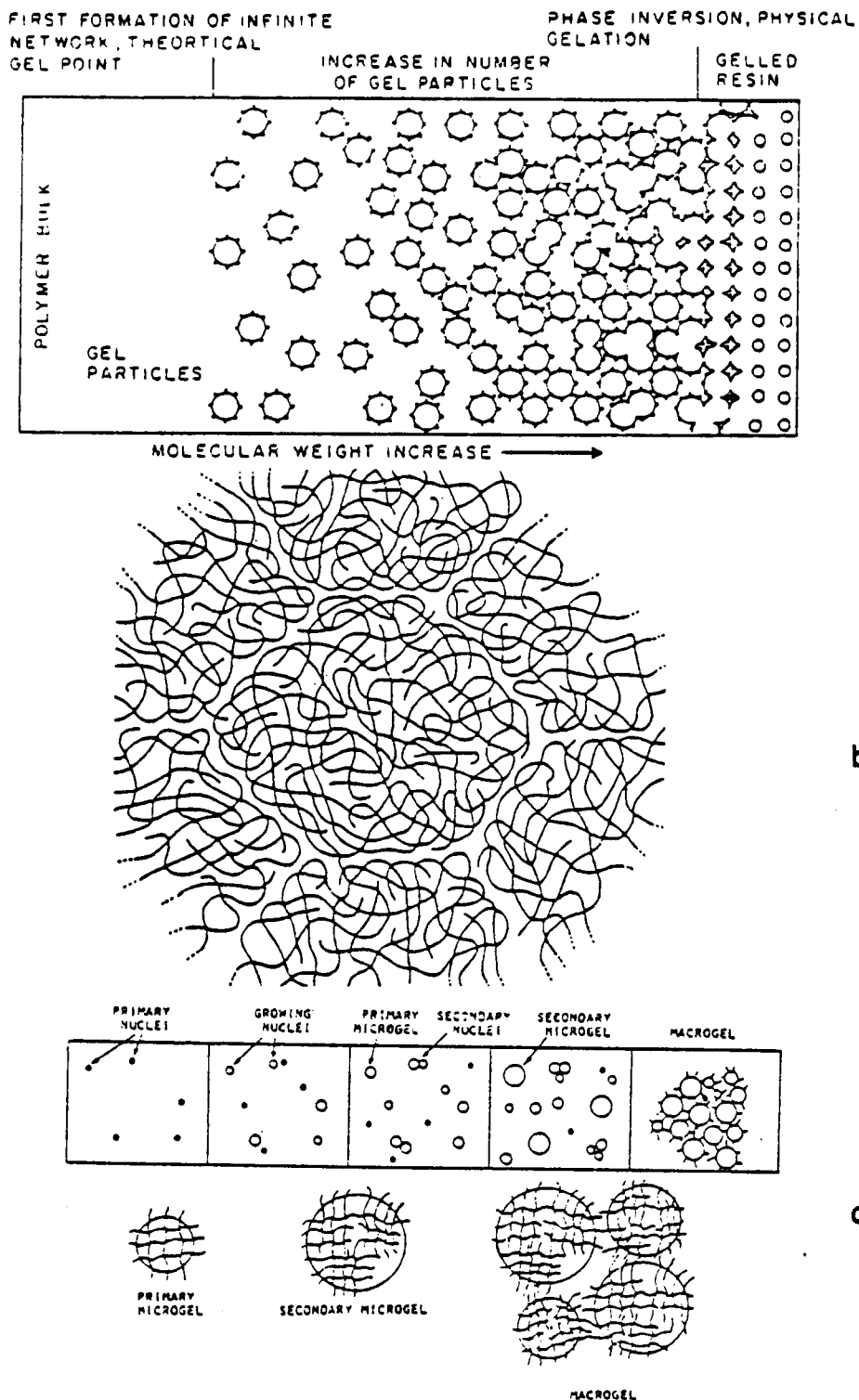


Figure 2.2. (a) Proposed model for gelation process by Bobalek et al. (b) Proposed formation for a gel ball by Labana et al. (c) Proposed model for network formation by Misra et al.

2.5 Effect of Characteristics of Constituents and Stoichiometry on Formation and Properties of Network Structure

The network structure of highly crosslinked polymer and its ultimate properties are greatly dependent on the molecular weight and molecular weight distribution of resins, the functionality and the stoichiometry of reactants.

Labana et al. (56) have widely investigated effects on the crosslinking density and tensile properties. They showed that the elongation to break and the tensile strength vary considerably with changes in molecular weight of resins, their functionality and stoichiometry of curing agents, but the same factors have little effect on the tensile modulus of the networks in the glassy state. The crosslinking density changes with the functionality and chemical structure of resins and curing agents. The ultimate elongation increases with increasing crosslinking density in the glassy state which is contrary to that of observed behavior in the rubbery state.

The effects of these factors on the network morphology of epoxy have also been studied by Misra et al. (73) from Scanning Electronic Microscopy. The SEM results showed that the dimple sizes observed on the etched surface increased with deviation from equivalent stoichiometry and there was also a marked difference in morphology observed

in networks when prepared from liquid resins as compared to those from solid or semi-solid resins (i.e., higher molecular weight of resins), the shell and core-type structures were present in samples from solid and semi-solid resins.

With thermoset resins, creep and dynamical mechanical properties can also vary a great deal, depending on the stoichiometry, the degree of crosslinking density and the morphology of network structure. Kim et al. (51) have studied the influence of stoichiometry on the creep behavior. The stoichiometric variation will vary the crosslinking density and morphology of network, therefore influencing their creep and dynamical mechanical behaviors. They indicated that the temperature dependence of shift factors for highly crosslinking density networks did not follow the WLF equation but rather were Arrhenius-type relationships (i.e., the data could be represented over the entire temperature range by plotting the shift factors against $1/T$). Kitoch and Suzuki (53) and Kaelble (48) also showed that the William-Landel-Ferry (WLF) equation was only applicable to networks with less crosslinking density.

2.6 Effect of Cure History on Formation and Properties of Network Structure

The cure history of crosslinked polymers is one of the most significant factors which greatly predominates the final network structure and properties in the practical applications. Some studies in investigating and developing

of cure history of thermosets have been reported in the early work on the dynamic mechanical properties of epoxy by Lewis and Gillham (65). Recently, Gillham and his co-workers (34, 64) have extensively investigated the cure behavior of epoxy by using Torsional Braid Analysis (TBA). They proposed a generalized time-temperature-transformation diagram which is shown in Figure 2.3. The diagram shows that three distinct phases are encountered in the curing process, which are liquid, rubbery and glassy states. As polymerization and crosslinking proceeds at certain cure temperatures, the resin will pass from a liquid through gelation into a rubbery state, then if the segments of network are immobilized by further chemical reaction (i.e., crosslinking density increase), the structure of network will therefore change to a glassy (vitrified) state. Since once the curing material vitrifies, the reaction will stop and a full cure will not be possible. This is the reason why the material usually needs the postcure for obtaining optimum properties.

Gillham et al. (64) also pointed out that the location of the thermal cure path during the cure cycle is very important since it will lead to different molecular networks in the cured material and so to different material behaviors. The general trend was also observed that the highest T_g is obtained for the lowest cure rate. They indicated that if the cure reaction was too rapid, the resulting network was less highly crosslinked.

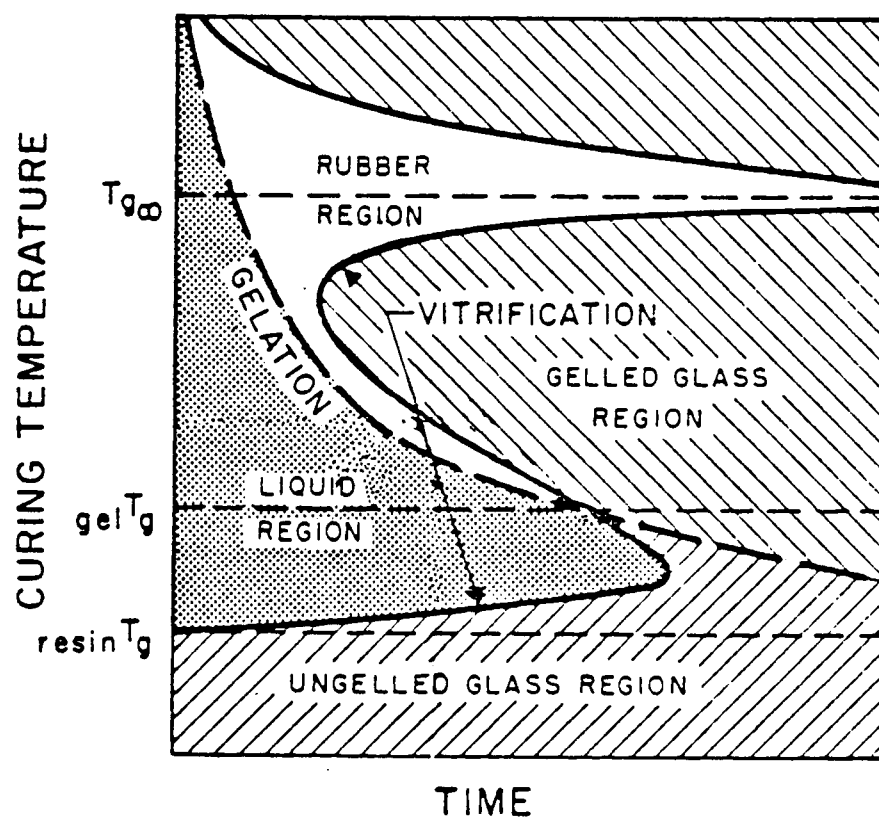


Figure 2.3. Time-temperature-transformation diagram for the thermosetting process.

Source: J. K. Gillham, Polym. Eng. Sci., 19, 676 (1979).

2.7 Characterization of Structural Properties of Cured Epoxies

Degree of Cure

The degree of cure is referred to the extent of consumption of the reactive groups during the reaction. This has been frequently used to index the degree of crosslinking (61). However, Dannerberg (20) has pointed out that the determination of the degree of cure is not satisfactory as the sole means of evaluation of the crosslinked network of thermosetting systems, because the values obtained in this way do not necessarily agree with the performance of the cured resins.

In general, complete cure is seldomly achieved due to the trapping of reactive molecules in the network at the vitrified state. These uncrosslinked or unreacted molecules embedded in the network have been proposed to become defects and flaws which will create rupture of weak regions during the network formation (5). Several investigators have reported that the degree of cure can be improved either by postcuring at a temperature higher than the original cure temperature (50, 64), or by employing a small proportion of nonreactive dilutents (105) which serve to enhance the mobility of segments.

Degree of Crosslinking

Crosslinking is the coupling of the molecules into a three-dimensional network through reactive sites. The

extent of crosslinking can be influenced by the functionality and the chemical structure of reacting materials (61, 67). The crosslinking will increase the glass transition temperature. A number of studies have been made to relate the degree of crosslinking to the shift of T_g (50, 73, 82). The crosslinking has little effect on the shear modulus of polymers below T_g , but at temperatures above T_g , the shear modulus is strongly dependent upon the extent of crosslinking (50). Nielsen (82) and Misra et al. (73) have claimed that increasing crosslinking results in increasing compressive modulus, creep resistance, hardness and Izod impact strength. However, increasing the crosslinking density will also result in decreasing resistance to crack propagation and increasing brittleness (15). Theoretically, one would expect tensile strength to increase with increasing crosslinking density; however, in some cases, the decrease in strength was also found (82). This has been presumably due to submicroscopic cracks developing from internal stresses which result from shrinkage or thermal changes, but nevertheless very little evidence or information is presently available.

It has been reported that crosslinking has a profound effect on other physical properties such as specific volume (35), thermal coefficient of expansion (32), thermal conductivity (82) and the swelling of polymers in liquids or vapors (50, 73). The broad distribution of molecular weight of resins results in the distribution of crosslinking

density. Their effects on the glass transition temperature and the characteristic creep time have also been reported by Misra et al. (73).

Glass Transition Temperature

Glass transition temperature is referred to the softening temperature in the highly crosslinked polymers, because the polymers do not apparently exhibit a sharp transition as that found in the thermoplastics (61). The glass transition temperature shifts progressively as the curing reaction proceeds. Generally the glass transition temperature of a crosslinked polymer can be affected by the degree of crosslinking (50, 82), chemical structure of reactants (68), curing temperature (74), and compositions of constituents (10). In most systems, Nielsen (82) has indicated that T_g exhibited in a complicating way. He proposed that the shift in the T_g was made up of two linearly independent effects, one is the degree of crosslinking and the other is the copolymer effect due to the curing agent. The crosslinking effect always increases T_g , while the copolymer effect can either increase or decrease T_g depending on the chemical nature of curing agents. Gillham (64) has reported that the glass transition temperature is greatly influenced by the thermal history of cure. The glass transition temperature of the system after isothermal cure is equal to the cure temperature. He also mentioned that the free volume of specimen increased as T_g increased.

This has been presumably a result of the glassy state being further from equilibrium at room temperature the higher the T_g . Therefore, it results in the decrease of density.

Morphology

Morphology has become a subject of interest recently. Many investigators (11, 56, 72, 90) have proposed that the curing reaction of a highly crosslinked polymer does not result in a homogeneous network structure, but a heterogeneous two-phase network occurs. They considered the network as a composite with highly crosslinking density phase embedded in a low crosslinked matrix. The morphological inhomogeneities of network could account for the low tensile strength of thermosets (56, 72). This discrepancy of low tensile strength has been presumably due to the incoherence of network structure.

The general model proposed for the mechanism of network formation has been discussed in the previous section. The size of microgels from several investigators seems not quite in accord with each other. Two levels of size have been reported in the literature, one ranging from 6 nm to 60 nm and the other ranging from 20 μm to 200 μm (72). Labana et al. (56) have indicated that the size of microgel varies with the molecular weight and reactivity of polymers. For instance in epoxy resins, the reactivity increases with the number of hydroxyl group present in the polymer chain. Misra et al. (73) have reported that an increase in the

molecular weight of epoxy would not only reduce its diffusivity but would also increase its reactivity. This combined effect resulted in a small size of the microgel. The size of microgels strongly affected by the foreign substrate and inclusions have been reported by Raich and Koustky (91). They observed a considerable increase in nodular size very near a glass-epoxy interface. The curing condition, as postulated, should also play an important role in affecting the homogeneity of network structure, but sufficient experimental evidence is so far not available.

2.8 Methods to Characterize Structural Properties of Cured Epoxies

Crosslinked network can have a great variety of structure. It is important to have techniques to characterize these structural parameters, such as crosslink density, glass transition temperature, degree of cure and morphology. Methods of studying network structure of crosslinked polymers are summarized below.

Chemical Methods

The infrared analytical method for the determination of epoxy groups in cured epoxy was used by Herzberg et al. (43). The absorption spectrum associated with oxirane ring ($\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ -\text{C}-\text{C}- \end{array}$) changes progressively when the curing reaction is proceeding. The degree of cure is calculated from the residual epoxy content. Another method to determine the

epoxy content was carried out by Tanaka and Kakiuchi in studies of kinetics of epoxy-acid anhydride system. They used the pyridine-pyridinium chloride method to titrate the epoxy content, and then to determine the extent of cure.

Swelling Method

Swelling method is quite successful to characterize the crosslinking density of lightly crosslinked polymer such as rubber or polymer above T_g . However, in the case of highly crosslinked polymer, Kenyon and Nielsen (50) have indicated that the swelling theory does not hold quite well, because the swelling is less than expected. Although the swelling method has this drawback, the generalization of theory still holds, and then the method is still quite often being used to characterize the network structure of highly crosslinked polymer.

Dynamic Mechanical Method

The dynamic mechanical measurement is a useful method to study the extent of crosslinking as functions of time and temperature (50, 64). The damping peak and the drastic drop in the shear modulus occurs at about the glass transition temperature. An empirical equation has been proposed by Nielsen (82) to estimate the degree of crosslinking for highly crosslinked polymer from the dynamic mechanical data obtained well above T_g is

$$\log_{10} G \approx 7.0 + \frac{293d}{Mc} \quad [2.8]$$

where d is the density of the polymer and M_c is the average crosslinking density. The dynamic mechanical methods have also been widely used by Gillham et al. (64) to measure the glass transition temperature and characterize the curing behavior during reactions.

Differential Scanning Calorimetry

Not only can the differential scanning calorimetry be used to characterize the kinetics of curing reaction, but can also be used to measure the glass transition temperature of the cured polymer. In general, T_g can be related to the degree of crosslinking. Thus the method can become a rapid and a useful way to study the crosslinked network structure.

Electron Microscopy

The morphology of network structures have been widely investigated by using electron microscopy (56, 72, 91, 110). Both the scanning and the transmission electron microscopy have been used. A fracture or etched surface can be examined in the SEM, while the fine structure can be examined under the TEM using carbon-platinum replicas of the sample surface.

2.9 Characterization of Mechanical

Properties of Cured Epoxies

A large number of different resins, curing agents, dilutents, etc. available has been made possible to the

preparation of cured epoxies with different properties in the industrial uses. They can be made highly flexible or hard and brittle, they can have high thermal stability or not. However in addition to the exact formulations for every specified use, the properties of cured epoxies has been reported associated with the composition of constituents and the thermal history of the cure cycle.

Many investigators have studied the effect of stoichiometry of reactants on the mechanical properties such as tensile properties and impact strength. Bell (10), Kim et al. (52), and Labana et al. (56) have studied the effect of M_c on the impact and tensile strength. Bell and Kim et al. reported that the impact strength increased as the molecular weight between crosslinks, M_c , increased, but the impact strength dropped as the M_c went over 1000. They also indicated that tensile properties such as ultimate tensile strength, elongation to break and Young's modulus were insensitive to M_c . The effects of stoichiometry of reactants and dilutents on the viscoelastic behavior of the amine-epoxy system have been investigated by Whiting and Kline (105), and Kim et al. (52). The effect of cure temperature on the tensile properties was reported by Morgan and O'Neal (74). They showed that the tensile properties are relatively insensitive to postcure, but a slight decrease with increasing cure temperature. The effect of crosslink density distribution on the mechanical properties of cured epoxies has been investigated by Misra et al. (73).

They indicated that the impact strength, tensile properties and the swelling were not affected by the distribution of crosslink density.

2.10 Residual Stresses

Residual stresses are stresses which permanently exist in a specimen in absence of external loading. They may be produced from the volumetric shrinkage on vitrification which gives rise to skin-core structure with built-in curing stresses during curing reactions (44). They may also arise from the inhomogeneous cooling which are responsible for thermal stresses.

Studies of residual stresses in metal or glass have had a long history (12, 24, 79, 104), since many applications were employed in extending the fatigue life of them by purposely introducing the specimen with surface compressive residual stresses. Recently studies of residual stresses in plastics have become of increasing importance in applications (14, 69), e.g., residual stresses can be frozen-in in injection molded parts when a hot melt is filled into a cold mold cavity (37). Han (41) has indicated that the quenching stresses sometimes relieve themselves by producing bubbles or sink marks in parts. An asymmetric residual stresses profile can arise after extrusion in the extruded sheet, which will lead to a warpage of the sheet (14), or in laminating process of FRP, the residual stresses associated with restrained shrinkage will distort or damage

the parts (84). Sc and Broutman (96) have studied the effect of residual stresses in polycarbonate and PMMA which results from quenching on their mechanical properties. It was noted that the residual stress can increase the notched impact strength of PC and PMMA because crazes were suppressed by residual compressive stresses near the surface of specimens which resulted in increasing the critical craze initiation stresses. The contractive stress of an amine-epoxy resin system occurred during the curing process was also investigated by Igarashi et al. (44). They have indicated that the volume contraction after gelation is effective in generating contractive stresses, while contraction before gelation is not effective.

Whether the residual stress within the material is harmful or favorable, it is primarily dependent on the residual stress pattern in certain applications (104). It has been suggested that tensile surface residual stresses usually promote fracturing, while compressive surface stresses counteract it. However, in some cases, residual stresses are so high that the member fails without the need for any additional stresses. Also in machining operations, any residual stresses is unfavorable because damage can be caused by the warpage of the finished part, or distorting by the relief of residual stresses.

Theoretical Development of Residual Stresses During Quenching

The development of residual stresses of glassy solids under quenching process has been described by many previous workers (37, 45, 60, 79). During the quenching process of a slab, the initial cooling of the surface layer is generally more rapid than the interior. In a very short time, the temperature difference between the surface and midplane will reach a maximum. Then the interior cools more rapidly than the surface until the isothermal condition throughout the plate is established. Thus initially, the thermal contraction of surfaces is greater than that of the midplane. This differential contraction tends to produce tensile stresses on the surface and compressive stresses in the midplane. However, in the later stage of cooling, stresses produced are of opposite sign. Generally each material in the cooling responds in different ways depending on the stress induced and the nature of the material. Now considering a thermoelastic solid (i.e., solid with elastic properties independent of temperature), stresses induced from two stages are cancelled by each other. Therefore no residual stresses will be produced, however, if elastic properties of solid are temperature dependent or the initial temperature is sufficiently higher than the softening temperature of solid. Most of the stresses induced initially tends to relax at high temperature, while stresses induced in the later stage will

remain. Thus a distribution of permanent stresses forms in the slab, with the compressive stresses on the surface balanced by tensile stresses in the interior.

Mathematical analysis of thermal stresses during cooling was firstly explored by Clerk Maxwell (67) early in 1850. He indicated that stresses induced tends to disappear at a rate depending on stresses themselves. He also pointed out that the time to relaxation is small in a fluid state and it will take longer in a solid state. Adams and Williamson (1) have firstly attempted to calculate the tempering stress in a glass plate. In the study of tempering glass, Bartenev (7) proposed a simple model to describe the thermorheological behavior of glasses. He considered that the glass above T_g behaves like a fluid being incapable of sustaining any shear stresses, but below T_g it behaves like a perfect elastic solid. With this simplification, he could quantitatively predice a parabolic law of residual stresses distribution in the tempered glass. A similar assumption was also made by O'Rourke and Saenz (83). They have developed a mathematical theory of residual stresses based on this simple model of symmetrically quenched spheres and cylinders in terms of relative retardation. Later on, Aggarwala and Saibel (3) presented more rigorous analysis of tempering stresses in an infinite glass plate. They specialized in the so-called Maxwell model applying it to the calculation of residual stresses. In this model, the viscosity assumed is infinite

below a critical temperature and zero above it. This model is essentially similar to the Bartenev's model. With this model, they expressed the stress-strain relation in the form of:

in shear response

$$\frac{\partial S_{ij}}{\partial t} + \frac{1}{\tau} S_{ij} = 2G \frac{\partial \lambda_{ij}}{\partial t} \quad [2.9]$$

in dilatational response

$$\tilde{\sigma}_{kk} = 3K(\tilde{\epsilon}_{kk} - 3 aT) \quad [2.10]$$

where

$$S_{ij} = \sigma_{ij} - \frac{1}{3} \sigma_{kk} S_{ij}$$

$$\lambda_{ij} = \epsilon_{ij} - \frac{1}{3} \epsilon_{kk} S_{ij}$$

$$G = 2G_0 \exp(-t/\tau)$$

$$\tilde{\sigma}_{kk} = \sigma_{11} + \sigma_{22} + \sigma_{33}$$

$$\tilde{\epsilon}_{kk} = \epsilon_{11} + \epsilon_{22} + \epsilon_{33}$$

$$a = a_0 + a_1 t$$

$$\tau = \text{the relaxation time defined as } \eta/G$$

and the equation of equilibrium is

$$\frac{\partial}{\partial x_j} \sigma_{ij} = 0 \quad \sigma_{ij} = \sigma_{ji} \quad [2.11]$$

which must be satisfied at all points throughout the volume. Since no external forces applied, the boundary condition is given as

$$\int_0^L \sigma_{22} dx_1 = 0 \text{ and } \int_0^L \sigma_{33} dx_1 = 0 \quad [2.12]$$

The temperature field in the cooling plate is governed by the equation of heat conduction:

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x_1^2} \quad [2.13]$$

which satisfies the initial condition and the boundary condition

$$T = T_0 \quad \text{at} \quad t < 0 \quad [2.14]$$

$$\frac{\partial T}{\partial x_1} = -\beta T \quad \text{at} \quad t > 0, x_1 = \pm L \quad [2.15]$$

where

$$\alpha = \text{thermal diffusivity, } \alpha = \frac{k}{C_p \rho}$$

$$T_0 = \text{the initial temperature}$$

$$\beta = \text{Nussult number, } \beta = hL/k$$

With the assumptions of the plate being symmetrically cooled, the stress in x_1 parallel to the direction of thickness being negligible and stresses in x_2, x_3 directions

being a function of x_1 only, they solved these equations and represented the solution in the form of:

$$\sigma_{22}(x_1, \infty) = \frac{E}{1-\nu} \left[a_0 T_{cr} \left(1 - \frac{\sin nL}{nL} - I_1 \right) + \frac{a_1 T_{cr}^2}{4} \left(1 - \frac{\sin 2nL}{2nL} - 2I_2 \right) \right] \quad [2.16]$$

where

$$I_1 = \int_0^{nx_1} \frac{\sin x}{\cos^2 x} \frac{\sin \frac{1}{2}(nL - x)}{\frac{1}{2}(nL - x)} \cos \frac{1}{2}(nL + x) dx$$

$$I_2 = \int_0^{nx_1} \frac{\sin x}{\cos^2 x} \frac{\sin(nL - x)}{nL - x} \cos(nL + x) + 1 dx$$

T_{cr} = the critical temperature

For small cooling rates, the equation can be reduced to

$$\sigma_{22}(x_1, \infty) = \frac{2E}{1-\nu} \left[a_0 T_{cr} n^2 \left(\frac{L^2}{3} - x_1^2 \right) + a_1 T_{cr}^2 n^2 \left(\frac{L^2}{3} - x_1^2 \right) \right] \quad [2.17]$$

Aggarwala and Saibel have pointed out that the parabolic law of the stress distribution is true only for slow rates of cooling. As the rate of cooling increases, the curve becomes steeper and steeper.

The theory of Aggarwala and Saibel is still defective on many counts. They neglected the effect of viscoelasticity and the temperature dependence of physical properties.

Lee et al. (60) have indicated that the over-emphasized subsurface residual stresses given by Aggarwala and Saibel is due to the neglect of the viscoelastic characteristic of glass. In considering the viscoelastic effect, Lee, Rogers and Woo (60) developed a theory of thermoviscoelastic stress analysis for the symmetrically cooled flat sheet problem. They assumed that the material responded to temperature change simply by a change in the time scale by a factor $4(T)$. The stress-strain relation for shear given in terms of relaxation modulus was written as

$$S_{ij}(x, \xi) = \int_0^{\xi} 2G(\xi - \xi') \frac{\partial \epsilon_{ij}(x, \xi')}{\partial \xi'} d\xi' \quad [2.18]$$

where

ξ is the reduced time expressed as

$$\xi(x, t) = \int_0^t \psi[T(x, t')] dt'$$

Assumptions which are made are the same as those of Aggarwala and Saibel. The solution for the thermal stress was given as

$$\sigma_{22}(x_1, t) = 3 \int_0^t R[\xi(x_1, t) - \xi'(x_1, t')] \frac{\partial}{\partial t} [\epsilon_{22}(t') - aT(x_1, t')] dt' \quad [2.19]$$

where

$R(\xi)$ is an auxiliary function first introduced by
Muki and Sternberg (76)

The residual stress in the viscoelastic case was thus given by

$$\sigma(x_1, \infty) = \sigma(x_1, t_1) - \sigma_e(x_1, t_1) \quad [2.19]$$

where

t_1 is the hardening time and σ_e is the elastic stress from time zero to t_1 .

The residual stress distribution can be solved by the numerical analysis of the above equations incorporating the temperature field in the plate. The procedure is very sophisticated. Details should be referred to in the literature (58, 59, 76, 98).

Methods to Measure Residual Stresses

Layer removal method. A method given for determining the residual stresses in a sheet material was developed by Treuting and Read (103), which is called the layer removal method. The method involves removing successive uniform layers of material from the surface of the test specimen and measuring the resulting curvatures. The method is based on the assumptions that the stress should not vary in the plane of the specimen but only through the thickness, and no external forces applied to the edges of the specimens.

Since the specimen deforms due to removing a layer from the upper surface to obtain another equilibrium state. Thus external forces and moments must be applied to the edges of the specimen to prevent deformation. These forces and moments are equal to the forces and moments acting on any cross section which can be represented as:

$$F_x(Z_1) = \int_{-Z_0}^{Z_1} \sigma_x(Z) dZ \quad [2.20]$$

$$M_x(Z_1) = \int_{-Z_0}^{Z_1} \sigma_x(Z) \left[Z + \frac{Z_0 - Z_1}{2} \right] dZ \quad [2.21]$$

An expression of relating the unknown stresses σ_x and the resulting curvature was derived by Treuting and Read as

$$\begin{aligned} \sigma_x(Z_1) = \frac{-E}{6(1-\nu)} \Bigg[(Z_0 + Z_1)^2 \left[\frac{d\phi_x(Z_1)}{dZ_1} + \frac{d\phi_x(Z)}{dZ_1} \right] \\ + 4(Z_0 + Z_1) [\phi_x(Z_1) + \nu\phi_y(Z_1)] - 2 \int_{Z_1}^{Z_0} [\phi_x(Z) + \\ \nu\phi_y(Z)] dZ \Bigg] \end{aligned} \quad [2.22]$$

where

ϕ_x , ϕ_y are curvatures, ν is the Poisson's ratio and E is the Young's modulus, and in case of $\sigma_x = \sigma_y$, the equation [2.22] can be reduced to

$$\sigma_x(Z_1) = \frac{-E}{6(1-\nu)}[(Z_0 + Z_1)^2 \frac{d\phi_x(Z_1)}{dZ_1} + 4(Z_0 + Z_1)\phi_x(Z_1) - 2 \int_{Z_1}^{Z_0} \phi_x(Z) dZ] \quad [2.23]$$

Photoelastic method. The optical phenomenon as well-known temporary or artificial double refraction which the science of photoelasticity is based on was first observed by Sir David Brewster in 1816. Many non-crystalline transparent materials such as glass, epoxy, phenolic and celluloid have been reported as showing these effects when they are stressed.

It was implicitly noted by Maxwell (67) the principal axes of optics at any point in the material coincide with the principal axes of stresses at the point. The stress-optical relation given by Maxwell is expressed as

$$R = \frac{2\pi ct}{\lambda}(\sigma_1 - \sigma_2) \quad [2.24]$$

where R is the relative retardation, c is the stress-optical coefficient, t is the thickness of the specimen, λ is the wavelength of light and σ_1 , σ_2 are principal stresses.

The relative retardation can be measured by a compensator and the stresses can thus be determined.

CHAPTER 3

EXPERIMENTAL DETAILS

3.1 Materials

General Characteristics

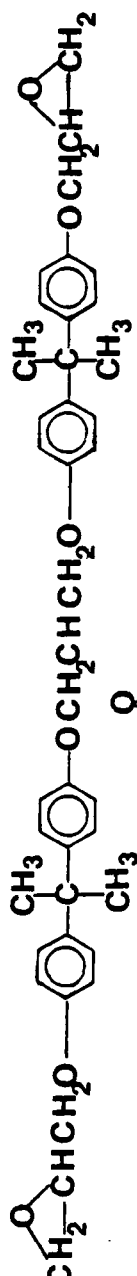
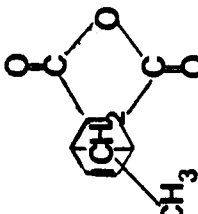
In the present research, a commercially available epoxy resin, diglycidyl ether of bisphenol A (EPON 828) and curing agent, nadic methyl anhydride (NMA), obtained from Shell Chemical Company, were studied. The EPON 828 have an average molecular weight about $370 \approx 384$ and a viscosity of about 120 centpoises at 25°C , while NMA whose chemical name is X-methyl-5-norbornene-2,3-dicarboxylic anhydride, is a low viscous and light yellow liquid. N,N-dimethylbenzylamine (BDMA) from Aldrich Chemical Company, was used as an accelerator. All materials were used as received without any purification. The structure of these materials is represented in Table 3.1.

Characterization of Material

The epoxy equivalent weight (WPE) was determined by the Hydrogen Bromide Method (22).

A weighed sample (about 0.5g) was dissolved in chlorobenzene. Add 4 to 5 drops of crystal violet indicator solution and titrate the solution with 0.1N HB_r in acetic acid to the blue-green end point of indicator. The weight per epoxide equivalent was calculated by the equation:

TABLE 3.1
CHEMICAL STRUCTURE OF REACTANTS

Compound	Chemical Structure
Diglycidal Ether Bisphenol A (EPON 828)	
Nadic Methyl Anhydride (NMA)	
Benzylldimethyl Amine (BDMA)	

$$\text{Weight per epoxide equivalent} = \frac{(\text{Weight of Sample})(1000)}{(S - B) (N \text{ of } HB_r)}$$

[3.1]

where

S: ml of HB_r used in titrating sample.

B: ml of HB_r used in titrating blank.

The properties of epoxy resin EPON 828 and NMA are presented in Table 3.2.

3.2 Characterization of Kinetics of Curing

Reaction by Differential

Scanning Calorimetry

Procedures

The kinetics of polymerization of DGEBA/NMA/BDMA systems were determined by the use of differential scanning calorimetry (DSC). A Perkin-Elmer DSC IB was used throughout the experiment.

Samples were prepared by mixing equivalents of epoxide (EPON 828) and anhydride (NMA) and stirred at slightly above ambient (25°C) temperature. The accelerator, BDMA was then added to the solution, and continued to stir for 5 minutes. About 20mg of the solution was transferred to aluminum micropans, covered and weighed. The same procedures were carried out for preparation of all the samples with varying concentrations of accelerator. A weighed sample pan and an empty reference sample pan were placed in the DSC cells, the flow rate of inert gas N_2 was

TABLE 3.2
PROPERTIES OF EPOXY RESIN AND CURING AGENT

Epoxy Resin	WPE (Weight per Epoxides)
EPON 828	190*
Curing Agent	EW (Equivalent Weight)
NMA	170**

*Epoxy resin was characterized by HBr-Acetic acid method.

**Source from Shell Chemical Company.

adjusted to about 15 ml/min. After 10 minutes at 300°k for preheat, the samples were scanned from 300°k to 500°k with various heating rates (1.25, 2.5, 5°C/min, respectively). Measurements were made by determining the power input to the sample container less that to a similar empty pan. With careful calibration of the Indium standard, the temperature and calorimeter output can be evaluated.

Data Analysis

Data were obtained from the recorder output as indicated schematically in Figure 3.1. The baselines were approximately evaluated from the DSC curve.

The total heat of reaction (area under DSC curve) will be calculated by the equation

$$\Delta H_{\text{rxn}} = \frac{(\Delta H_{\text{In}})(W_{\text{In}})(A_{\text{sample}})(R_{\text{sample}})(S_{\text{In}})}{(W_{\text{sample}})(A_{\text{In}})(R_{\text{In}})(S_{\text{sample}})} \quad [3.2]$$

where

ΔH_{In} = heat of fusion of Indium

A = area under DSC curve

W = weight of sample or Indium

S = chart speed

R = range of run

The heat of fusion of Indium is 68 cal/gm.

To analyze the kinetics of reaction from the DSC curve, the basic assumption made is that the heat of

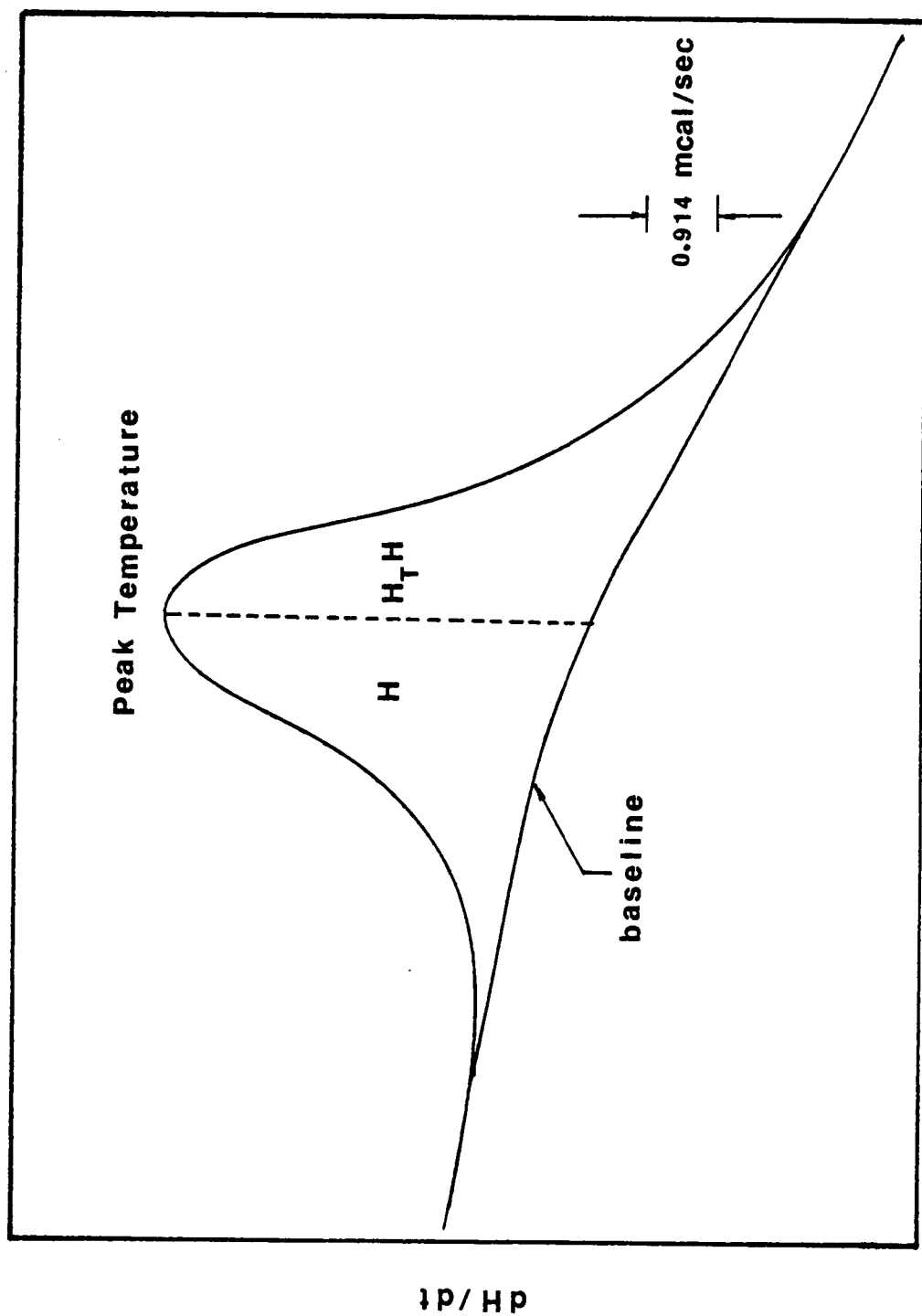


Figure 3.1. A typical DSC scan showing heat of reaction and peak temperature.

reaction evolved at any time is proportional to the number of moles of reactant consumed. So that the Arrhenius rate equation becomes (84):

$$\frac{1}{H_T} \frac{dH}{dt} = A e^{-E_a/RT} \left(\frac{H_T - H}{H_T} \right)^n \quad [3.3]$$

where

H_T : total heat of reaction (cal/gm)

H : heat of reaction at given time and temperature

E_a : Arrhenius activation energy (kcal/mole)

A : Arrhenius frequency factor

n : order of reaction.

Two approaches based on the Arrhenius equation are used to analyze the DSC data.

(a) The simplest way is when reaction order n is known or assumed, the equation [3.3] in logarithmic form becomes:

$$\log \frac{dH}{dt} \frac{1}{H_T} - n \log \frac{H_T - H}{H_T} = - \frac{E_a}{RT} + \log A = \log k \quad [3.4]$$

Then a plot of $\log \frac{dH}{dt} \frac{1}{H_T} - n \log \frac{H_T - H}{H_T}$ vs. $\frac{1}{T}$ or $\log k$ vs. $\frac{1}{T}$

should be a straight line with slope $-\frac{E_a}{R}$ and intercept $\log A$.

(b) The peak temperature at the maximum of the DSC curve shifts to a lower temperature as the heating rate

decreases. If we differentiate equation [3.3] with respect to T and let the value equal to zero.

$$\left[\frac{d \frac{dH}{dt}}{dT} \right]_{\max} = 0 \quad [3.5]$$

we obtain at the peak temperature

$$\frac{E_a}{n} = \left[\frac{RT^2}{(H_T - H)\omega} \right] \frac{dH}{dT} \left(\frac{dH}{dT} \right)_{\max} \quad [3.6]$$

where

ω : the heating rate ($^{\circ}\text{C}/\text{min}$)

so that $\frac{E_a}{n}$ can be calculated directly.

In using these analyses, it is assumed that the reaction be described by simple n th order Arrhenius equation. Such an assumption is not usually justified for a complex reaction. However, as indicated by Peyser and Bascom (86), the reaction of the system of anhydride-epoxy appears to follow this simple Arrhenius kinetics.

3.3 Characterization of Cured Epoxies

Sample Preparation

The various formulations and different cure schedules are described in Table 3.3. Series A was prepared using different compositions of EPON 828 with NMA to examine the

TABLE 3.3
COMPOSITIONS AND CURE SCHEDULES OF EPOXY SAMPLES

Sample No.	NMA/Epoxy Ratio	Cure Schedule	Sample No.	NMA/Epoxy Ratio	Cure Schedule
A-1	0.5	100°C 5 hrs precure 150°C 6 hrs postcure	B-7	1.0	163°C 6 hrs isothermal cure
A-2	0.7	same as above	B-8	1.0	177°C 6 hrs isothermal cure
A-3	0.8	same as above	C-1	1.0	95°C 2 hrs precure 150°C 1 hr postcure
A-4	0.9	same as above	C-2	1.0	95°C 2 hrs precure 150°C 2 hrs postcure
A-5	1.0	same as above	C-3	1.0	95°C 2 hrs precure 150°C 4 hrs postcure
A-6	1.2	same as above	C-4	1.0	95°C 2 hrs precure 150°C 6 hrs postcure
B-1	1.0	80°C 6 hrs isothermal cure	C-5	1.0	95°C 2 hrs precure 150°C 10 hrs postcure
B-2	1.0	95°C 6 hrs isothermal cure	C-6	1.0	95°C 2 hrs precure 150°C 15 hrs postcure
B-3	1.0	108°C 6 hrs isothermal cure	D-1	0.5	same as series A, but quenched in ice water
B-4	1.0	120°C 6 hrs isothermal cure	D-2	0.8	same as above
B-5	1.0	135°C 6 hrs isothermal cure	D-3	1.0	same as above
B-6	1.0	150°C 6 hrs isothermal cure	D-4	1.2	same as above

effect of stoichiometry. To study the effect of curing temperature, series B was prepared by varying the casting temperature in a constant composition. To investigate the effect of postcure, samples were made by changing the time of postcure, which was in series C. Finally, to study the effect of residual stresses on the mechanical behavior of cured epoxies, series D was prepared with the same condition of series A, but quenching samples in ice water when the cure finished. All the samples were prepared by casting into molds made by a machine shop (see Figure 3.2), which were cured in a compression molding machine.

Determination of Swelling

The swelling of the crosslinked materials in solvents is considered to be related to the degree of crosslinking density. A swelling agent chloroform, CHCl_3 , was used to swell the cured epoxy samples. The method for swelling measurement was involved with placing weighed samples in a desiccator which contained solvent as specified. The samples were not immersed in solvent but contacted with the vapor of solvent only. The advantage of this method is to eliminate the cracking of specimens which has been observed as the specimen is immersed in the solvent. The swelling equilibrium established rapidly and the reproducibility is good.

The desiccator is kept at a constant temperature (25°C) for 12 hours. The gain of weight of the sample was

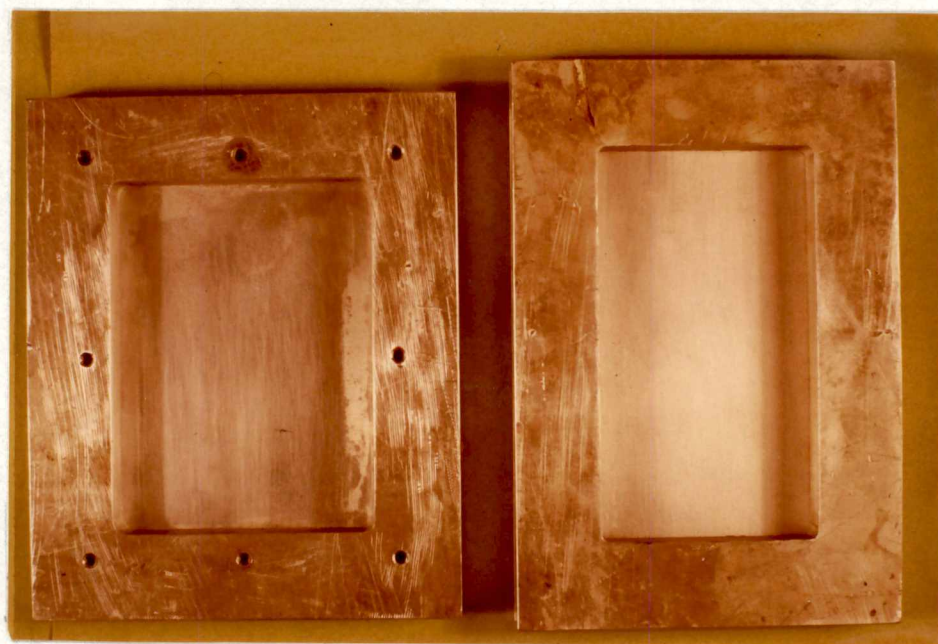


Figure 3.2. Photograph of molds for casting epoxy samples.

determined. The swelling ratio q_s was calculated by the formula

$$q_s = \frac{W_s - W_r}{W_r} \quad [3.7]$$

where

W_s : the weight of swollen sample

W_r : the weight of dry sample

The effective crosslinking density can be evaluated by employing the Flory-Rehner equation as mentioned in Chapter 2, if the theoretical formulation may be accepted and the Flory-Huggins interaction parameter χ is known.

Glass Transition Temperature Measurement

The glass transition temperature of epoxies was measured by using Differential Scanning Calorimetry. Since DSC yield a thermogram of rate of heat absorption, dH/dt , which is proportional to the specific heat of the sample. The discontinuity in the thermogram is associated with the softening point in the crosslinked networks.

The samples were finely powdered, then placed in the DSC sample pan, and were scanned from 30°C to 200°C. The transition region shown in the thermogram embraces about 30°C, so for practical purposes, the glass transition temperature is taken as the point of intersection of the extrapolated baseline at the low temperature and the tangent

to the curve at the inflection point, which is expressed as in Figure 3.3.

Measurement of Density

Density of samples were measured in the density gradient column made by Sodium Bromide--Water solution in the range of density of 1.200 to 1.250 g/cm³.

Morphology

The morphology of network structure of cured epoxy specimen were studied by using an AMR model 900 Scanning Electron Microscope. Samples were cut into small square pieces, and the surface of specimens polished. After etching the specimen in the 1M aqueous solution of chromic-sulfuric acid at 90°C for 10 hours, the etched specimens were coated on the surface with a very thin layer of gold, then they were examined under the SEM. A non-etched specimen was also examined for reference.

3.4 Measurement of Residual Stresses in Epoxy Specimen

Layer Removal Method

The measurement due to Treuting and Read (103) involves removing successive uniform layers of materials from the upper surface of the test specimen and measuring the resulting curvature as schematically shown in Figure 3.4.

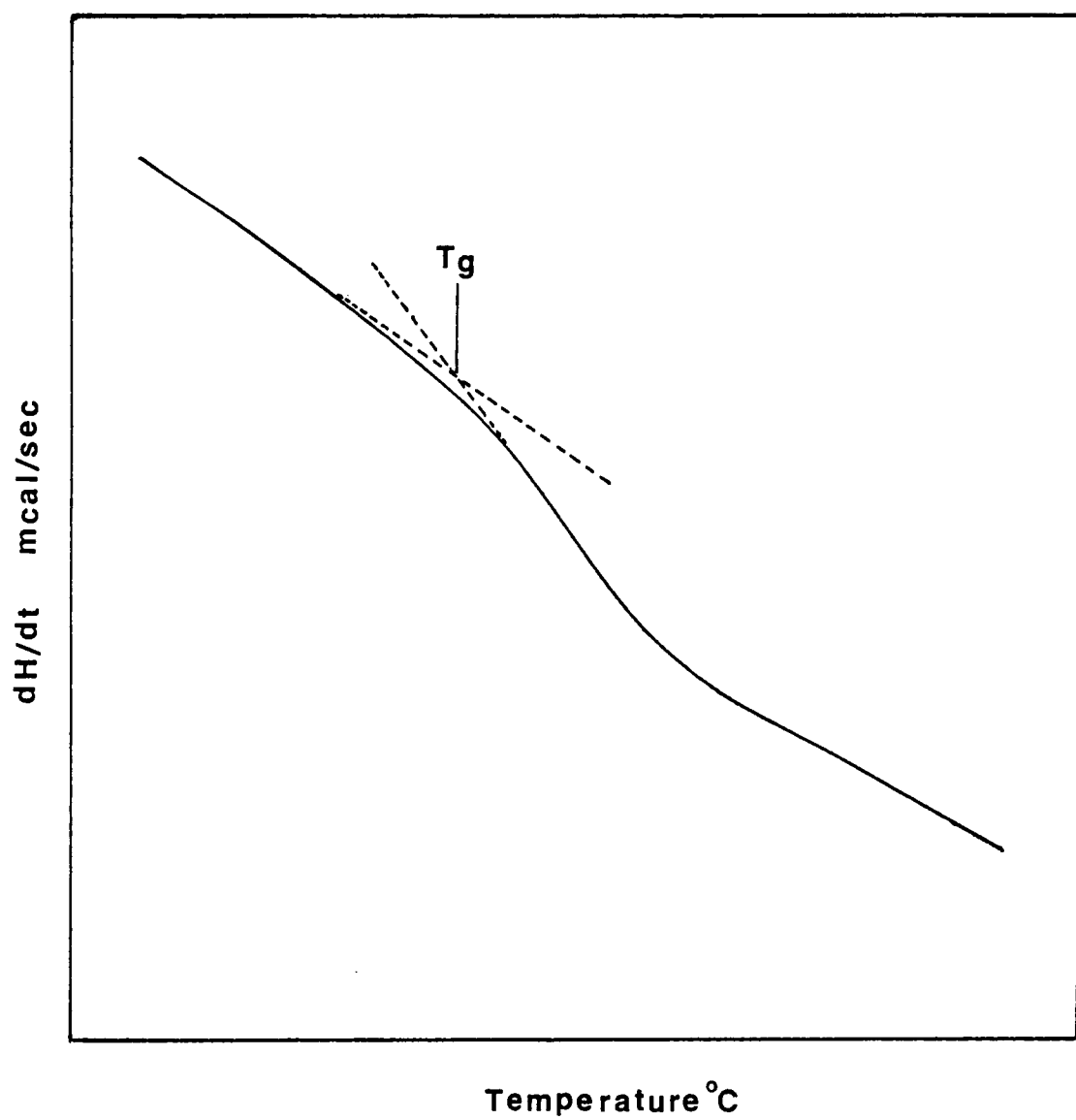


Figure 3.3. A typical DSC scan ($2.5^{\circ}\text{C}/\text{min}$) of cured epoxy showing glass transition temperature.

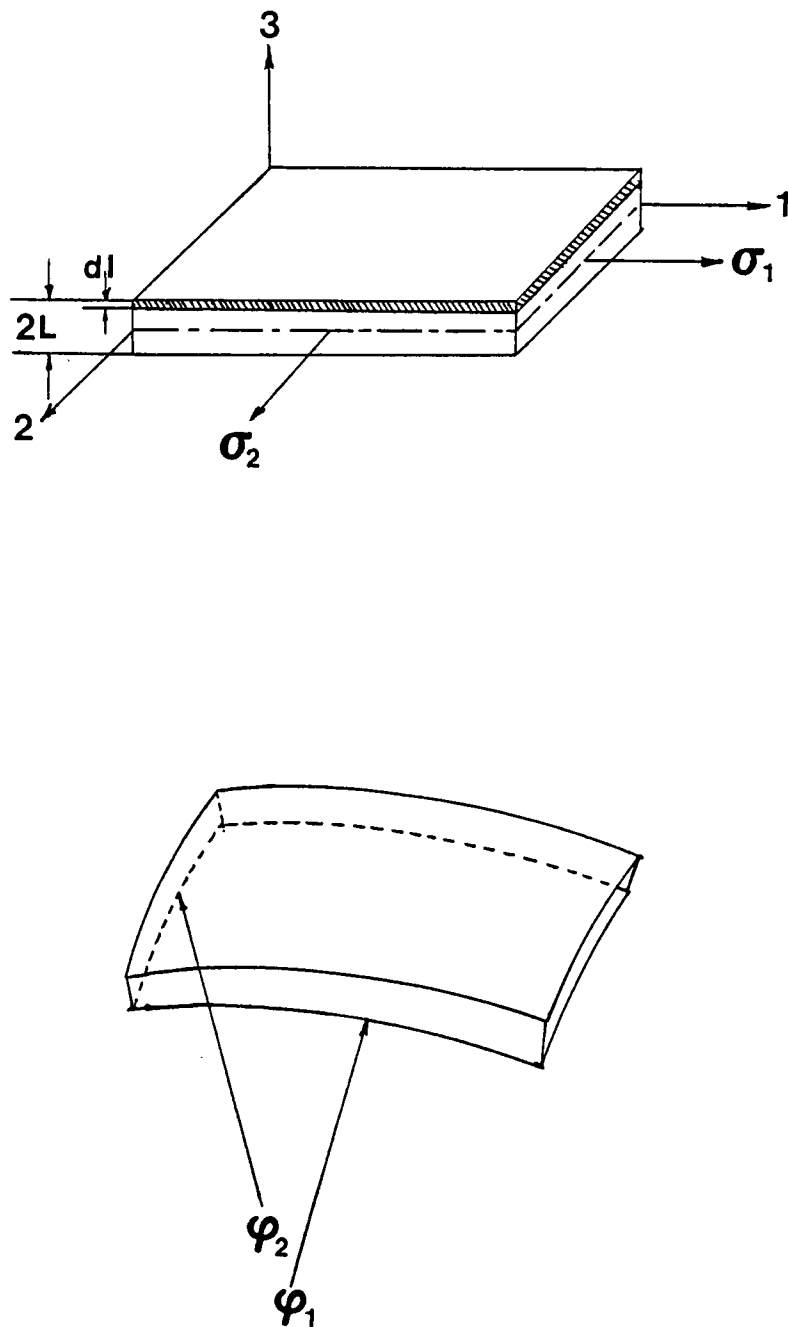


Figure 3.4. Schematic diagram for layer removal method to measure residual stress.

Quenched plate samples were prepared with thicknesses of 1/4" and 1/2". A milling process was used throughout this investigation as shown in Figure 3.5. One problem possibly occurs during the milling operation. The structural deformation induced by machining may affect the residual stresses distribution under investigation. This effect can perhaps be greatly reduced by postfinishing with fine grade sand paper.

The curvature was determined by measuring the sagitta of a chord of known length on optical microscope with a Filar Lens to measure the distance. The curvature was calculated by the equation:

$$\frac{L^2}{4} + (r - a)^2 = r^2 \quad [3.8]$$

where

L: the length of the chord

a: the distance of sagitta

r: the radius of the curvature

and the curvature is defined as

$$\phi = \frac{1}{r} \quad [3.9]$$

After five successive reductions in thickness and measuring curvatures, the curvature versus distance characteristics of the original midsurface of the plate at $z = 0$ were plotted.

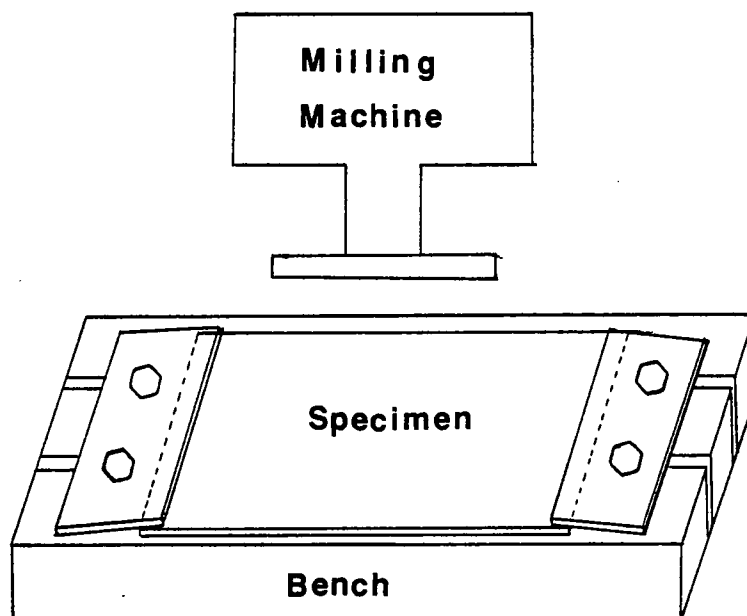


Figure 3.5. Schematic diagram of milling process for removing layers.

On the basis of Equation [2.23] shown in the previous chapter, it requires the two further functions

$$\frac{d\phi(Z)}{dZ} \text{ and } \int_{Z_1}^{Z_0} \phi(Z)dZ \text{ in order to calculate the residual}$$

stresses. Both can be obtained from the curve by graphical differentiation and integration at convenient intervals. These permit evaluation of $\sigma_x(Z)$ by Equation [2.23], and the complete stress distribution of $\sigma_x(Z)$ will be obtained.

Photoelastic Method

The distribution of residual stresses in the specimen of quenched epoxy sample were studied by using the photoelastic method. The set-up of an instrument of this method, which is shown in Figure 3.6, is similar to that of birefringence measurement.

The specimen for measurement was prepared by slicing it out of a quenched plate of sample. The specimen was then polished by a grinding wheel with the range of grinding powder from 9.5 μm to 1 μm , which gives a clearly optical transparency.

The specimen was placed on the holder. While moving the analyzer from one edge of specimen through another, the phase difference (or retardation) between two mutually perpendicular planes polarized light wave emerging from the sample was determined with a Babinet compensator. According to the stress-optical law, the stresses were calculated from the equation:

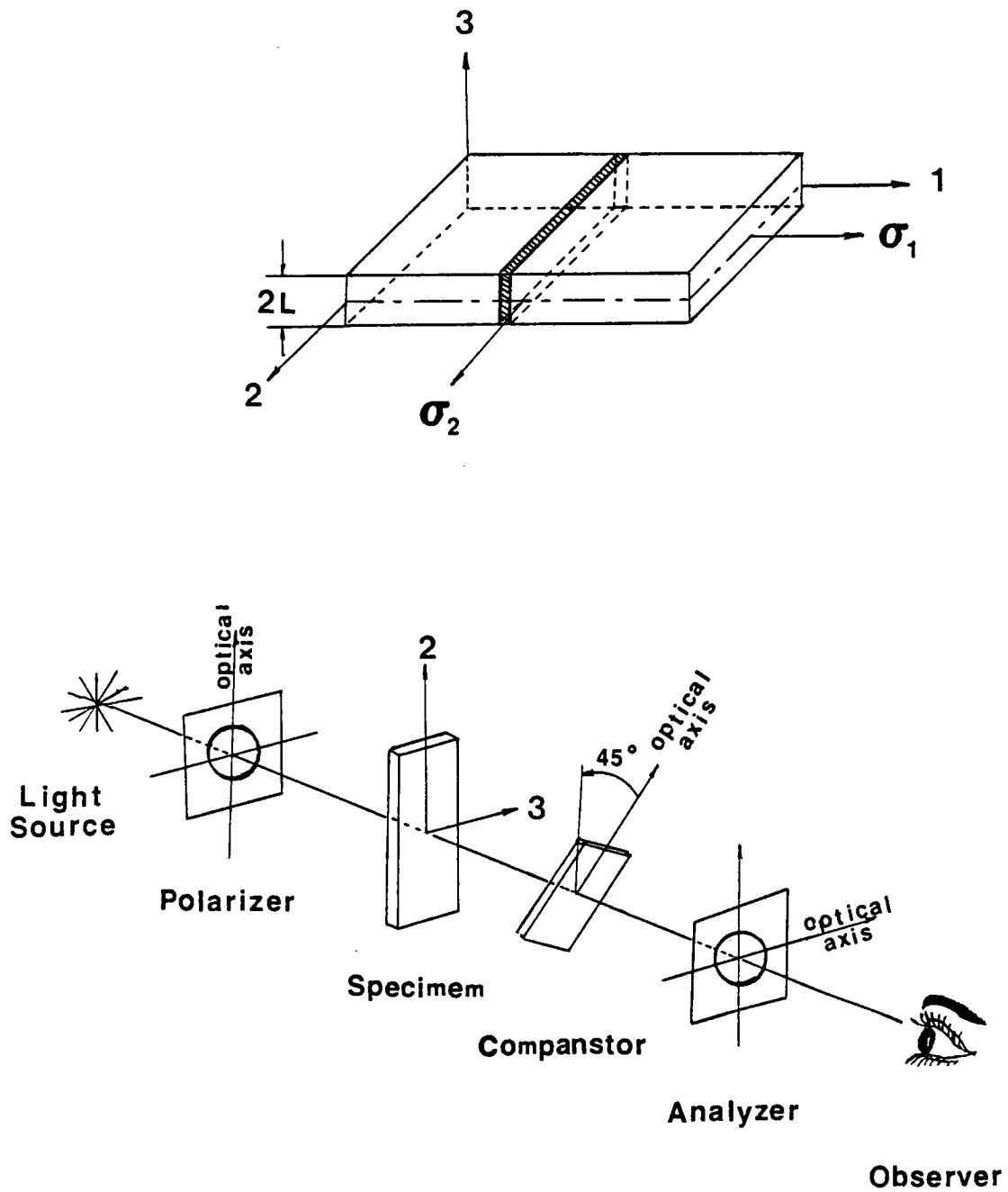


Figure 3.6. Schematic diagram for photoelastic method to measure residual stress.

$$R = \frac{2\pi tc}{\lambda}(\sigma_1 - \sigma_2) \quad [3.10]$$

where t is the thickness of specimens, c is the stress-optical coefficient, λ is the wavelength of the light and σ_1, σ_2 are principal stresses. The stress-optical coefficient of epoxy resins, c , given by Laven (63), is about $0.828 \times 10^{-12} \text{ cm}^2/\text{dynes}$.

A procedure of measuring the remaining retardation of a subslice from the original slice as shown in Figure 3.7 was also carried out. The approach will be discussed in Chapter 7.

3.5 Mechanical Properties Measurement

Tensile Testing

Tensile measurements were made by using an Instron Tensile Tester at room temperature, according to ASTM test D-638-58T, type 1.

Test specimens were prepared by cutting pieces out of a large plate and shaping them into the specified tensile bars as shown in Figure 3.8. In all cases, 5 specimens per sample were tested. The tensile tests were carried out with a crosshead speed of $0.05"/\text{min}$. The force-elongation curves obtained were used to evaluate the Young's modulus, ultimate tensile strength and ultimate elongation.

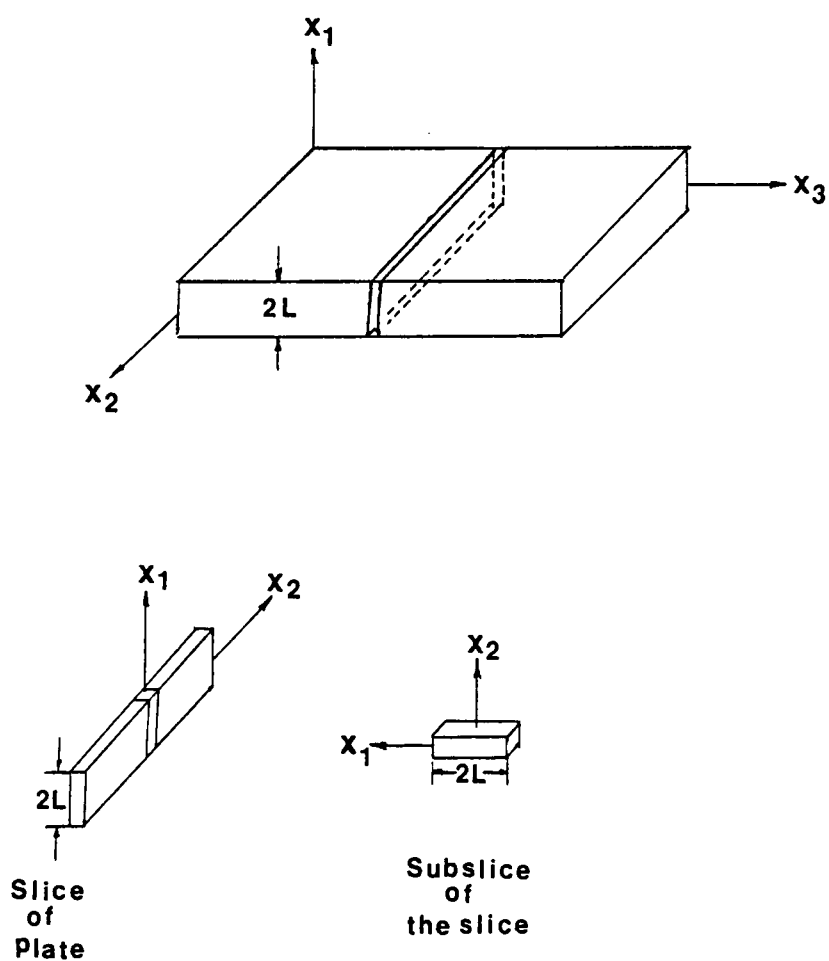
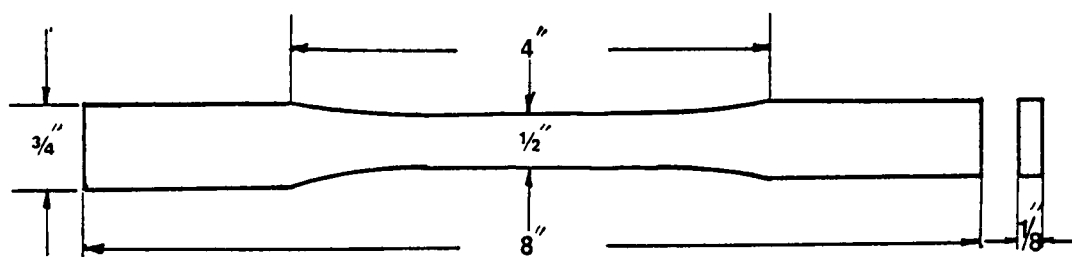
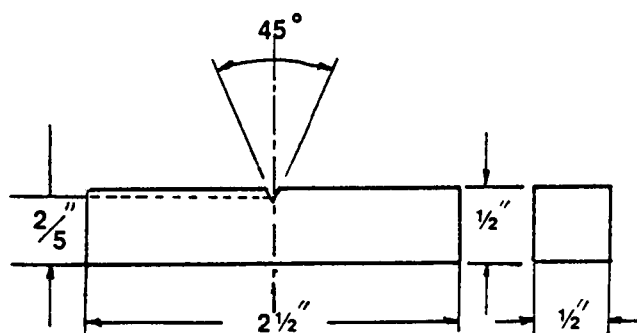


Figure 3.7. Schematic diagram for subslicing a slice of slab.



(a)



(b)

Figure 3.8. Test specimen geometries: (a) tensile specimen, (b) Izod impact specimen.

Impact Strength

Impact tests were conducted by using Tinus-Olsen Impact Tester according to ASTM D-256-73, method A (Izod type, notched). The impact strength is usually expressed in joules per meter of notch width of specimens at failure. Specimens were prepared with the same procedures as in the case of the tensile specimens but are made with a notch of 0.1 inch on the Izod bars. Five specimens of each sample were tested to take the average value.

CHAPTER 4

KINETICS OF POLYMERIZATION OF EPOXY RESIN DURING CURING REACTION

4.1 Characterization of Curing Reaction by Using DSC

The determination of epoxy cure kinetics by differential scanning calorimetry has been dealt with by several workers (25, 87, 89). Two techniques were generally carried out by them, one is the isothermal scan method, the other is the dynamic scan method. From a practical point of view, the isothermal scan gives more useful information than the dynamic scan, because the former one directly provides the extent of polymerization as a function of time at a given temperature. However, there are some difficulties encountered in the analysis of the isothermal data. Since if a very rapid cure reaction occurs, the initial several percentages of the scan become unmeasurable, therefore the total heat of reaction cannot be obtained with sufficient accuracy and the results become less reliable. However, as far as the kinetic parameters are concerned, the dynamic method turns out to be a useful and a relatively quick method to measure the kinetics of the curing reactions.

Both methods were examined in our experiments and typical dynamic and isothermal scan curves are shown in Figure 3.1 (p. 50) and Figure 4.1. The total heat of reaction and the glass transition temperature are listed in Table 4.1 and Table 4.2 along with the experimental conditions. As noted for the dynamic scans, it indicates that there is no clear trend for the total heat of reaction with varying the experimental conditions. After the initial scan, the samples were rescanned to obtain the glass transition temperatures which are also shown in Table 4.1. It shows that T_g increases as the concentration of the catalyst increases, also T_g increases as the heating rate decreases. On the other hand, for the isothermal scans as noted in Figure 4.1, the curves rapidly rise for high temperature scans, but they slowly level off for the low temperature scans. The total heat of reactions can only be approximately determined for high temperature scans. It is quite difficult to integrate the curves for low temperature scans. As same as the procedures of the dynamic scan, the glass transition temperatures obtained are listed in Table 4.2. The glass transition temperature increases as the cure temperature increases, but when the cure temperature reaches 140°C , the T_g slightly decreases. It is quite surprising that the result is consistent with that of the molded samples in the later experiments. A residual extherm was also observed for low cure temperatures when the sample was

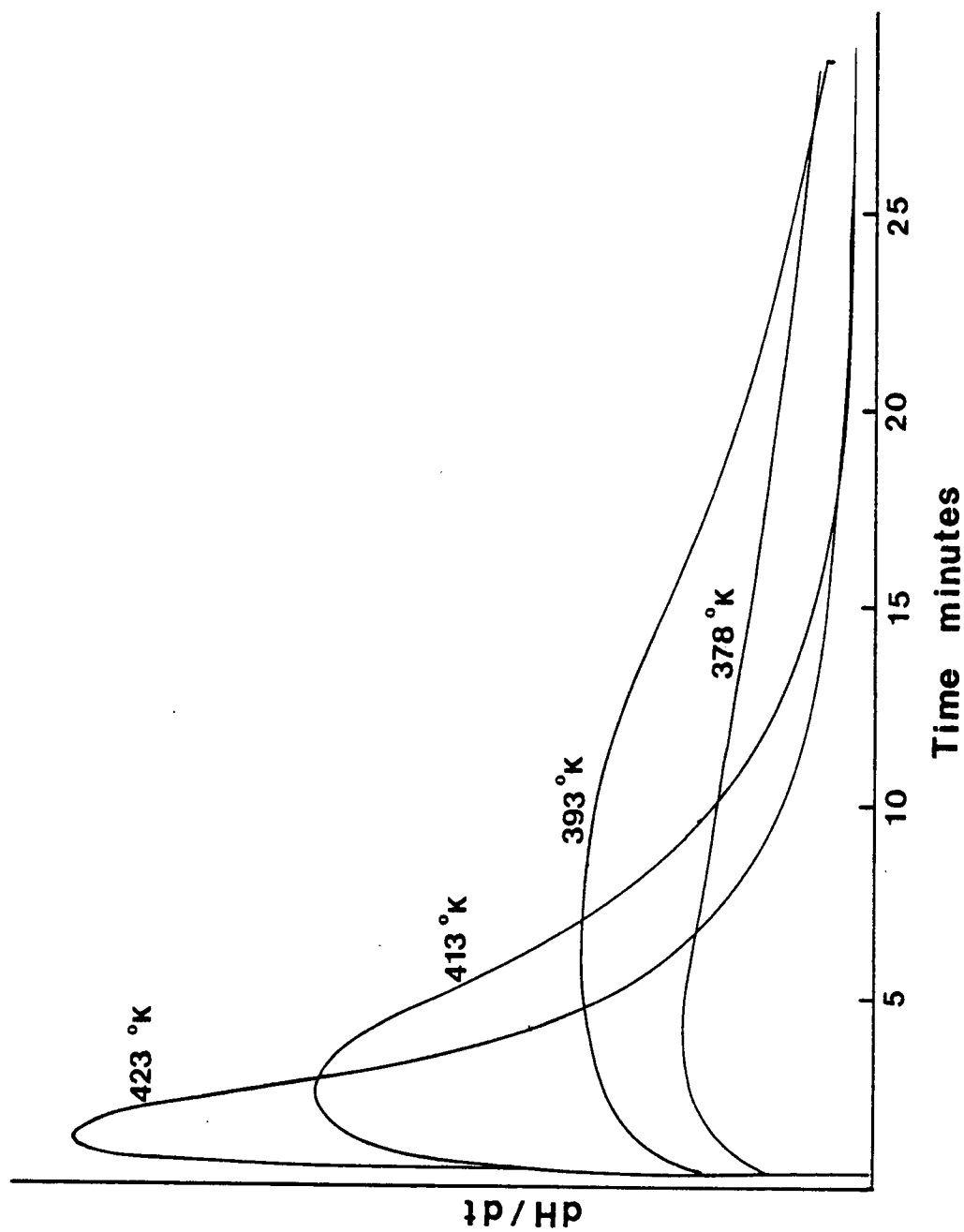


Figure 4.1. Isothermal DSC runs at various cure temperatures.

TABLE 4.1
TOTAL HEAT OF REACTION AND GLASS
TRANSITION TEMPERATURE FOR
DYNAMIC SCAN

Experiment No.	Scan* Rate °C/min	BDMA ml/g	Weight mg	Total Heat of Reaction cal/gm	T _g °C
1	5	0.02	20	42.3	116
2	5	0.015	18	42.3	107
3	5	0.01	18	37.8	98
4	5	0.005	18	37.9	77
5	2.5	0.01	18	40.0	99
6	1.25	0.01	18	41.9	107

*Dynamic DSC run from 300°K to 475°K.

TABLE 4.2

TOTAL HEAT OF REACTION AND GLASS
TRANSITION TEMPERATURE FOR
ISOTHERMAL SCAN

Experiment No.	*Isothermal Cure Temperature °C	Weight mg	Total Heat of Reaction cal/g	T _g °C
1	100	18	-----	76
2	105	18	-----	93
3	120	18	-----	109
4	135	18	55.15	109
5	140	18	51.36	105
6	150	18	41.58	103

*BDMA in all samples is 0.01 ml/g of resins
In isothermal scan, samples were placed in DSC
cell at specified temperature for an hour.

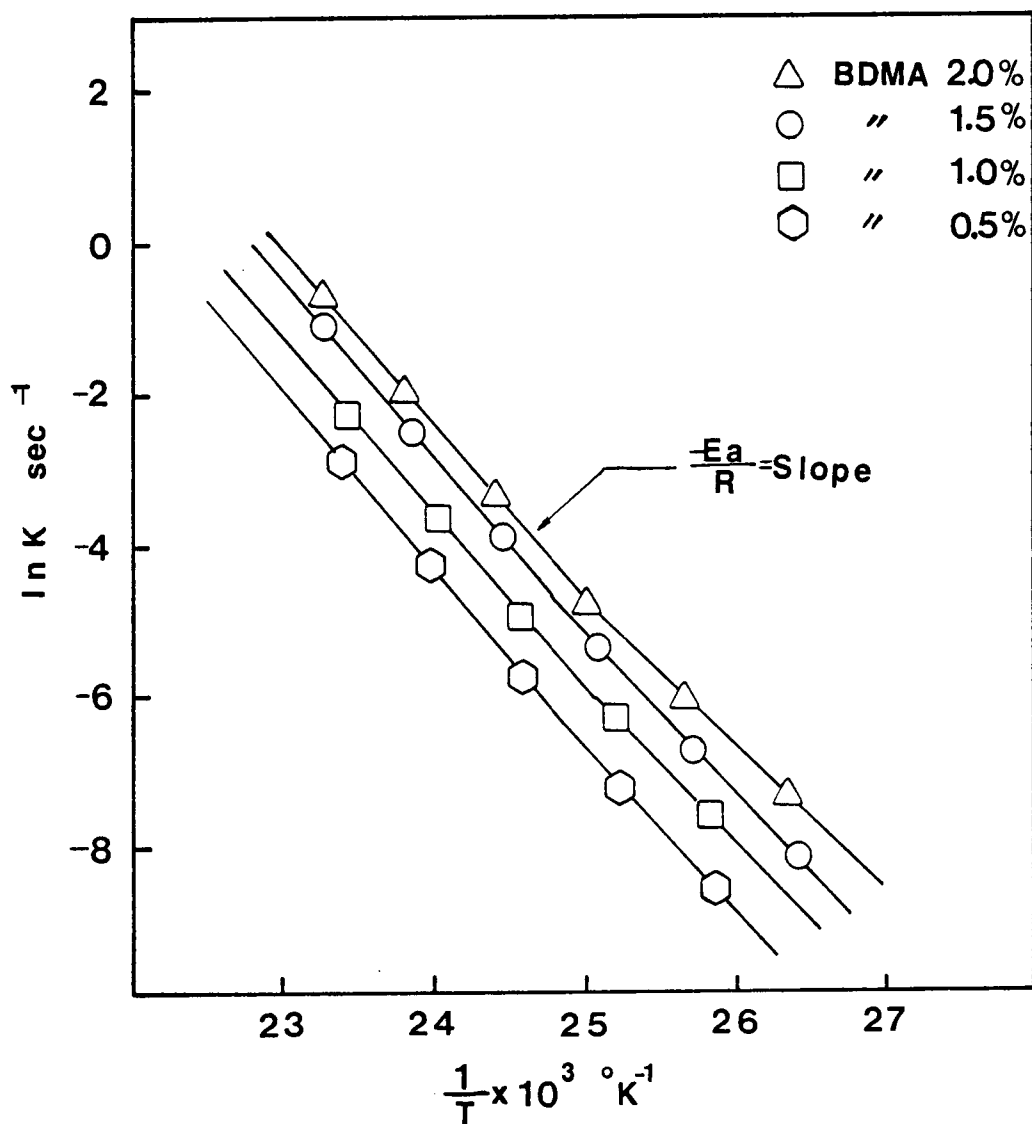


Figure 4.2. Plots of DSC dynamic run (5°C/min) with various concentrations of catalyst BDMA.

rescanned. This indicates that the curing reaction was not completed for low temperatures.

As described previously in Chapter 3, two approaches were used to analyze the data obtained from the DSC curves and then evaluated the kinetic parameters of the epoxy curing reactions. The results were plotted in Figure 4.2 and Figure 4.3. As noted in Figure 4.2 the effect of the catalyst concentration on the reaction rate is shown. The straight lines are reasonably parallel to each other which indicates the activation energy is more or less constant in all cases, and in Figure 4.3 it also shows the effect of heating rates on the reaction rates. Note that all the lines are approximately parallel to each other, except there exhibits two stages in the low heating rates. This two-stage phenomenon has also been seen by Peyser and Bascom. However, for high heating rates, a two-stage reaction cannot be detected. This is probably due to the fact that the transition of the two-stage reaction is very slight and not detectable with the present equipment.

The values of the activation energies were obtained from the slopes of the lines, and with the extrapolation of lines to $1/T$ equal to zero, the frequency factor $\ln A$ was determined. The results are listed in Table 4.3 and Table 4.4. All the activation energies are more or less constant with the values about 50 kcal/mole and only a slight variation in each case. So it turns out to be quite consistent with the assumption of a second-order kinetics which is

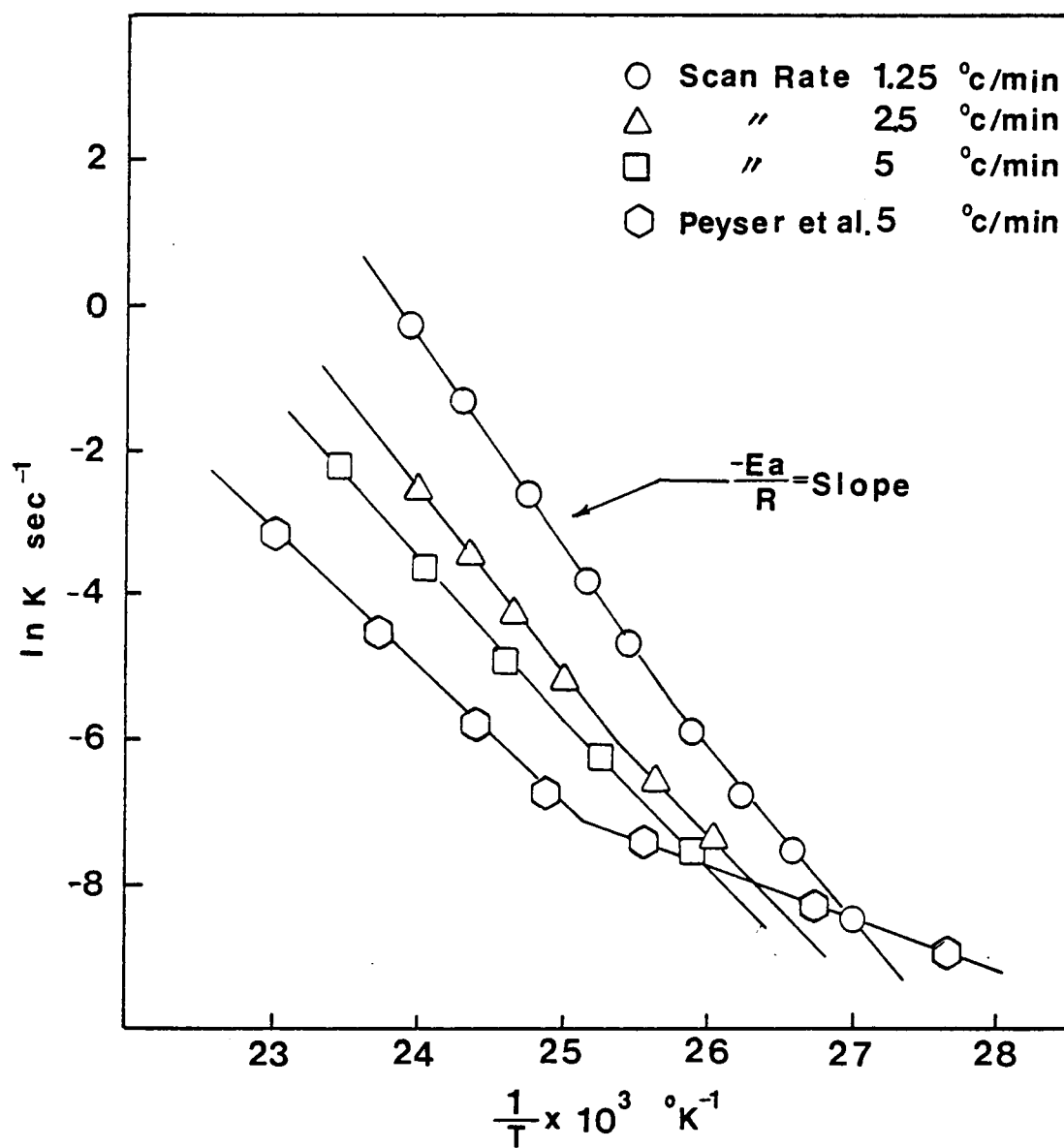


Figure 4.3. Plots of DSC dynamic run data with different scan rates.

TABLE 4.3
ACTIVATION ENERGY BY PEAK TEMPERATURE METHOD*

Experiment No.	Heating Rate °C/min	BDMA ml/g	Peak Temperature °K	$\frac{E_a}{n}$ Kcal/mole	E_a n=2 Kcal/mole
1	1.25	0.01	390	26.4	52.8
2	2.5	0.01	402	27.9	55.8
3	5	0.01	412	24.3	48.6
4	5	0.005	416	27.5	55.0
5	5	0.015	407	26.5	53.0
6	5	0.02	404	25.6	51.2
Peyser et al.	5	0.03	420	20.7	41.4

$$* \frac{E_a}{n} = \left[\frac{RT^2}{(H_T - H)\omega} \right] \frac{dH}{dt} \bigg|_{\max}$$

ω : Heating rate

TABLE 4.4
ACTIVATION ENERGY BY EQUATION [3.4]*

Experiment No.	Heating Rate °C/min	BDMA ml/g	Ea Kcal/mole	In A sec ⁻¹
1	1.25	0.01	57.8	69.4
2	2.5	0.01	52.9	61.4
3	5	0.01	48.8	54.9
4	5	0.005	47.8	53.4
5	5	0.015	47.7	54.8
6	5	0.02	45.9	53.2
Peyser et al.	5	0.03	36.7	39.4

$$*\ln \frac{dH}{dt} \frac{1}{H_T} - n \ln \left(\frac{H_T - H}{H_T} \right) = - \frac{Ea}{R} \frac{1}{T} + \ln A = \ln K \quad [3.4]$$

being made. As compared the values of activation energies calculated from both methods, their results are in accord with each other. Also noted that the maximum temperature of DSC scan curves increases as the heating rate increases and decreases as the amount of the catalyst increases, the explanation of this result has been quite controversial in the literature. It will be discussed later.

4.2 Discussion

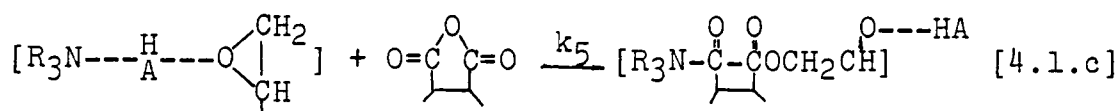
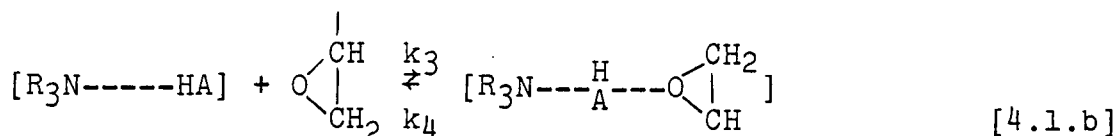
Cure Mechanism of DGEBA/NMA/BDMA System

As noted previously, the system used throughout the experiments consists of reacting diglycidal ether bisphenol A epoxy resins with the curing agent, nadic methyl anhydride, and used benzyldimethylamine as catalyst.

First, I would like to point out that the work here is not intended to be a detailed investigation of the mechanism of the reactions, but only a study of the correlation of kinetic parameters determined by the differential scanning calorimetry. Based on this kinetic characterization, then we can go further to study their structure-properties relationships.

However, it is convenient to start with briefly describing the cure mechanism of this system. As described in Chapter 2, several investigations (27, 29, 101, 102) have studied the epoxy-anhydride system in the presence of tertiary amine as the catalyst. The mechanism generally

can be represented in three stages as proposed by Tanaka and Kakiuch:



In their study of epoxy-anhydride polymerization system, Feltzin et al. (27) indicated that the reactions of type [4.1.b] were rate controlling, and the rate was first-order with respect to epoxy concentration. However, Tanaka and Kakiuchi (101) found that second order kinetics prevailed in a variety of epoxy-anhydride systems and suggested that the reactions of type [4.1.c] were rate controlling. Finally, Peyser and Bascom (86) concluded that the kinetics of the DGEBA/NMA/BDMA system to be initially first order and presumably controlled by reactions of type [4.1.b], but in the latter stage it exhibits second order kinetics controlled by reactions of type [4.1.c]. As indicated by Peyser and Bascom, an increase in reaction rate occurred at about 12% conversion, they argued that an autocatalytic reaction exist at the beginning of the reaction. Thus a

first order kinetics occurred at the initial stage of reaction. Since it only occurs in a small amount of reaction system, this seems reasonable that the overall reaction can be presumed to be a second-order kinetics mechanism, and we proceed to evaluate our results on this basis.

Activation Energy of Reactions

As noted in Table 4.2 (p. 72), the total heat of reaction greatly varies with different cure temperatures. This indicates that the uncertainties of measurement of heat of reaction cause difficulties in the analysis of isothermal DSC runs.

Activation energies obtained are nearly constant with the values about 50 kcal/mole for different experimental conditions. Although there are some slight changes with the concentration of catalyst, they can be explained through arguing that the reaction rate is controlled by the reaction [4.1.b] in the initial stage of reaction which is only dependent on the concentration of catalyst. Thus they might result in a slight change for the overall activation energy. Nevertheless, it is still quite consistent with the assumption made that the reaction can be described by simple second-order kinetics and an Arrhenius-type equation. Comparing the activation energies to those of Peyser and Bascom, it was found that the activation energies they measured were about 40 kcal/mole, which are less than ours.

This is possible due to the different preparation of samples and the different sources of material. (They used epoxy resin DER-332 from Dow Chemical Company.)

As previously mentioned, the peak temperature increases as the heating rate increases. An explanation has been given by Peyser and Bascom (87). They claimed that the reaction became diffusion controlled after the initial stage of reaction. Therefore for the fast heating rate, the reaction cannot keep up with itself and thus falls behind the heating rate. However, evidently for the system we studied, this retardation seems to have no effect on the determination of activation energies.

Glass Transition Temperature

As noted in Table 4.1 (p. 71), the glass transition temperature increases as the heating rate decreases, which has also been observed by Fava (25), Peyser and Bascom (87). Gillham et al. who used torsional braid analysis to scan the samples with different heating rates, found the same trend. It was suggested that the lower heating rate samples stayed for a longer time at the higher temperature period and were given a greater amount of postcuring which resulted in their higher T_g .

In the isothermal scans we find that T_g increases with curing temperature, but slightly decreases when the temperature is up to 140°C. This tendency was also observed by Gillham et al. (64) using isothermal TBA scan.

They mentioned that the highest T_g was obtained for the lowest cure rate. As seen from later experiments of the molded samples, if the cure temperature is too high, the resulting network is less highly crosslinked and a dark hue in the samples can be seen. These slight changes are possibly due to a change of cure mechanism of reaction or thermal degradation.

CHAPTER 5

NETWORK STRUCTURAL PROPERTIES OF EPOXY RESINS

The mechanical properties and performance of cross-linked polymers are governed by their structure especially that of the network. The network varies considerably with changes in prepolymer molecular weight, functionality, stoichiometry of curing agent, extent of curing reaction and thermal history of cure. In this study two of these were investigated, the stoichiometry of the curing agent and the thermal history of cure. Characterization of morphology, crosslink density, glass transition temperature and density will be studied. The methods used to carry out these measurements have been described in Chapter 3.

5.1 Swelling

Results

The effect of stoichiometry, defined as the ratio of equivalent weight of the curing agent to react with one mole of epoxy group, on the swelling ratio of the cross-linked epoxy system in series A is plotted in Figure 5.1. The swelling ratio was defined in Chapter 3 as the ratio of the weight of swollen polymer to the weight of dry polymer.

The swelling ratio dramatically decreases with increasing the stoichiometric ratio of NMA and is minimum

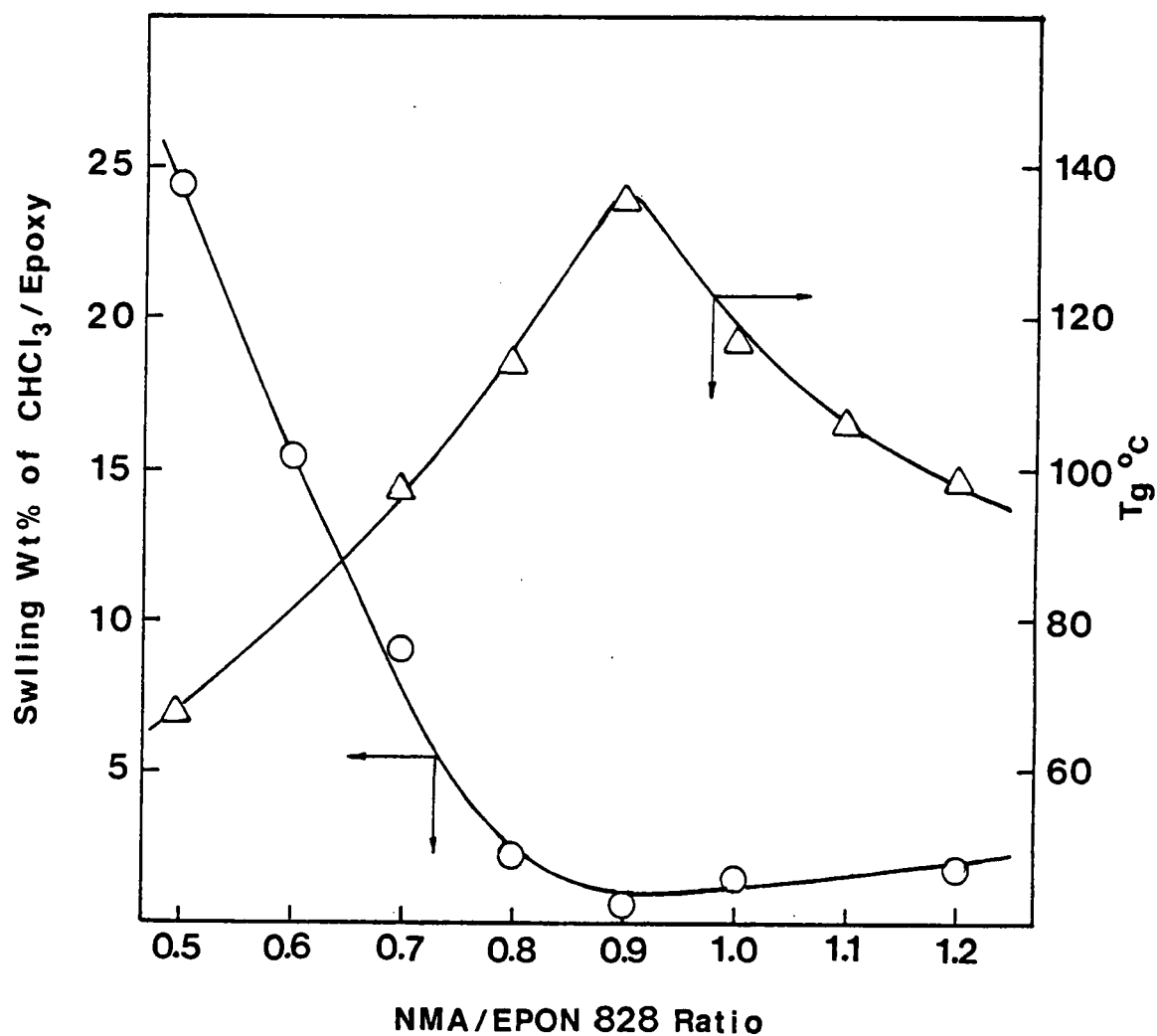


Figure 5.1. Swelling ratio and glass transition temperature of cured epoxies as a function of NMA/EPON 828 ratio.

at a stoichiometry of 0.9. As soon as the stoichiometric ratio is above 0.9, the swelling ratio slightly increases again.

The epoxy samples in series B are cured isothermally at temperatures ranging from 80°C to 180°C. The swelling ratio is plotted versus the cure temperature for epoxy samples in series B in Figure 5.2. The swelling ratio decreases with increasing cure temperature; however, it exhibits an upturn in the range of 110°C to 150°C. The swelling ratio slightly decreases again at cure temperatures higher than 160°C.

The effect of the time of postcure on the swelling of the epoxy system in series C is shown in Figure 5.3. The swelling ratio dramatically decreases in the first period of postcure, and then levels off as the time is further increased.

Discussion

The swelling ratios are generally considered to be a measure for the degree of crosslinking. The results shown in Figure 5.1 seems to reflect that the network has the most highly crosslinked structure at the stoichiometric ratio of 0.9. However, if the ratio deviates from this value either because of excess of the epoxy resin or excess of the curing agent, the network should become less crosslinked. This trend is similar to that observed by Dannerberg and Harp (20) for different but related epoxy systems. It is

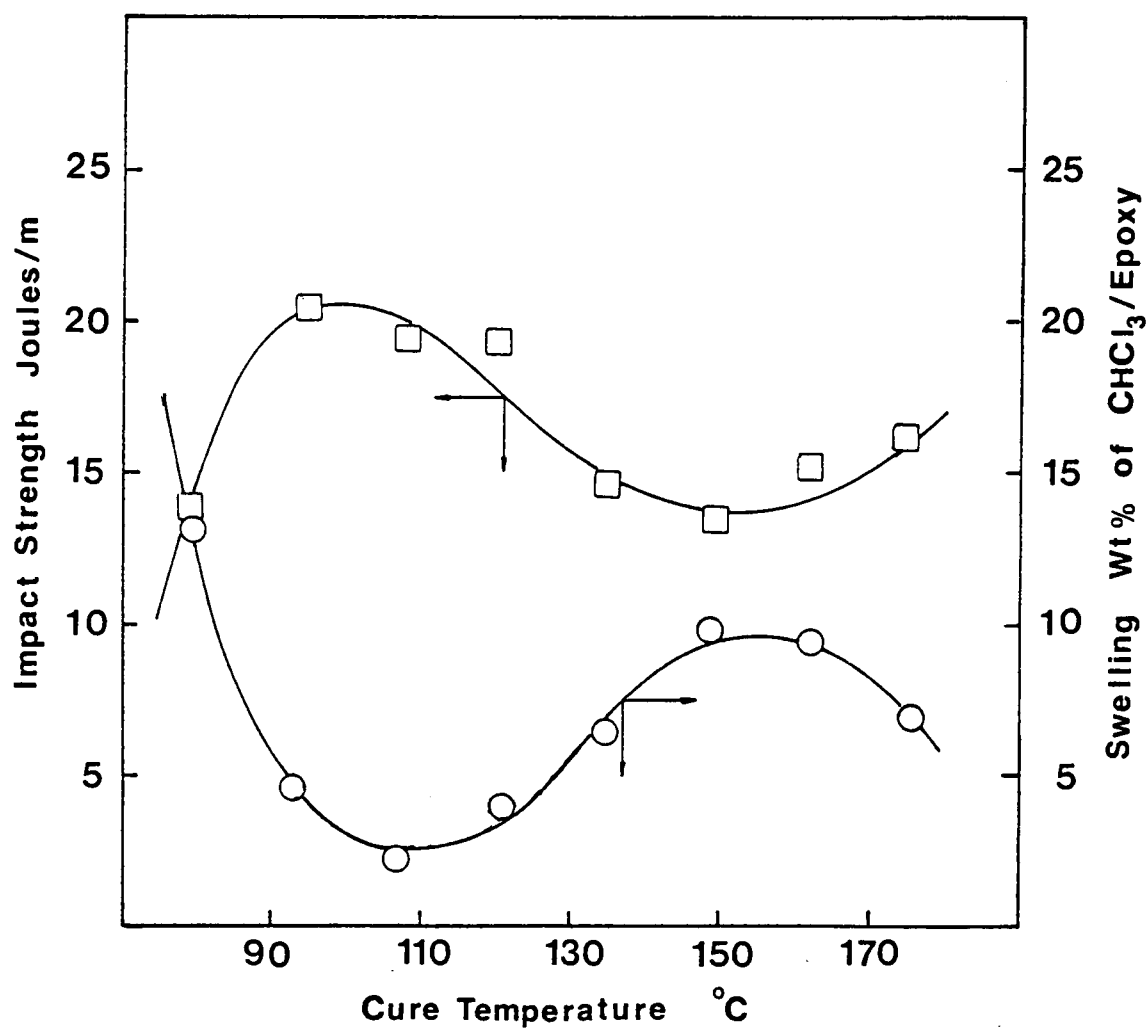


Figure 5.2. Swelling ratio and glass transition temperature of cured epoxies as a function of cure temperature.

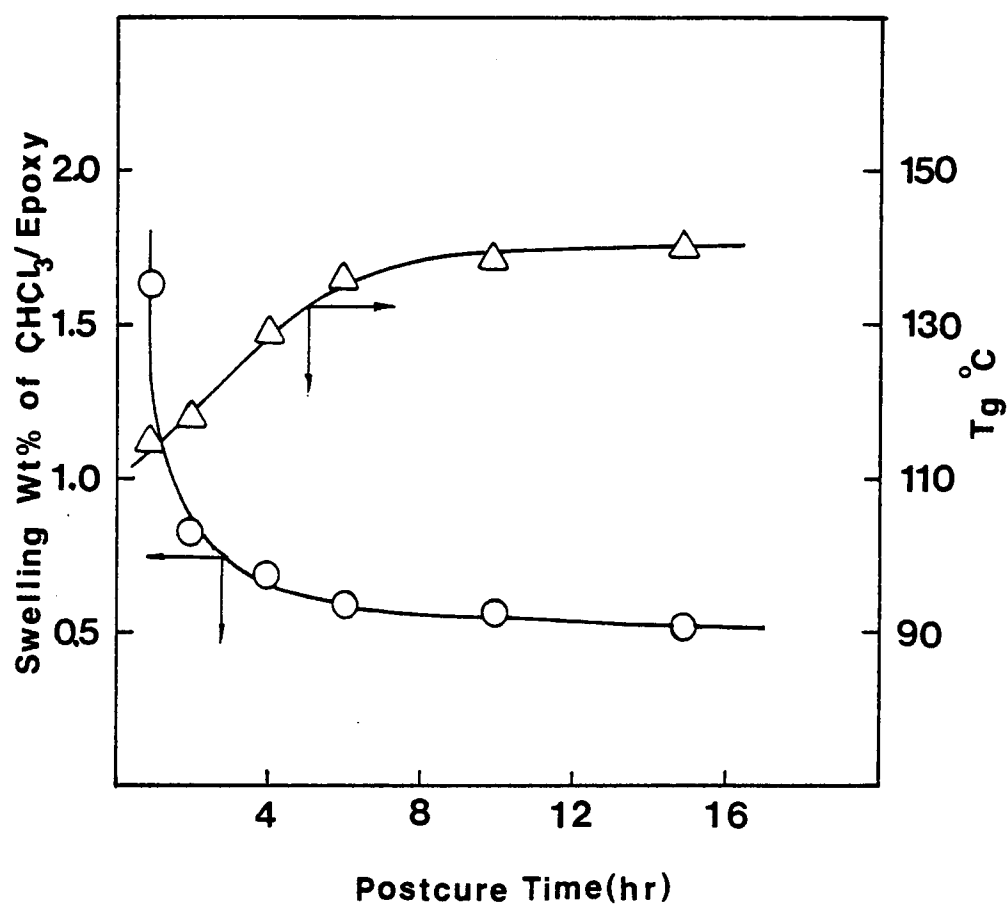


Figure 5.3. Swelling ratio and glass transition temperature of cured epoxies as a function of postcure time.

apparent that an increase of the curing agent provides more reactive sites to form the crosslinks which leads to a decrease of molecular weight between crosslinks. Thus the network becomes tighter and tighter. However, if the curing agent exceeds the equivalent amount of epoxy resins, it may create more structural weakness associated with the unreacted curing agents or chain ends embedded in the network matrix. It is evident that both excess in epoxy prepolymer or excess in curing agents are easily attacked and swollen by chemical agents.

It is observed that the swelling value decreases for lower cure temperatures. The increase of cure temperature tends to increase molecular mobility which increases the curing reaction and thus increases the crosslinking density. However, a peculiar result can be seen at high cure temperatures. The swelling value tends to increase at cure temperatures over 110°C . A similar result was also observed by Cuthrell (18). He has claimed that a high cure temperature results in a lower degree of cure, as indicated by the density, hardness and glass transition temperature. Lewis et al. (64) have also argued that the resulting less crosslinked network is probably due to competing curing reactions which result in different networks. Thermal degradation and volatilization of curing agent could also give significant effects. Thermal degradation of our epoxy system has been reported by Anderson (4). He indicated that nadic methyl anhydride (NMA) itself

decarboxylates by heating it to about 200°C. The degradation of the epoxy resin such as DGEBA type was also found in the temperature range 200-250°C by Neiman et al. (81). It is believed that both degradation in epoxy resins and NMA are reasons why we have a yellowish brown colored specimen at high cure temperatures. Another cause of less crosslinked network is due to the evaporation of the curing agent. A few drops of liquid were observed to stick on the upper press during the curing process. We believe that those drops are the curing agent NMA, since the vapor pressure of NMA is much higher than that of epoxy resin which reportedly (109) is about 1.5 mm Hg at 102°C. A slight decrease of the swelling ratio was again observed at cure temperatures higher than about 160°C. The cause of this downturn is not well understood. It is possible that an increased rate of reaction due to the increase of cure temperature overtakes the effect of thermal degradation and evaporation of the curing agent.

As noted in Figure 5.3, a highly crosslinked network can be achieved for 6 hours postcuring at 150°C. After that time the network seems unchanged. It is suggested that the full cure can be almost attained for 6 hours post-cure in our epoxy systems.

It should also be pointed out that the conversion of these swelling values to the average molecular weight between crosslinks M_c is difficult. This is partly because of the knowledge of the Flory-Huggins interaction parameter

which is difficult to determine, and partly because of the inherent low sensitivity of the swelling theory for highly crosslinked systems. In theory, the swelling of a non-polar crosslinked polymer in a non-polar solvent can be related to M_c by the equation (3):

$$-[\ln(1 - \phi_2) + \phi_2 + \chi\phi_2^2] = \left(\frac{V_1}{VM_c}\right)\left(1 - \frac{2M_c}{M}\right)\left(\phi_2^{1/3} - \frac{\phi_2}{2}\right) \quad [5.1]$$

where ϕ_2 is the volume fraction of polymer in the swollen polymer, V_1 is the molar volume of the solvent, V is the specific volume of the polymer, M is the molecular weight of the polymer before crosslinking, and χ is the Flory-Huggins interaction parameter. This theory has been reported by Kenyon and Nielsen (50) and Misra et al. (72) not to give a satisfactorily accurate determination of M_c in a highly crosslinked polymer such as epoxy. The average molecular weight between crosslinks M_c obtained from the swelling value is significantly less than that theoretically predicted from stoichiometry.

5.2 Glass Transition Temperature

Results

The effect of the stoichiometry, isothermal cure temperature of reaction and time of postcure on the glass transition temperature of their respective crosslinked epoxy systems in series A, B and C are plotted in Figures 5.1, 5.2 and 5.3. It is interesting to note that all the

results exhibits an inverse correlation between the glass transition temperature and the swelling ratio. A plot of the glass transition temperature versus swelling ratio for all three series of epoxy samples A, B, C is also shown in Figure 5.4. The glass transition temperature increases with the decrease of swelling value. In particular, the T_g sharply increases with a small amount of change of the swelling value in the range of small values of swelling.

Discussion

The glass transition temperature increases with increasing stoichiometry until it becomes a maximum at a stoichiometry of 0.9 and then decreases with excess of the curing agent. The trend in results is in good agreement with those reported by Fellers and Golovoy (26), and Selby and Miller (94). These observations reveal that the glass transition temperature of crosslinked polymers like the swelling ratio is essentially associated with the crosslinking density of the network. T_g tends to increase as the crosslinking density increases. However, as indicated by Nielsen (82), it should be pointed out that the factors which result in the shift of T_g are due not only to the influence of the degree of crosslinking but also the influence of the copolymer effect. Both in the excess of epoxy resins and curing agents, the unreacted molecules are acting as a type of dilutents. Thus they may make contributions to the shift of glass transition temperature.

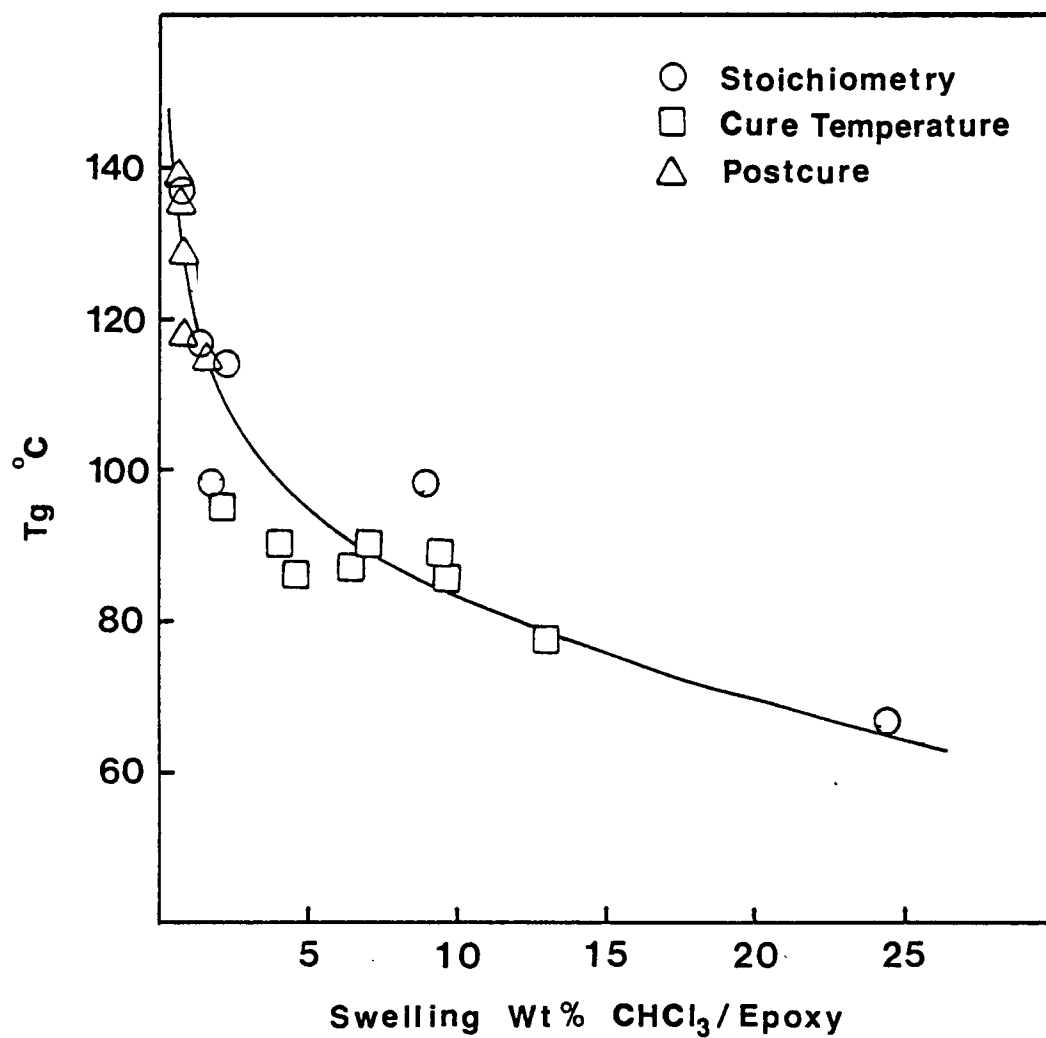


Figure 5.4. Glass transition temperature of cured epoxies as related to swelling ratio.

Similarly, Figures 5.2 (p. 86) and 5.3 (p. 87) show an inverse correlation between the glass transition temperature and the swelling ratio with respect to the effect of cure temperature and time of postcure. It appears that a high glass transition temperature corresponds to a low swelling ratio. In other words, the higher the cross-linking density, the higher the T_g will be. As shown in Figure 5.2 (p. 86), an increase of cure temperature tends to increase the T_g . While at high cure temperatures thermal degradation also results in a decrease of the T_g . In practice, this exothermic effect can be eliminated by going through a two-step process which is precuring at a low temperature and then postcuring at a high temperature. It should be noted that a residual exotherm was observed in the DSC for samples cured at temperatures below 100°C. This apparently reveals that the reaction has not been completed at low cure temperatures. As noted by Gillham (34, 36), this under-cure is a consequence of the vitrification which stops the reaction. Further reaction can only occur if the cure temperature is increased to overcome the thermal motions for vitrification. This is the reason why the post-cure above $T_{g\infty}$ which is defined by Gillham as the maximum glass transition temperature of the cured system, is needed in order to develop an optimum network structure. It can be seen in Figure 5.3 (p. 87) the glass transition temperature greatly improves by postcuring at 150°C. Figure 5.4 shows the correlation of the glass transition temperature

and the swelling ratio. It is interesting to note that the glass transition temperature seems more sensitive to network structure than the swelling ratio. The T_g exhibits an observable increase even with a very small amount of change of the swelling value in the highly crosslinked range.

5.3 Density

Results

The density of the crosslinked epoxy systems in all three series A, B, C, is reported in Tables 5.1 and 5.2. It reveals no clear trend in effects of the stoichiometry and the cure temperature. However, the density tends to decrease with increasing the time of postcure. A correlation plot of density versus glass transition temperature is also shown in Figure 5.5 for all three systems. The density of crosslinked epoxies seems to decrease with an increase of the T_g .

Discussion

The effect of stoichiometry and cure temperature reveals no clear trend on the density of crosslinked epoxies. It may be due to the fact that many factors such as the original density of reactants, the crosslinking density, the exothermic effect and the cooling rate from the mold after the curing process is completed, are all expected to affect the final density of cured epoxies. These combined effects result in no clear trend. As noted

TABLE 5.1

GLASS TRANSITION TEMPERATURE AND
DENSITY OF EPOXY RESIN SERIES A

Sample No.	Glass Transition Temperature °C	Density* g/cm ³
A-1	67	1.217
A-2	98	1.218
A-3	114	1.216
A-4	137	1.217
A-5	117	1.221
A-6	98	1.228

*Density of EPON 828 and NMA

EPON 828 $D_4^{20} = 1.17$

NMA $D_4^{20} = 1.22$

TABLE 5.2

GLASS TRANSITION TEMPERATURE AND DENSITY
OF EPOXY RESIN SERIES B AND C

Sample No.	Glass Transition Temperature °C	Density g/cm ³
B-1	78	1.234
B-2	86	1.229
B-3	95	1.227
B-4	90	1.226
B-5	87	1.230
B-6	86	1.232
B-7	89	1.224
B-8	90	1.229
C-1	115	1.216
C-2	118	1.215
C-3	129	1.215
C-4	136	1.214
C-5	139	1.213
C-6	139	1.214

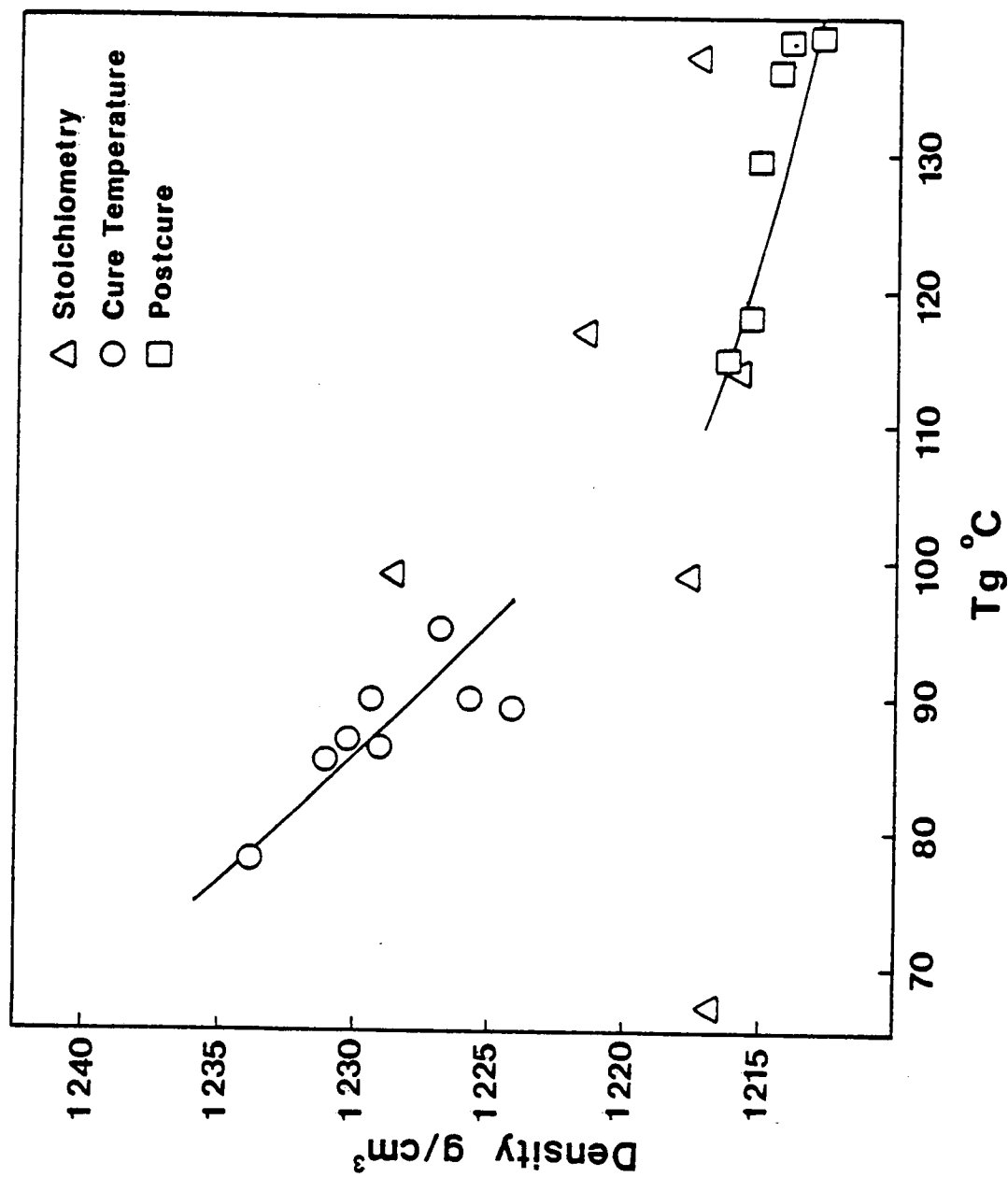


Figure 5.5. Density of cured epoxies as related to glass transition temperature.

in Table 5.1, a sharp increase of density occurs at the stoichiometry of 1.2. It is believed that the high density of the curing agent NMA which reportedly is 1.22 g/cm^3 makes a large contribution to this rise of density.

It should be pointed out that the density does increase in comparison with the value calculated from the original density of reactants. However, the non-equilibrium nature of the glassy state would also make a significant effect on the final density of cured epoxies. As noted in Table 5.2 and Figure 5.5, the density seems to decrease as the glass transition temperature of crosslinked epoxies increases. This may be due to the cooling through a glass transition which leads to a supercooled state. This phenomenon is well known in glassy solids. The state is further from equilibrium at the higher the T_g . The same observation has also been reported by Gillham (35). He argued that the higher free volume at room temperature of the more highly crosslinked polymer resulting from the non-equilibrium state through cooling is responsible for its lowering of density. From this point of view, it seems to be consistent with the results we observed.

5.4 Color

Result

The color of samples vary with the cure temperature. This is shown in Figure 5.6. The color of samples becomes brown and then dark as the cure temperature increases.



Figure 5.6. Photograph showing colors of cured epoxies at various cure temperatures.

Discussion

The inherent exothermic nature of the thermosetting reaction, if not well controlled, can cause serious effects on its appearance and properties of epoxies. Since the evolution of heat at the beginning of reaction is so rapid that the accumulation of heat increases rapidly due to the poor conductivity of epoxies, this will result in an increase of temperature and turn to the thermal degradation of samples which can be seen in Figures 5.6 and 5.7. The exotherm could cause the thermal degradation and the volatilization of NMA which has been discussed in the previous section. It has also been proved that the effect will lead to a less crosslinked network structure.

5.5 SEM Studies of Etched Surfaces

Results

We have examined the etched smooth-faced surface of epoxy samples of series A, which were prepared with varying the stoichiometry of curing agent, using Scanning Electron Microscopy. A globular structure can be seen in micrographs as shown in Figures 5.8 and 5.9. The average spheroidal size varies with the stoichiometric ratio of the curing agent as shown in Figure 5.10. The size of the spheroids varies from 0.1 μm to 0.7 μm . The size seems to decrease with increasing the stoichiometric ratio of NMA and is a minimum at the ratio of 0.9. After that the size of the spheroids tends to increase again. Some globules

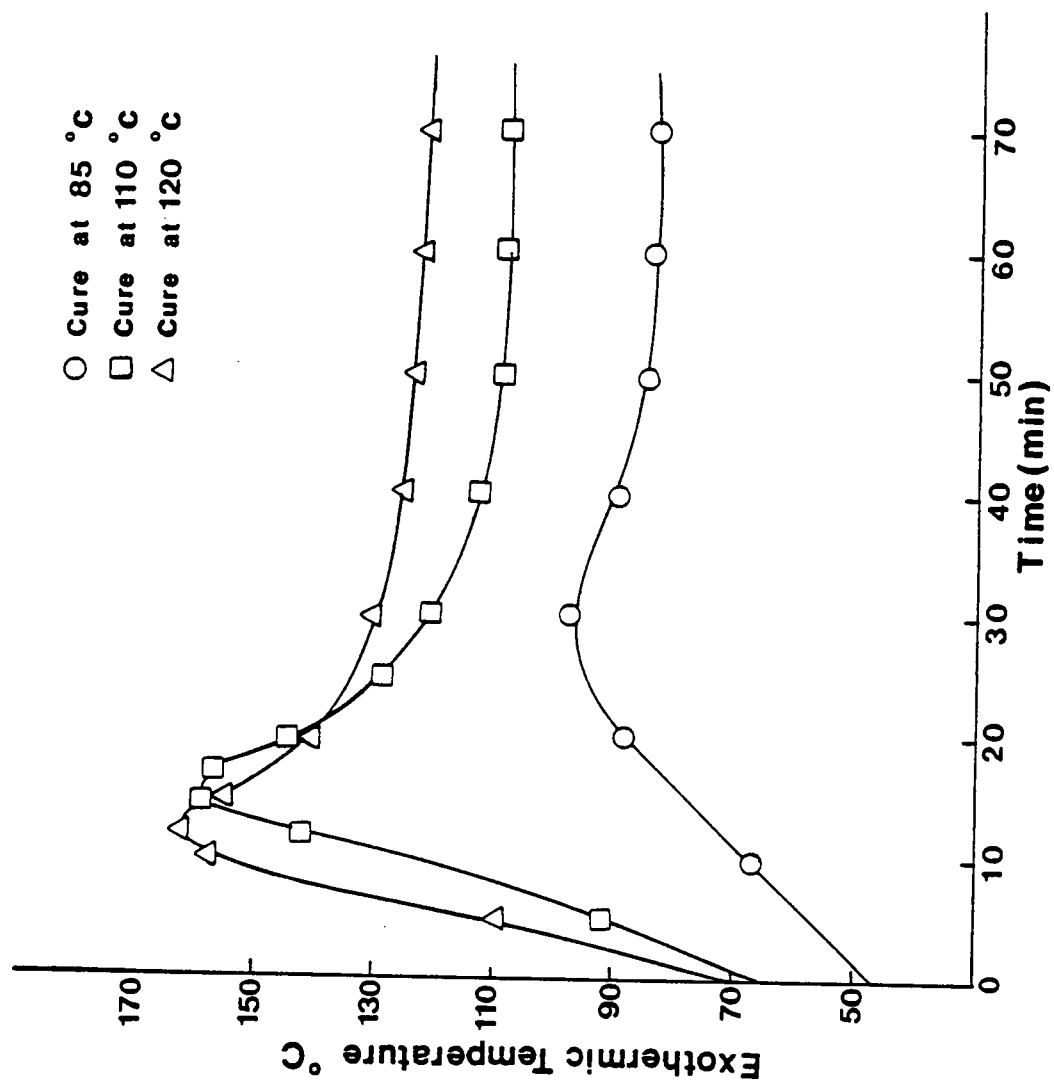


Figure 5.7. Plots of exotherm profile at various cure temperatures.

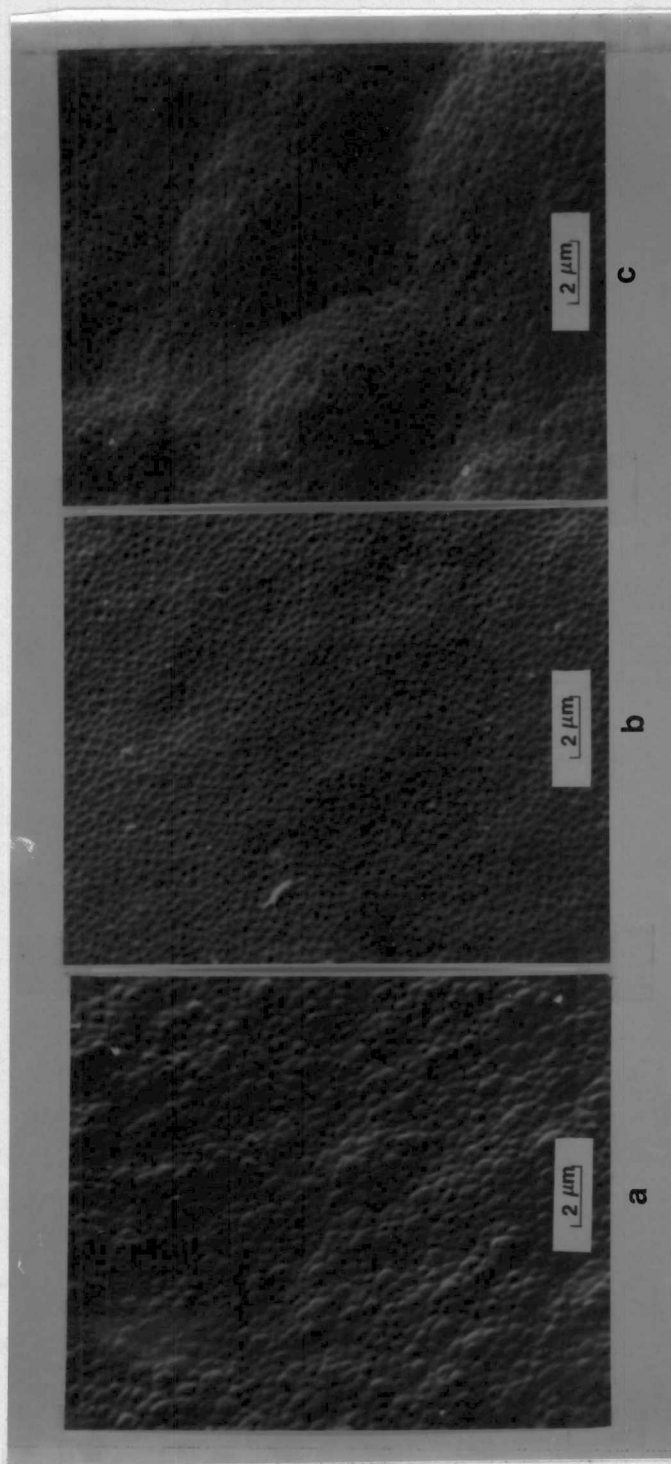


Figure 5.8. SEM micrographs showing globular structure of $\text{CrO}_3\text{-H}_2\text{SO}_4$ etched surface of cured epoxy samples having different stoichiometric ratio of NMA to EPON 828: (a) 0.5/1 (b) 0.7/1 (c) 0.8/1.

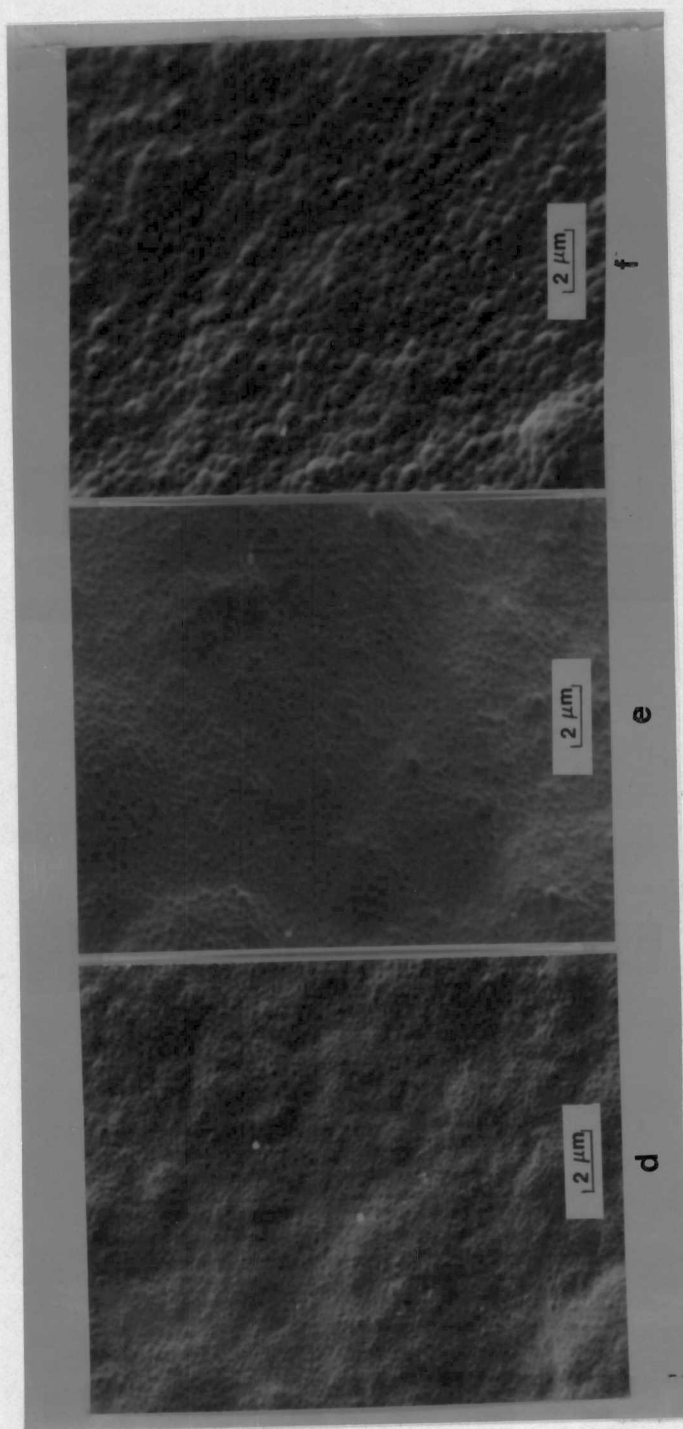


Figure 5.9. SEM micrographs showing globular structure of $\text{CrO}_3\text{-H}_2\text{SO}_4$ etched surface of cured epoxy samples having different stoichiometric ratio of NMA to EPON 828: (d) 0.9/1 (e) 1.0/1 (f) 1.2/1.

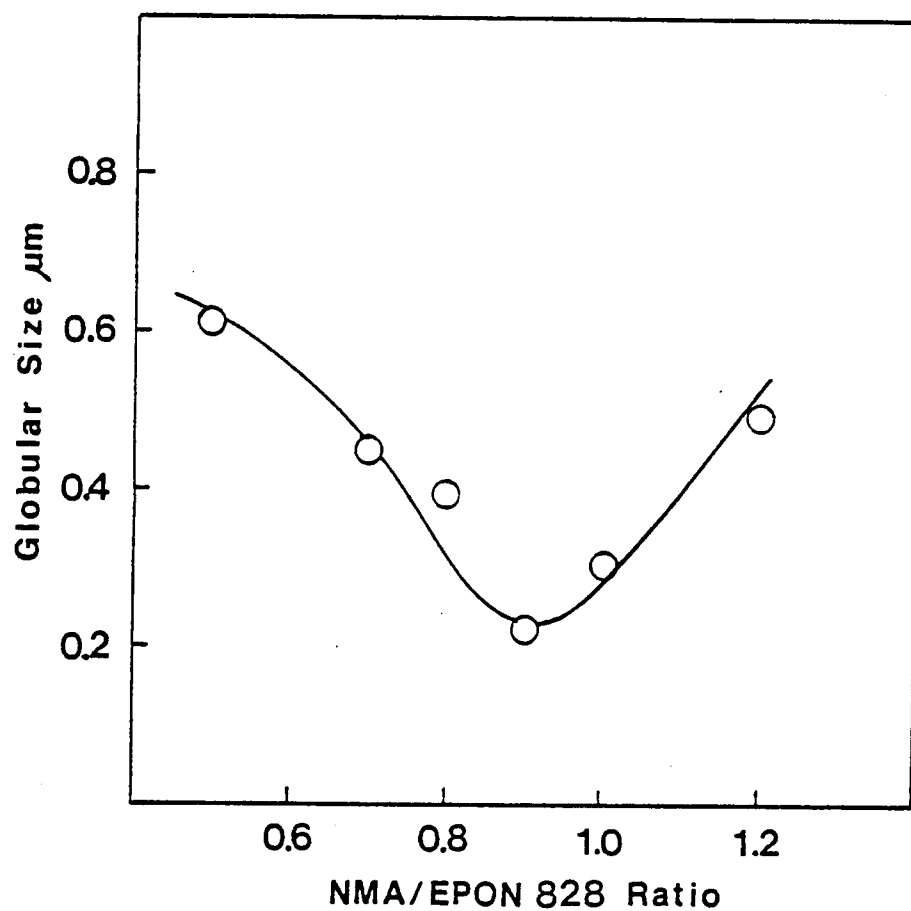


Figure 5.10. Globular size of cured epoxies as a function NMA/EPON 828 ratio.

are also observed in the low magnification of micrographs shown in Figure 5.11. The range in size is from 2.5 μm to 50 μm .

The globular structure of epoxy samples of varying cure temperature and time of postcure in series B and C were also observed under the SEM. The micrographs are shown in Figures 5.12 to 5.14. At a lower cure temperature the size of the spheroids seems to exhibit only a slight variation with an average domain size about 0.5 μm . However, the gross appearance of morphology becomes rough and irregular at high cure temperatures.

Two samples undergoing postcure were also examined. The micrographs are shown in Figure 5.14. A relatively regular distribution of globules with the size about 0.3 - 0.4 μm are observed.

Discussion

Our observation accords with many investigators (56, 73, 91, 110). A distinct two-phase structure was observed under the SEM on the etched surface of our epoxy systems. The micrographs shown in Figures 5.8 and 5.9 clearly exhibit regularly sphere-shaped dimples or globules throughout the etched surfaces with the size ranging from 0.1 μm to 0.7 μm depending on the composition of epoxy systems. The depressed regions or dimples on the surface of networks have been generally presumed to be due to the etching of regions of lower local crosslinking density (56, 73).

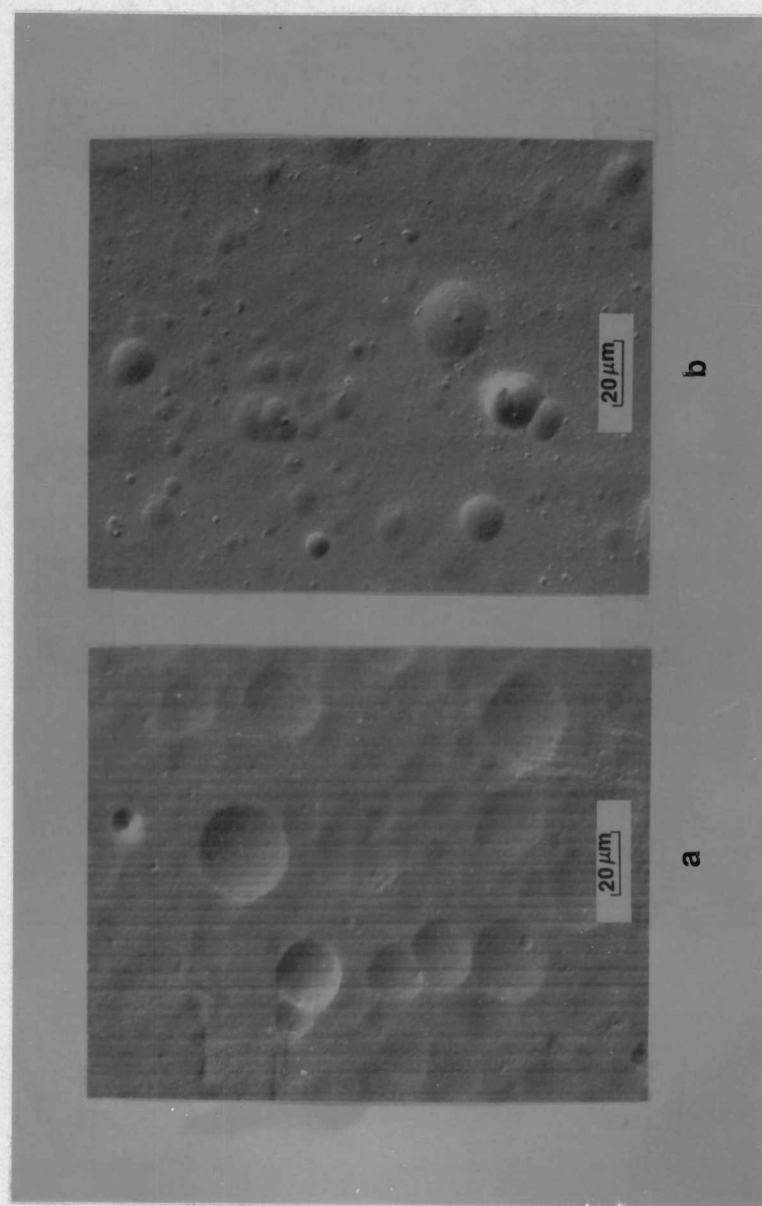


Figure 5.11. SEM micrographs of etched epoxy samples with low magnification (500x): (a) 0.7/l (b) 0.9/l.

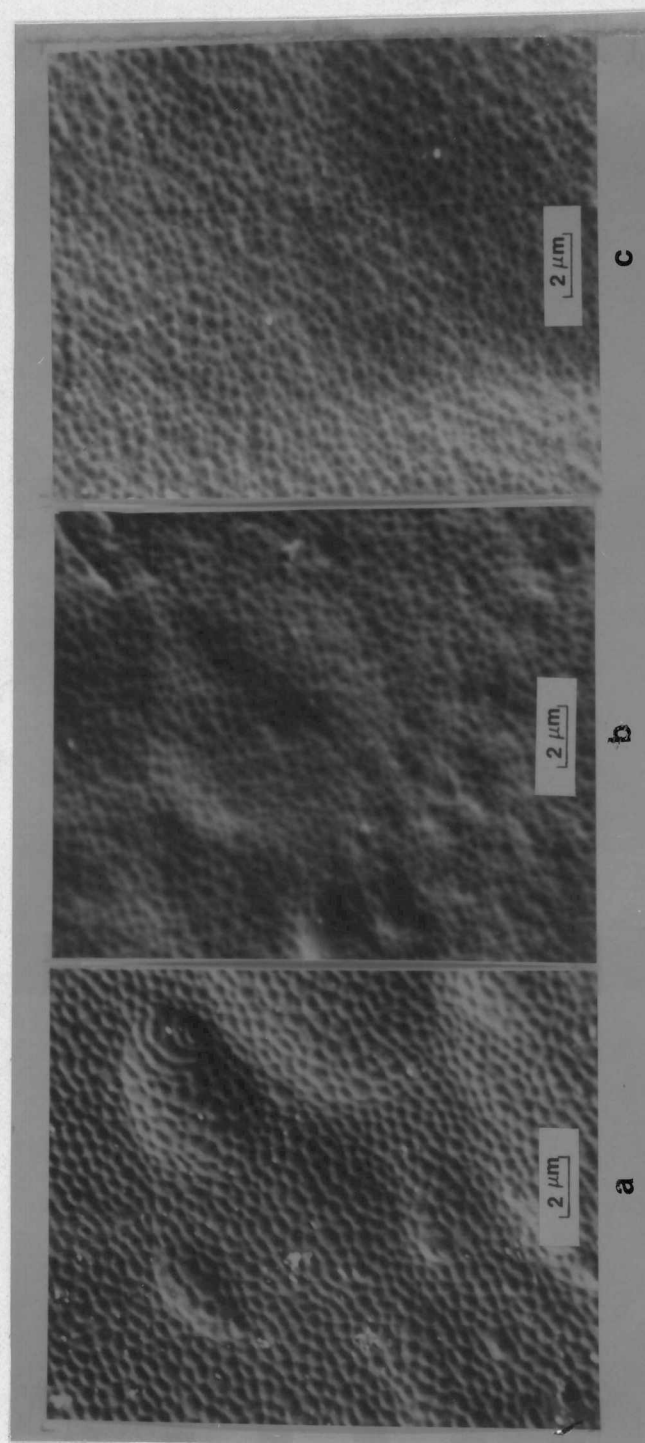


Figure 5.12. SEM micrographs of etched epoxy samples cured at various temperatures: (a) 80°C (b) 93°C (c) 107°C.

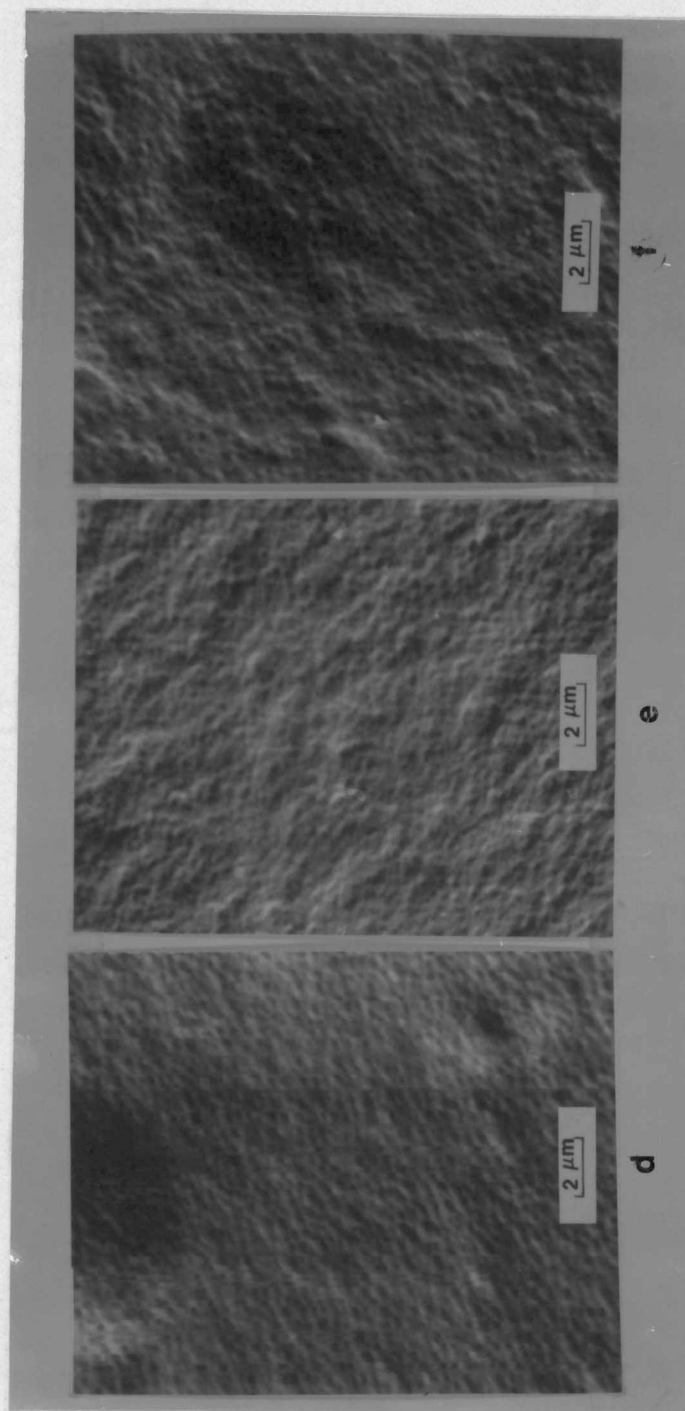


Figure 5.13. SEM micrographs of etched epoxy samples cured at various temperatures: (d) 121°C (e) 135°C (f) 150°C.

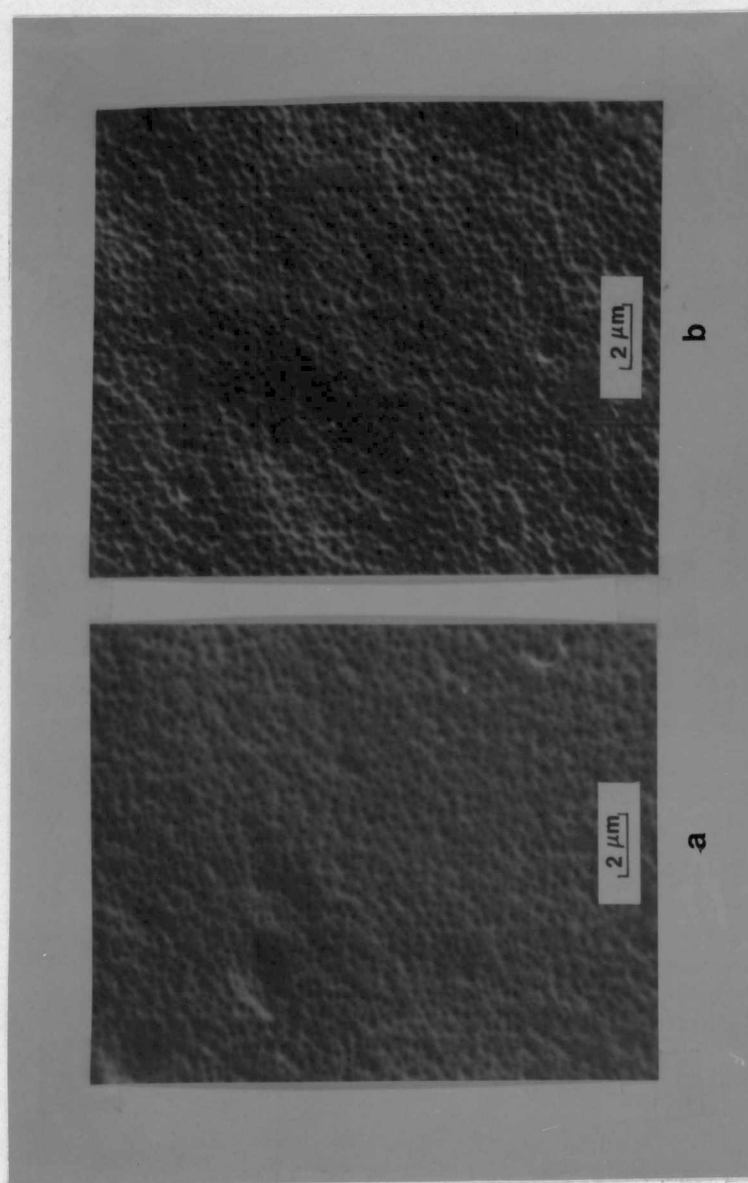


Figure 5.14. SEM micrographs of etched epoxy samples having postcure at 150°C: (a) 1 hr (b) 15 hr.

These regions are preferentially oxidized by a strong oxidizing agent such as chromic-sulfuric acid which was used in our etching process. The globules have been referred to in many different ways by many investigators with terms such as "micelles" (23), "floccules" (18), "modules" (91), "gel balls" (56), and "microgels" (11).

In general, several levels of sizes of globules have been reported in the literature. Labana et al. (56) have claimed that the diameter of so called gel balls is about $0.01 - 0.015 \mu\text{m}$. Rachich and Koutsky (91) described the nodules having sizes with a range from $0.01 \mu\text{m}$ to $0.66 \mu\text{m}$. Aspbury and Phillips (7) found the finest structure of microgels about 4 nm to 15 nm . Cuthrell (18) has reported that the average floccular diameter ranges from $0.5 \mu\text{m}$ to $50 \mu\text{m}$ depending on cure temperatures. Misra et al. (73) argued that there were two size ranges. One of the sizes varied from $10 \mu\text{m}$ to $70 \mu\text{m}$ under the SEM, while the other had a much finer scale with a range of $0.02 \mu\text{m}$ to $0.2 \mu\text{m}$ in a Transmission Electron Microscopy. Our results from the SEM using different magnifications show two levels of dimple sizes ranging from $0.1 \mu\text{m}$ to $0.7 \mu\text{m}$ and from $2.5 \mu\text{m}$ to $50 \mu\text{m}$. The difference of the sizes between these observations is not well understood. It can be assumed that a number of factors such as various epoxy systems, etching agents, experimental procedures used in the SEM or TEM are all possibly involved.

Misra et al. have argued that the presence of microgels in two levels is due to the mechanism of network formation. According to the mechanism suggested by Bobalak et al. (11), Solomon (97) and Labana et al. (56), this is a microgel particle produced by microgelation prior to the gel point, which will then coalesce or flocculate to form the microgel after total gelation of the system. They therefore proposed a model considering the formation of macrogels in three stages: formation of the primary microgel, the secondary microgel and then the macrogel. They used the term primary microgel to refer to microgels in the size of 0.01 μm to 0.05 μm , whereas secondary microgels are above 1 μm . In view of our results, the sizes fall into the range between the primary and secondary microgel. This seems to indicate that it is difficult to differentiate microgels simply into these two categories because the size of microgels may depend on many factors.

Agglomeration of microgels in the range of size from 2.5 μm to 50 μm randomly distributed throughout the surface can be seen in Figure 5.11 (p. 106). This is similar to those observed by Misra et al. This can probably be referred to as the macrogel.

The domain size observed tends to increase with an increase in the amount of excessive curing agent. These observations are consistent with those of Misra et al. In the excess of epoxy resin case, we also observe that the size tends to increase with an increase in the amount of

excess epoxy resins. These results differ from those of Misra et al., who claimed that an increase of excess epoxy did not cause significant changes in the morphology observed at equal stoichiometry. As noted by Racich and Koutsky (90), increases of the crosslinking density should result in decreasing domain sizes. Crosslink density increases with an increase of curing agent as has been shown in the previous section. This seems to indicate that the domain size should also decrease in the excess epoxy case due to the increase of crosslink density. Thus it can be seen that the size of domain should vary either with excess of curing agent or an excess of epoxy resin.

The domain size at the macro level does not exhibit a clear trend with varying stoichiometry of the curing agent.

The effect of the cure temperature on the domain size seems less significant as compared to that of the stoichiometry. Since samples in series of B and C are in the same stoichiometry of 1.0, their sizes are all about 0.4 - 0.5 μm . It may be suggested that the stoichiometry probably dominates the size of domain. As seen in the micrographs in Figure 5.13, the appearance becomes rough and irregular at high cure temperatures. It is possible that this is due to exothermic effects which can give rise to the inhomogeneous reactions within the samples. Thus it results in the roughness and irregularity of the network as observed.

The exothermic effect is largely reduced in a two-stage postcuring process. It can be seen that the appearance of the surface looks regular even postcuring at 150°C. The domain size also reveals no significant difference from variation of the time of postcure.

The size of microgel is greatly governed by the reactivity and diffusivity of reactants. Labana et al. (56) have reported that the formation of microgel resembles a nucleation process in crystallization, which includes the formation of nuclei and the growth of nuclei. These mechanisms are controlled by the reactivity and diffusivity of nuclei. The reactivity of reaction increases with an increase of the functionality of reactants (56), or an increase of catalysts (90). These all tend to decrease the size of microgels since higher reactivity may cause the gelation of the entire mixture to occur at an earlier stage. On the other hand, the increase of cure temperature may increase not only the rate of reaction, but also the capability of diffusivity of reactions. It has been indicated (56, 70) that the higher diffusivity will result in larger microgels. The mechanism of the formation of microgels must be very complicated. However in view of our results, it may be suggested that the stoichiometry of systems governs the size of domains, and the combined effect of reactivity and diffusivity due to the increase of cure temperature has only a slight effect on the size of domain.

However, the exothermic effect could cause roughness and irregularity of the morphology.

CHAPTER 6

MECHANICAL PROPERTIES OF CURED EPOXIES

6.1 Small Strain Elastic Properties

Results

Tensile properties of cured epoxies were determined using an Instron Tensile Tester. The tests were carried out at room temperature and at a crosshead speed of 0.05 inches per minute. The sample length between clamps was 4 inches. A typical stress-strain behavior of epoxy samples is shown in Figure 6.1. The stress rises almost linearly with increasing strain up to the breaking point, and rupture occurs at only a few percentages of strain. The elastic modulus E is obtained from the slope of curves at zero strain. Results for cured epoxy specimens of series A and B are reported in Table 6.1 and Table 6.2. The modulus of all samples has a value of about 1.7×10^{10} dynes/cm² and seems unchanged.

Discussion

The stress-strain behavior of epoxies samples is almost linear obeying Hooke's law in a small strain. The samples fail at very low strains less than about 5%. It implies that the epoxies fracture in a brittle manner. The Young's modulus obtained for all samples varies only slightly. It seems to indicate that the stoichiometry and

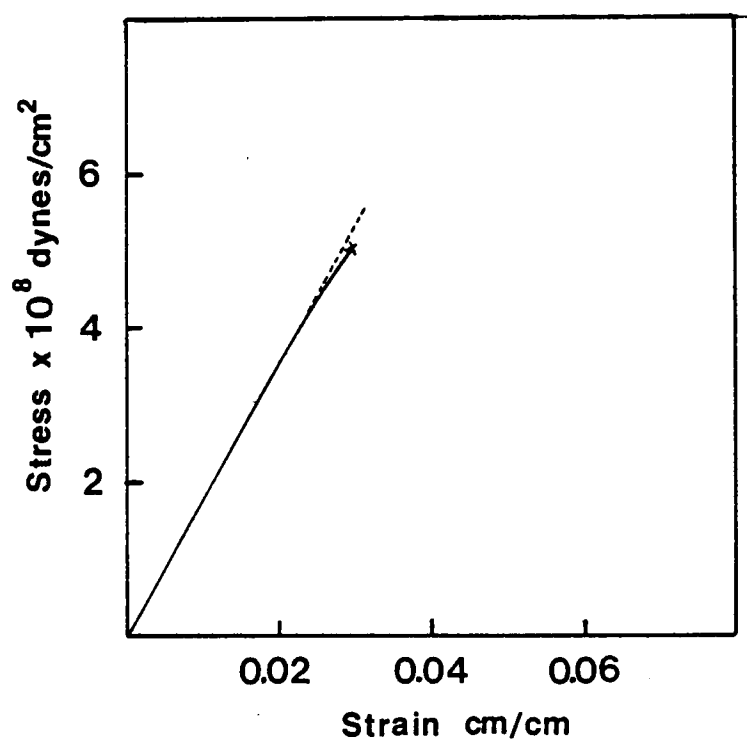


Figure 6.1. A typical force-elongation curve for cured epoxy sample.

TABLE 6.1
EFFECT OF NMA TO EPON 828 STOICHIOMETRY
ON TENSILE PROPERTIES

NMA/EPON 828 Ratio	Ultimate Tensile Strength σ_b $\times 10^{-8}$ dynes/cm ²	Young's Modulus E $\times 10^{-10}$ dynes/cm ²	Elongation to Break γ_b %
0.5	6.4	1.7	3.6
0.7	6.4	1.8	3.7
0.8	5.6	1.8	3.2
0.9	4.9	1.7	2.2
1.0	5.5	1.8	3.2
1.2	6.0	1.8	3.6

TABLE 6.2
EFFECT OF CURE TEMPERATURE ON TENSILE PROPERTIES

Cure Temperature °C	Ultimate Tensile Strength σ_b x 10 ⁻⁸ dynes/cm ²	Young's Modulus E x 10 ⁻¹⁰ dynes/cm ²	Elongation to Break γ_b %
80	5.6	1.8	3.3
93	5.6	1.7	3.3
107	5.8	1.7	3.6
121	5.8	1.8	3.9
135	6.4	1.7	4.2
150	6.9	1.7	4.7

cure temperature does not affect the small strain elastic properties. It also indicates that the Young's modulus is insensitive to the crosslinking density of networks. This observation has also been reported by many investigators (10, 52, 56, 73).

6.2 Ultimate Tensile Properties

Results

The ultimate tensile properties such as ultimate tensile strength, σ_b , and elongation to break, γ_b , are shown in Table 6.1 and Table 6.2. These vary with increasing the stoichiometry. A minimum of σ_b and γ_b appears at the stoichiometry of 0.9. The effect of the cure temperature on the ultimate properties seems not significant except at high cure temperatures.

Discussion

The tensile strength decreases with the stoichiometric ratio of NMA and is minimum at stoichiometry of 0.9. The properties increase again with an excess of curing agent. The trend of the tensile strength is similar to that observed by Kim et al. (52), but the trend of the elongation to break seems reversed. However in contrast, Labana et al. (56) indicated that both σ_b and γ_b exhibited a convex shape of relations to the stoichiometry of curing agent. The reason for this inconsistency is not well understood. It may be due to the different preparation of

samples or due to the inherent variation of tensile measurements.

In Table 6.2 the ultimate properties are unaffected by varying the cure temperature except at the higher cure temperature. It appeared that the thermal degradation in the tensile specimens was not significant even at higher cure temperatures. But it is believed that volatility of curing agent is still significant. Therefore the ratio of epoxy to NMA should be decreased. This may explain why an increase of σ_b and γ_b is observed. In view of our results, it appears that the ultimate properties are relatively unaffected by varying the cure temperature, but could be strongly influenced by the stoichiometry of epoxy systems.

6.3 Impact Strength

Results

The effect of the stoichiometry on the impact strength is plotted in Figure 6.2. It shows that the impact strength increases with an increase of the curing agent and is a maximum at the stoichiometry of 0.9. It then decreases with the stoichiometry over 0.9. The influences of the cure temperature and the time of post-cure on the impact strength are also shown in Figures 6.3 and 6.4. The impact strength varies with the cure temperature in a manner as that observed in the plot of the glass transition temperature versus the cure temperature which

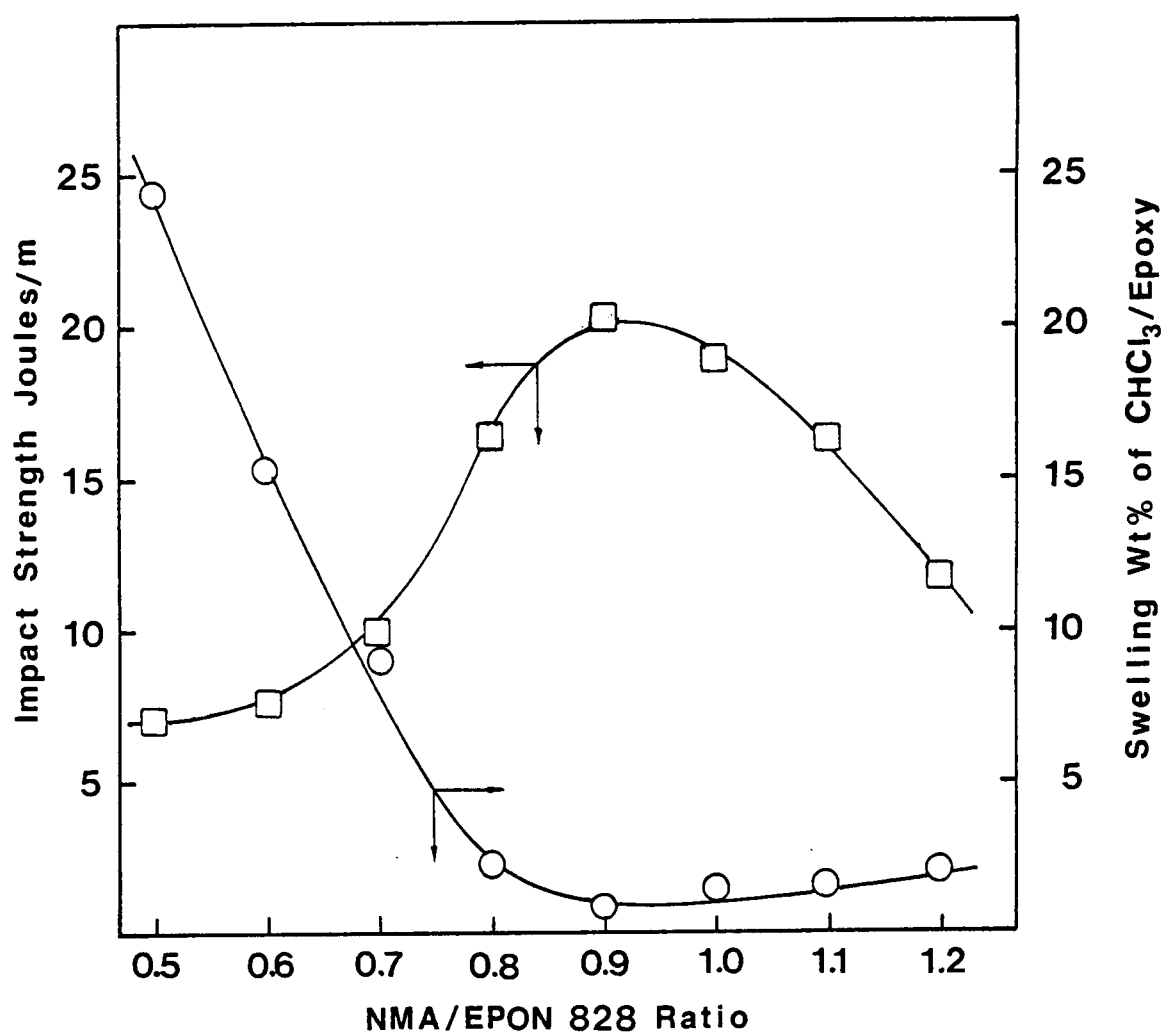


Figure 6.2. Impact strength and swelling ratio of cured epoxies as a function of NMA/EPON 828 ratio.

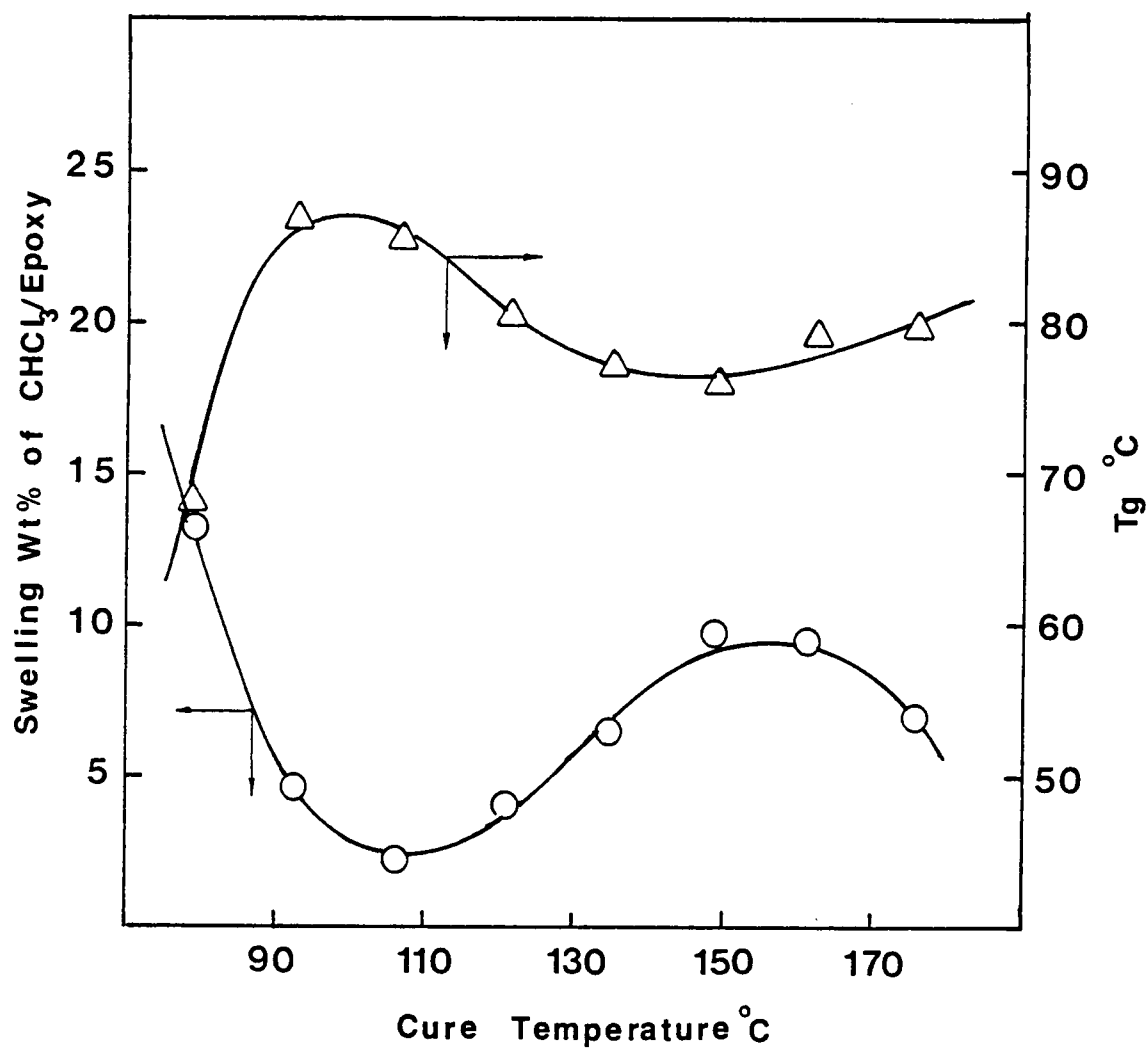


Figure 6.3. Impact strength and swelling ratio of cured epoxies as a function of cure temperature.

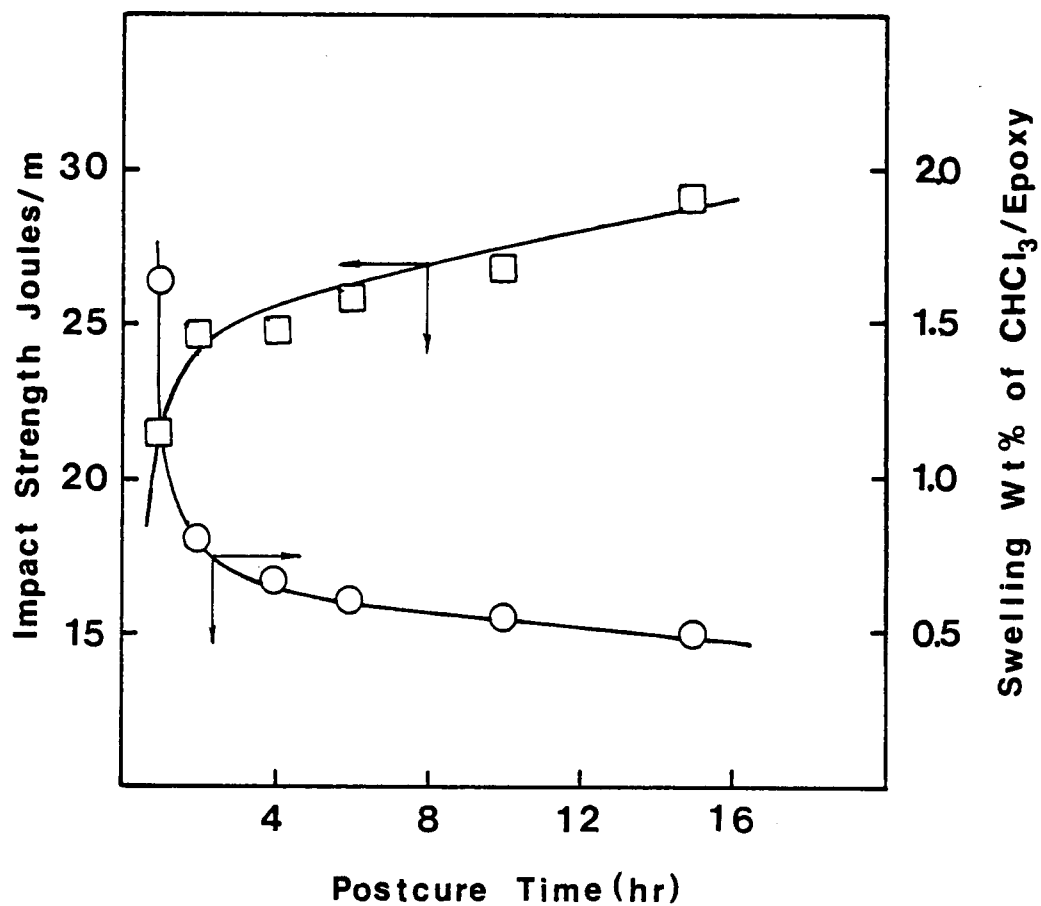


Figure 6.4. Impact strength and swelling ratio of cured epoxies as a function of time of postcure.

described in Chapter 4. The postcure shows to increase the impact strength.

Discussion

The impact strength for all epoxy samples we have seen exhibits trends similar to those of the glass transition temperature described in Chapter 4. It indicates that the impact strength is sensitive to the crosslinking density of networks. In other words, the crosslinking density of the network structure determines the performance of the highly crosslinked polymers. The trend in results is in good agreement with those reported by Kim et al. (52).

CHAPTER 7

RESIDUAL STRESSES IN CURED EPOXY

7.1 Origins of Residual Stresses in Epoxy

The residual stresses produced in cured epoxy during the curing process can primarily come from two sources. One of them is from the contractive stresses due to the volume contraction after the gelation of curing reaction (44), the other is from the thermal stresses due to density changes occurring during the inhomogeneous cooling process when casted samples are cooled from the curing temperature to the ambient temperature. The generation of contractive stresses is greatly affected by the thermal cure cycle of the process. The time to vitrify in the curing reaction varies with the curing temperatures. Thus as a consequence of the exothermic reactions, improper curing temperature will lead to the core vitrifying before the outer layers or vice versa (36). Built-in curing stress will then occur. The cooling stresses are governed by the rate of cooling, the faster the rate of cooling the greater will be the stresses developed. The temperature dependence of material properties such as elastic modulus, thermal expansion coefficient is responsible for the occurrence of the residual stresses. In addition, several other factors such as elastic anisotropy, orientation textures or heterogeneity of structure are also possibly involved.

7.2 Theoretical Solution of Residual Stresses Distribution Due to Non-homogeneous Cooling

Thermal Stresses Development

Thermal stresses arise when a piece of material is cooled inhomogeneously. This is due to the effect of temperature differential within the body which results in non-uniform volume change due to the variations in rates of thermal contraction of different parts. As a result of temperature dependent behavior of elastic properties of material, a distribution of residual stresses is formed after the specimen has been cooled below solidification. Many investigators (58, 59, 60, 76) have extensively described the development of thermal stresses during the cooling process.

The extent of stresses persisting within the slab largely depends upon temperature dependent properties such as the thermal expansion coefficient, heat capacity, thermal conductivity and Young's modulus, and also depends upon the cooling conditions such as the cooling medium and thickness of the slab. However as far as the theoretical modeling is concerned here, we assume that the material is isotropic and the effects of viscoelasticity, yielding and volume relaxation are neglected.

Theoretical Solution

Theoretical solution of the residual stresses developed during quenching has been treated by several workers (3, 45, 60).

A simple model approached by Aggarwala and Saibel is based on the assumption that the material behaves like a Maxwell solid in its thermomechanical response, that is, the material properties drastically change at some critical temperature (e.g., glass transition temperature). A more sophisticated theory developed by Lee et al. (60) considered the detailed viscoelastic effects of temperature near the transition range.

It is difficult to apply Lee's theory to epoxies as the detailed experimental data on the relaxation modulus and density as a function of time is not available. However in the case of quenching an epoxy sample from above its softening temperature to the ambient temperature, the material goes through from an incompressibly rubbery state to a compressibly elastic state. Since the modulus in the rubbery state is relatively low as compared to the modulus in the glassy state, the contribution to the residual stress due to the low modulus in the rubbery state is small, probably negligible. However in the glassy state, the material behaves like an elastic solid. Based on these assumptions, an analytical solution is given in Appendix. Only the final result will be given. The equation for the residual stresses is expressed as:

$$\sigma(X_1, \infty) = \frac{-E}{1-\nu} \left[\frac{1}{L} \int_0^L a[T(X_1, t_1) - T(X_1, 0)] dX_1 - a[T(X_1, t_1) - T(X_1, 0)] \right] \quad [7.1]$$

Where E is the Young's modulus of elasticity, ν the Poisson's ratio, a the thermal expansion coefficient, $2L$ the thickness of the slab, and t_1 the time which the level solidifies. E and ν will be considered to be independent of temperature, whereas a is assumed to be a linear function of temperature.

The integration term in Equation [7.1] is the expression of the average strain throughout the whole thickness during the thermal history of inhomogeneous cooling at a solidification time at a specified depth of slab. The second term represents the strain change during homogeneous cooling from above T_g to well below T_g .

As noted in Equation [7.1], the temperature profile in the cooling slab must be known throughout the calculation. The reason is that the thermal contraction of the material is governed by the temperature field in the plate. The heat conduction equation for temperature field in a cooling slab can be written as in the dimensionless form.

$$\frac{\partial \bar{T}}{\partial t} = \alpha \frac{\partial^2 \bar{T}}{\partial \bar{X}_1^2} \quad [7.2]$$

where $\bar{T} = T - T_1 / T_0 - T_1$, T_0 is the initial oven temperature, T_1 is the temperature of the surrounding cooling medium, and $\bar{X}_1 = X_1 / L$, $\bar{t} = kt / L^2$. k is the thermal diffusivity, i.e., $\alpha = k / \rho C \rho$. The initial condition is

$$\bar{T} = 1 \quad \text{for } -1 < \bar{X}_1 < 1 \quad \text{at } \bar{t} < 0 \quad [7.3]$$

If one assumes Newton's Law of cooling that the heat flux is proportional to the temperature differential between the surface and the cooling medium, this leads to the boundary conditions of

$$\frac{\partial \bar{T}}{\partial \bar{X}_1} = -\frac{\beta}{L} \bar{T} \quad [7.4]$$

where β is the Nusselt number defined as hL/k , h is the heat transfer coefficient and k the thermal conductivity. The solution for the temperature profile has been given by Carslaw and Jaeger (16) in the form of:

$$\frac{T - T_1}{T_0 - T_1} = \sum_{n=1}^{\infty} \frac{2\beta \cos(\alpha_n X_1)}{[(\beta^2 + \alpha_n^2) + \beta] \cos \alpha_n} \exp(-\alpha_n^2 t) \quad [7.5]$$

where α_n are the roots of the Equation, $\alpha \tan \alpha = \beta$, which is based on a Fourier series representation which gives more rapid convergence as the time increases.

Calculation of the residual stresses based on these equations has been carried out on the IBM/360 with the computer programs as indicated in the Appendix. It is noted that properties of the material dramatically changes at the transition temperature. As soon as the temperature is below T_g , it will rapidly solidify. Thus first we need to know how long the time is that elapsed from the beginning of quench to T_g . The second program was run to obtain the time for each position in slab to vitrify. We then substitute the temperature profile for each level and integrate the average strain by Simpson's method. The residual stress distribution can be computed by the third program.

Predicted Results for Residual Stresses

Figure 7.1 shows the temperature profile with various assumed heat transfer coefficients over half the thickness of slabs at seven time values in the dimensionless form. The results illustrate the influence of Nusselt number, β , or the thermal gradient in the cooling plates. As Nusselt number increases, that is, the quench becomes more severe, the thermal gradient will increase. Since the Nusselt number is defined as the heat transfer coefficient h times the thickness of slab L and divided by the thermal conductivity k , so that if heat transfer coefficient or thickness increases, or thermal conductivity decreases, the thermal gradient will become greater and greater. These

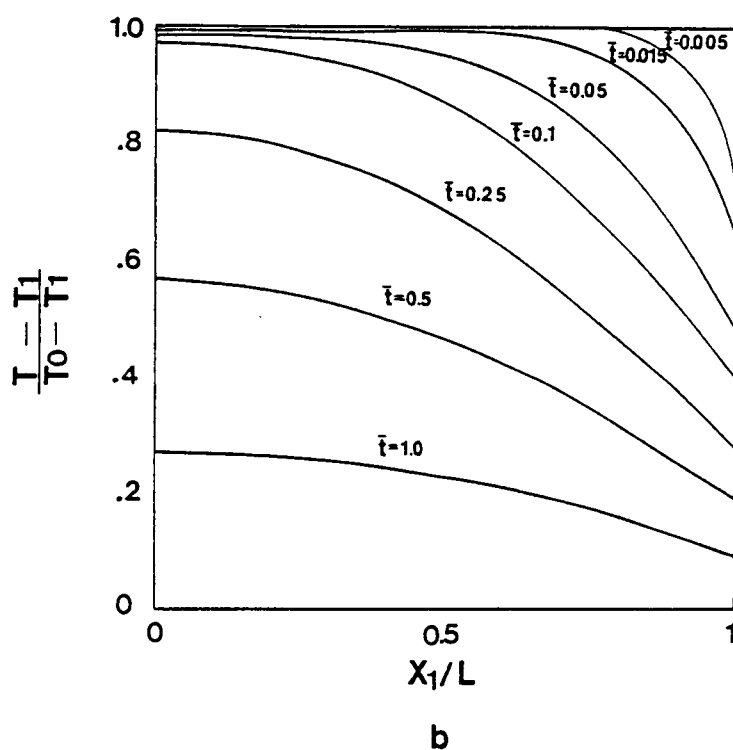
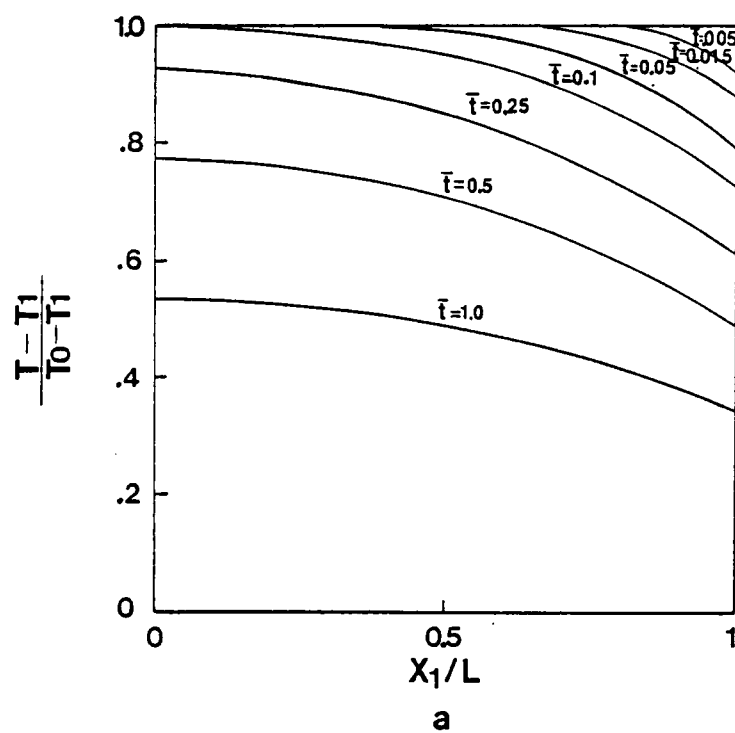


Figure 7.1. Dimensionless temperature profile for different Nusselt number (a) 0.979 (b) 3.528.

will thus affect the residual stress distribution of the slab after the cooling is completed. Figure 7.2 shows the theoretical solutions for the residual stress distribution in a 0.5 inch thick slab with various heat transfer coefficients. The severer the quenching occurs, the steeper is the shape of the residual stress distribution developed. The stresses both on the surfaces and in the center also increase. Figure 7.3 illustrates the effect of the thickness of slabs on the residual stresses. It should be pointed out that calculations of residual stresses above are under the assumptions that material properties below T_g are temperature independent (see Table 7.1).

7.3 Experimental Results of Residual Stress Distribution

Layer Removal Method

From successive removal of layers from quenched samples by carefully machining procedures, curvatures of samples which due to the bending resulted from a release of a stress were measured from the optical microscope. According to Treuting and Read's method, the residual stress distributions for different thicknesses and various quenching conditions are calculated as reported in Tables 7.2 to 7.7. The resulting residual stress distributions are shown in Figures 7.4, 7.5 and 7.6. The results appear to reveal a similar trend as obtained from the theoretical solutions.

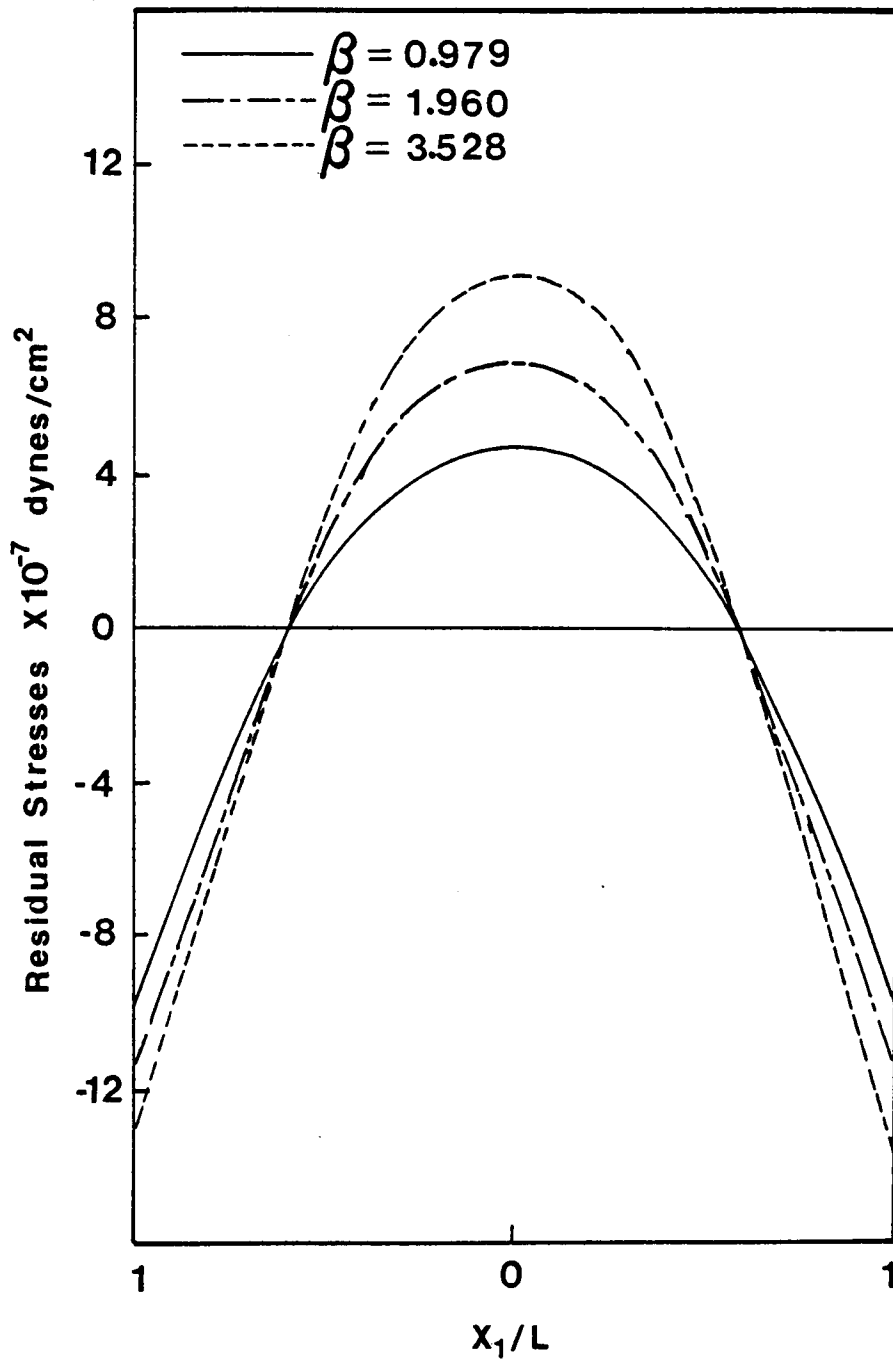


Figure 7.2. Theoretical solution of residual stress distribution for various Nusselt numbers.

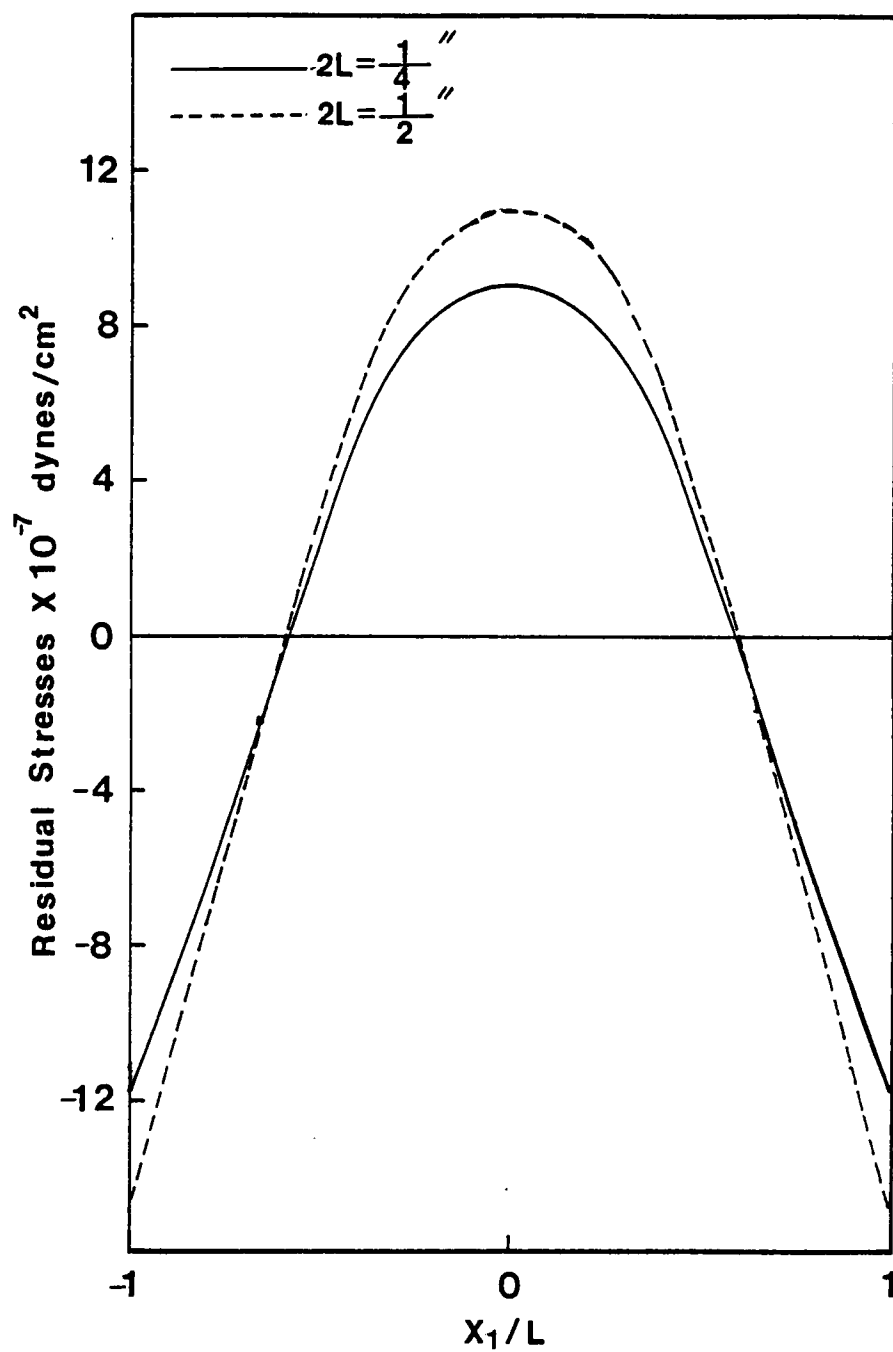


Figure 7.3. Theoretical solution of residual stress distribution for different thicknesses of slabs.

TABLE 7.1
 REPRESENTATIVE PROPERTIES OF EPOXY
 IN STRESS ANALYSIS

Young's Modulus (E)	3.45×10^{10}	dynes/cm ²
Poisson's Ratio (ν)	0.35	
Critical Temperature (T _{cr})	135	°C
Thermal Conductivity (k)	4.5×10^{-4}	cal/sec/cm/°C
Thermal Expansion Coefficient (α)	5.5×10^{-5}	cm/cm°C
Material Fringe Value (f)	1.93×10^7	dynes/cm ² cm•fringe

TABLE 7.2
DATA OF MEASURED CURVATURE FOR A $\frac{1}{4}$ " THICK SLAB
UNDER ICE WATER QUENCHING

No. of Layer	Z_1 cm	Z_1/Z_0^*	L cm	σ cm	r cm	ϕ cm ⁻¹
0	0.321	1.00	10.05	0.0107	1175.5	8.51×10^{-4}
1	0.191	0.60	10.04	0.094	133.3	7.50×10^{-3}
2	0.129	0.40	10.03	0.144	86.9	1.15×10^{-2}
3	0.084	0.26	10.01	0.176	71.4	1.14×10^{-2}
4	0.065	0.20	10.00	0.188	66.7	1.55×10^{-2}

* $Z_0 = 0.321$

TABLE 7.4
DATA OF MEASURED CURVATURE FOR A $\frac{1}{2}$ " THICK SLAB
UNDER ICE WATER QUENCHING

No. of Layer	Z_1 cm	Z_1/Z_0^*	L cm	σ cm	r cm	ϕ cm ⁻¹
0	0.671	1.0	10.06	0.016	1562.3	0.64×10^{-3}
1	0.494	0.74	10.06	0.040	307.7	3.25×10^{-3}
2	0.388	0.58	10.05	0.081	153.8	6.50×10^{-3}
3	0.277	0.41	10.05	0.093	134.2	7.45×10^{-3}
4	0.161	0.24	10.04	0.118	105.3	9.51×10^{-3}

* $Z_0 = 0.671$ cm

TABLE 7.5
CALCULATION OF RESIDUAL STRESSES FOR A $\frac{1}{2}$ " THICK SLAB
UNDER ICE WATER QUENCHING

Z_1 cm	Z_1/Z_0	Z_0+Z_1 cm	$(Z_0+Z_1)^2 \frac{d\phi(Z_1)}{dZ_1}$	$4(Z_0+Z_1)\phi(Z_1)$	$-2 \int_{Z_1}^{Z_0} \phi(Z) dZ$	$\phi(Z_1)$ dynes/cm ²
0.6	0.895	1.271	-2.527×10^{-2}	0.636×10^{-2}	-8.56×10^{-5}	-1.68×10^8
0.5	0.746	1.171	-2.263×10^{-2}	1.405×10^{-2}	-6.92×10^{-4}	-0.82×10^8
0.4	0.597	1.071	-2.271×10^{-2}	2.142×10^{-2}	-1.08×10^{-3}	-0.21×10^8
0.3	0.447	0.971	-2.049×10^{-2}	2.796×10^{-2}	-2.38×10^{-3}	0.45×10^8
0.2	0.298	0.871	-1.460×10^{-2}	3.031×10^{-2}	-4.07×10^{-3}	1.03×10^8
0.1	0.149	0.771	-1.324×10^{-2}	3.238×10^{-2}	-6.14×10^{-3}	1.15×10^8

TABLE 7.6

DATA OF MEASURED CURVATURE FOR A $\frac{1}{4}$ " THICK SLAB
UNDER LIQUID NITROGEN QUENCHING

No. of Layer	Z_1 cm	Z_1/Z_0^*	L cm	σ cm	r cm	ϕ cm ⁻¹
0	0.339	1.0	10.05	0.0435	285.7	3.50×10^{-3}
1	0.233	0.69	10.05	0.885	140.8	7.10×10^{-3}
2	0.181	0.53	10.01	0.140	88.5	1.13×10^{-2}
3	0.109	0.32	9.99	0.216	57.1	1.75×10^{-2}
4	0.033	0.096	9.98	0.278	44.6	2.24×10^{-2}

* $Z_0 = 0.339$ cm

TABLE 7.7
CALCULATION OF RESIDUAL STRESSES FOR A $\frac{1}{8}$ " THICK SLAB
UNDER LIQUID NITROGEN QUENCHING

Z_1 cm	Z_1/Z_0	Z_0+Z_1 cm	$(Z_0+Z_1)^2 \frac{d\phi(Z_1)}{dZ_1}$	$4(Z_0+Z_1)\phi(Z_1)$	$-2 \int_{Z_1}^{Z_0} \phi(Z) dZ$	$\phi(Z_1)$ dynes/cm ²
0.30	0.886	0.639	-2.261×10^{-2}	0.639×10^{-2}	-3.06×10^{-4}	-1.78×10^8
0.25	0.739	0.589	-2.445×10^{-2}	1.366×10^{-2}	-7.44×10^{-4}	-1.02×10^8
0.20	0.591	0.539	-1.832×10^{-2}	2.113×10^{-2}	-1.23×10^{-3}	-0.14×10^8
0.15	0.443	0.489	-1.774×10^{-2}	2.641×10^{-2}	-2.45×10^{-3}	0.55×10^8
0.10	0.295	0.439	-1.542×10^{-2}	3.073×10^{-2}	-3.89×10^{-3}	1.01×10^8
0.05	0.148	0.389	-1.057×10^{-2}	3.377×10^{-2}	-6.47×10^{-3}	1.48×10^8

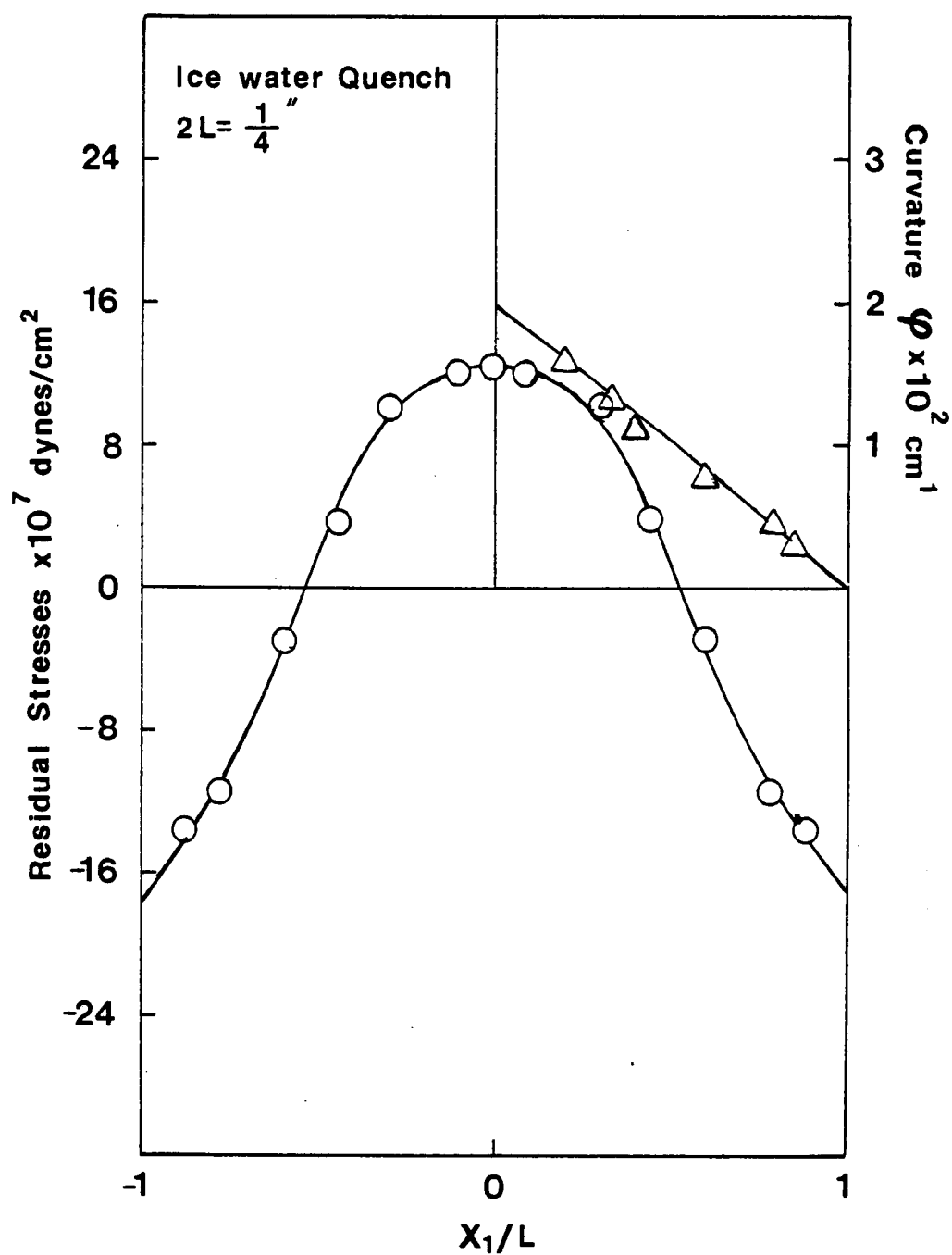


Figure 7.4. Measured curvature and calculated residual stress for a $\frac{1}{4}''$ thick slab under ice water quenching.

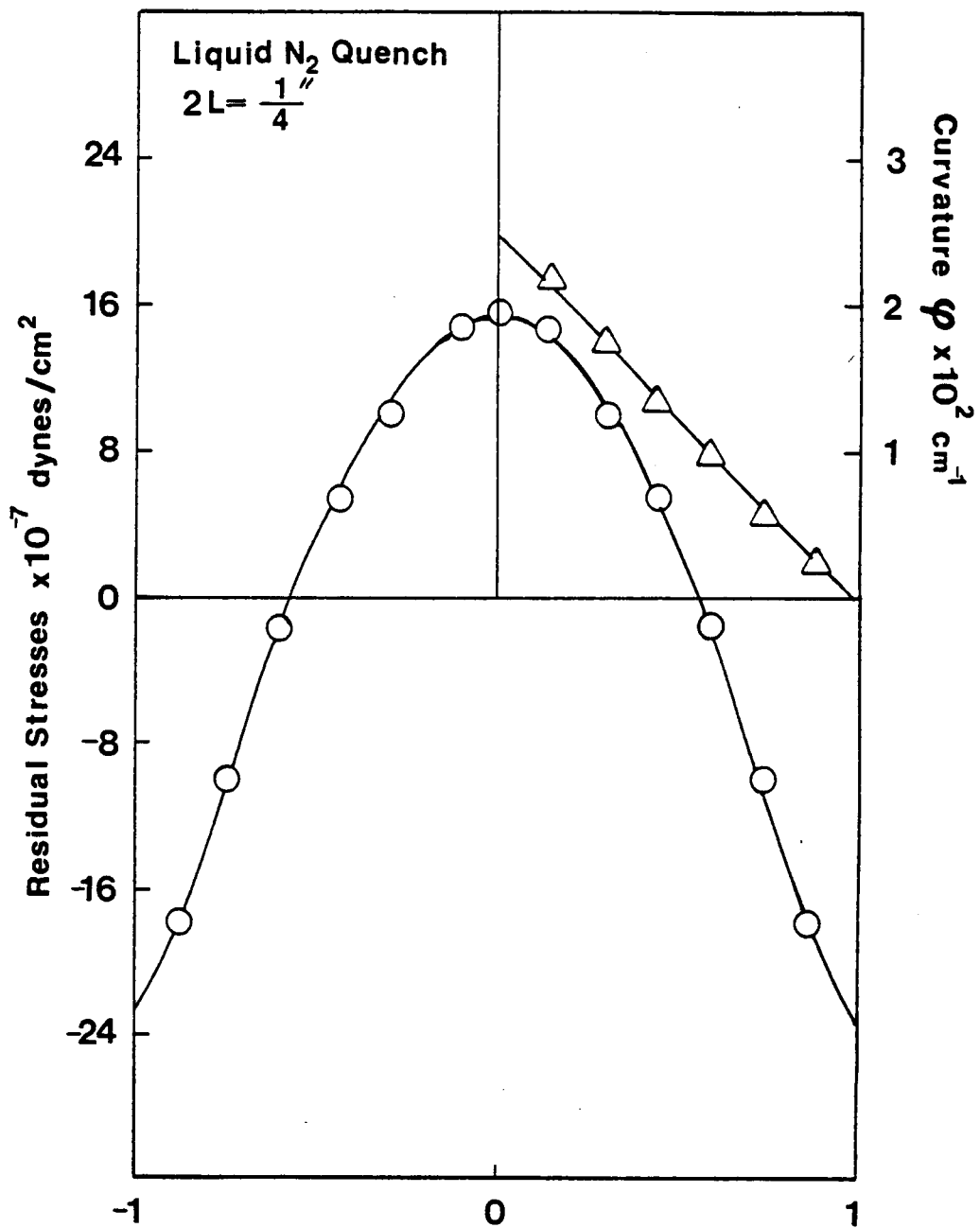


Figure 7.5. Measured curvature and calculated residual stress for a $\frac{1}{4}''$ thick slab under liquid N₂ quenching.

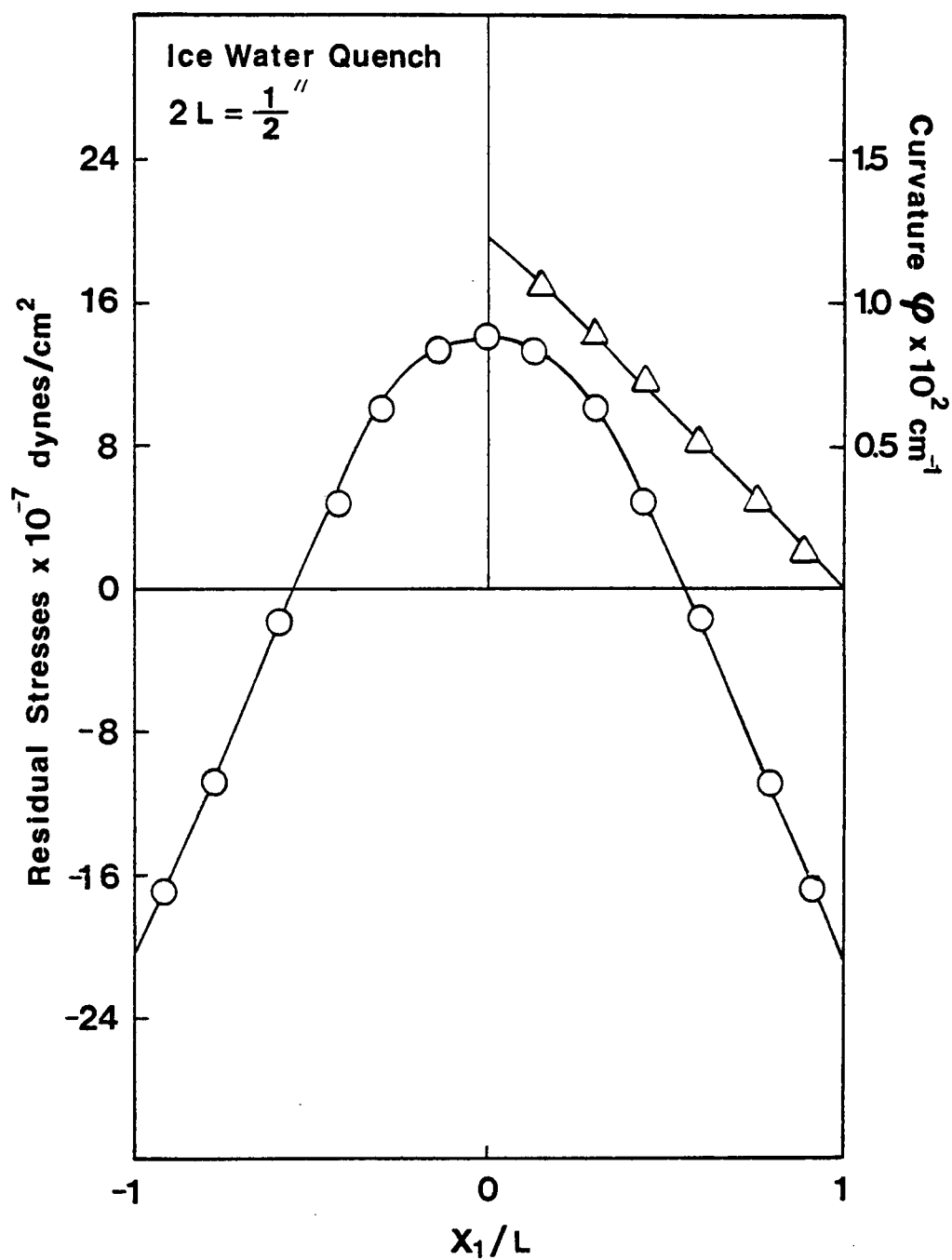
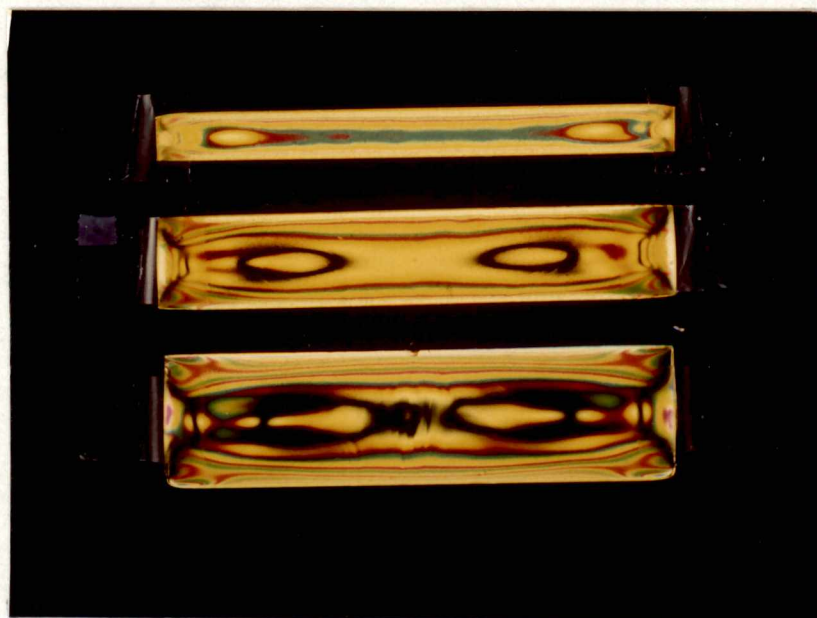


Figure 7.6. Measured curvature and calculated residual stress for a $\frac{1}{2}$ " thick slab under ice water quenching.

Photoelastic Method

The measurements of the residual stress distribution of quenched samples were made in the photoelastic apparatus which is similar to the birefringence measurement. The specimens were viewed with white light in a plane polariscope. The principal axes of stresses which have been examined reveal them to be reasonably parallel to the Cartesian coordinate system of slabs. The isochromatic fringes can be easily distinguished from the isoclinic fringes with white light because the isochromatics are colored with the exception of fringes of zero order, while the isoclinics are all black. In the pictures shown in Figure 7.7, the isochromatic fringes pattern for various conditions and thicknesses of specimens can be clearly observed. All fringes are more or less parallel to one direction of specimens except those of near the ends. Figure 7.8 shows the results with various quench conditions which are calculated from the stress-optical law by use of the relative retardation measured from a Babinet compensator. As may be seen in Figure 7.8, the residual stress distributions across section of specimens appear to be all on the compressive side. In the sense, this is contradictory to the condition of static equilibrium. They are internally self-balanced, that is, the tensile forces at any cross-section should be equal to the compressive forces.



a



b

Figure 7.7. Photographs of fringe pattern of plates with thicknesses of $\frac{1}{4}$ ", $\frac{1}{2}$ ", $\frac{3}{4}$ " under (a) ice water quench and (b) liquid N_2 quench.

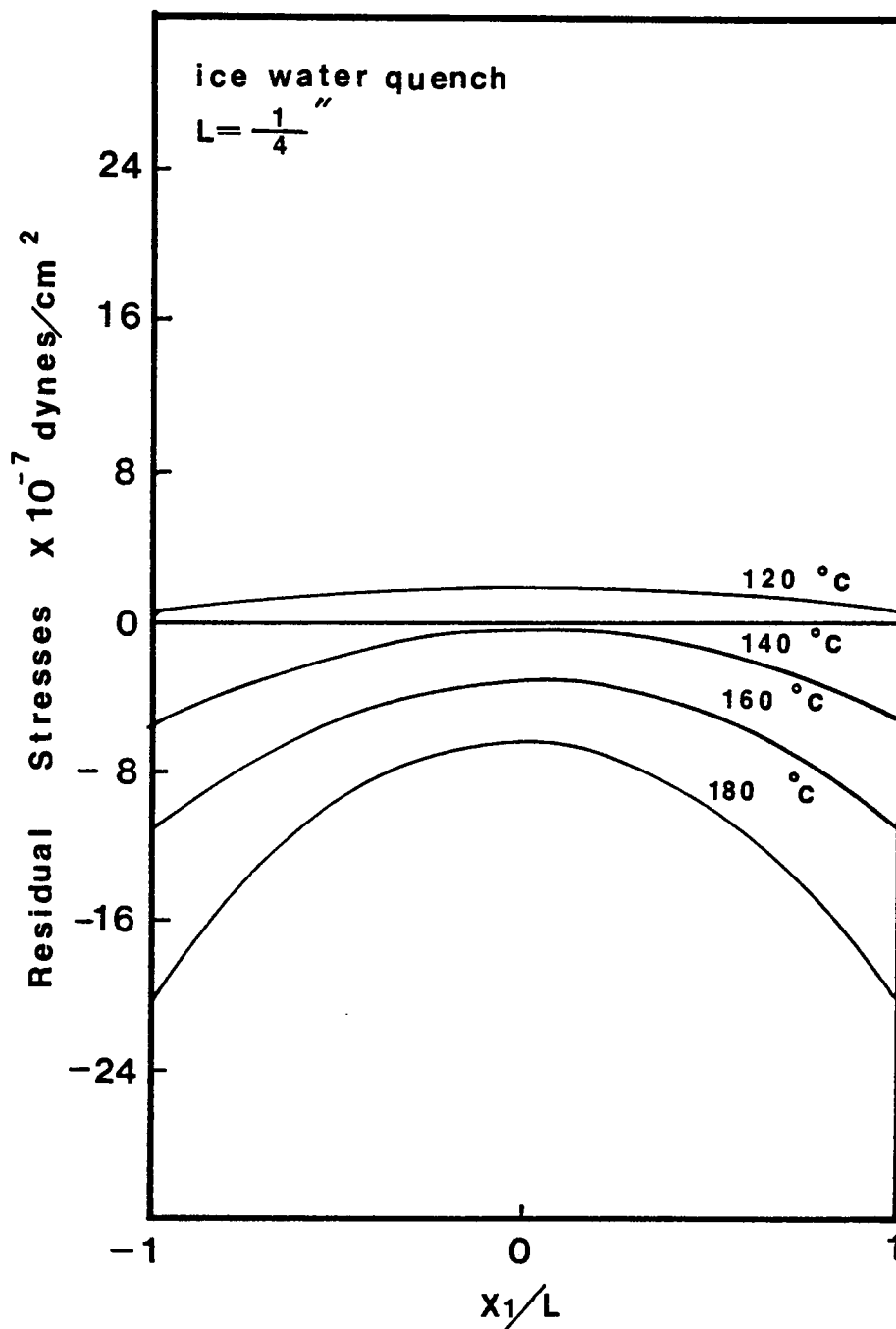


Figure 7.8. Plots of measured total residual stress by photoelastic method for $\frac{1}{4}''$ slab under ice water quenching at various initial oven temperatures.

These peculiar results may arise several questions that if 1. a plastic deformation yielding may involve due to a very rapid cooling, 2. some anisotropy effect such as molecular orientation may be introduced. During the quenching process, the transient temperature distribution will frequently result in the development of transient stresses large enough to cause plastic flow which may give rise to molecular orientation. The total birefringence due to quenching may include the internal stresses due to the thermal straining, plastic yielding deformation and molecular orientation. All these factors will contribute to retardation measurements and give the total combined effects. This may be the reason why an unbalanced residual stress pattern is obtained.

We have tried to separate these effects experimentally by measuring the retardation by two stages. First a total retardation is measured through a cross-section of specimen cut out of the plate, then a subslice is removed from the specimen and the remaining retardation measured. It is assumed that the total retardation can be divided into two parts, one is the retardation due to the residual thermal stresses, the other is the retardation due to the plastic deformation and orientation. It can be expressed as

$$R_t = R_r + R_s$$

[7.6]

where R_t is the total retardation, R_r is the retardation due to the residual thermal stresses, and R_s is the retardation due to the sum of plastic deformation and orientation. As noted the residual thermal stresses in a slab are similar to a slab subjecting to a pure bending, they can be released by cutting; however, the frozen in molecular orientation cannot be released by cutting or slicing. In this manner, we can probably separate these two effects and get the residual stress purely due to thermal gradient.

Based on these assumptions and carried out in experiments, the results of residual stresses distribution are shown in Figures 7.9, 7.10 and 7.11. In these Figures, it can be seen that the second effect seems more profound in the center of the slab than near the surface. After subtracting the second effect from the total retardation, the residual stresses distribution shown in the Figures becomes balanced. It is surprising that the results revealed fit the assumption being made. The influence of varying cooling conditions and thicknesses on the residual stress distribution is also shown in the Figures. They indicate the same trend as those obtained from the layer removal method. A comparison of results obtained from theoretical solution, photoelastic method and layer removal method are plotted in Figures 7.12 and 7.13. A residual stresses distribution for various thicknesses of slabs under a slow cooling from the curing temperature is also shown in Figure 7.14.

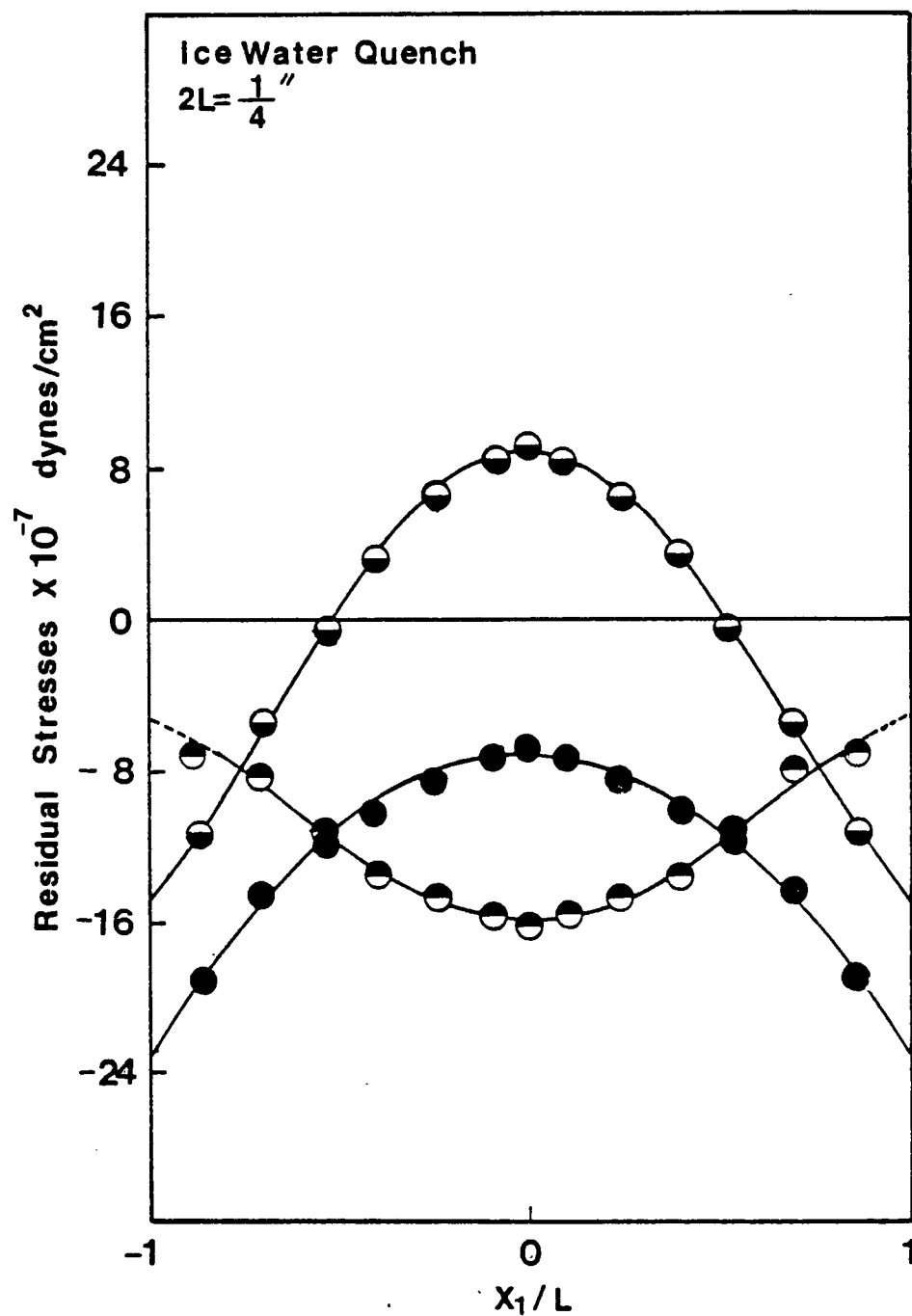


Figure 7.9. Plots of measured residual stress: ● total effect ◐ effect due to molecular orientation ○ effect due to thermal stress ($\frac{1}{4}''$ slab, ice water quench).

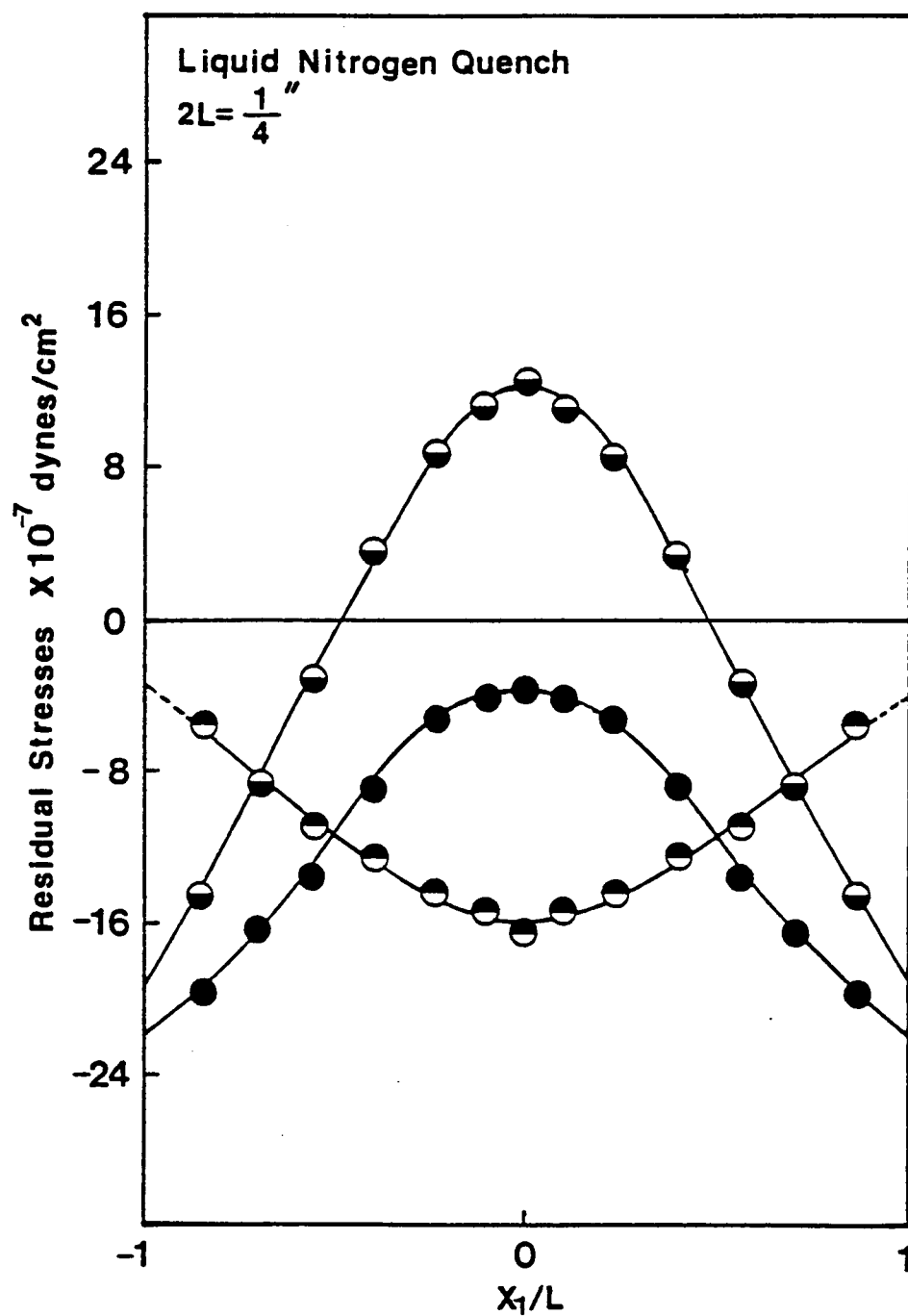


Figure 7.10. Plots of measured residual stress: ● total effect ○ effect due to molecular orientation ● effect due to thermal stress ($\frac{1}{4}''$ slab, liquid N_2 quench).

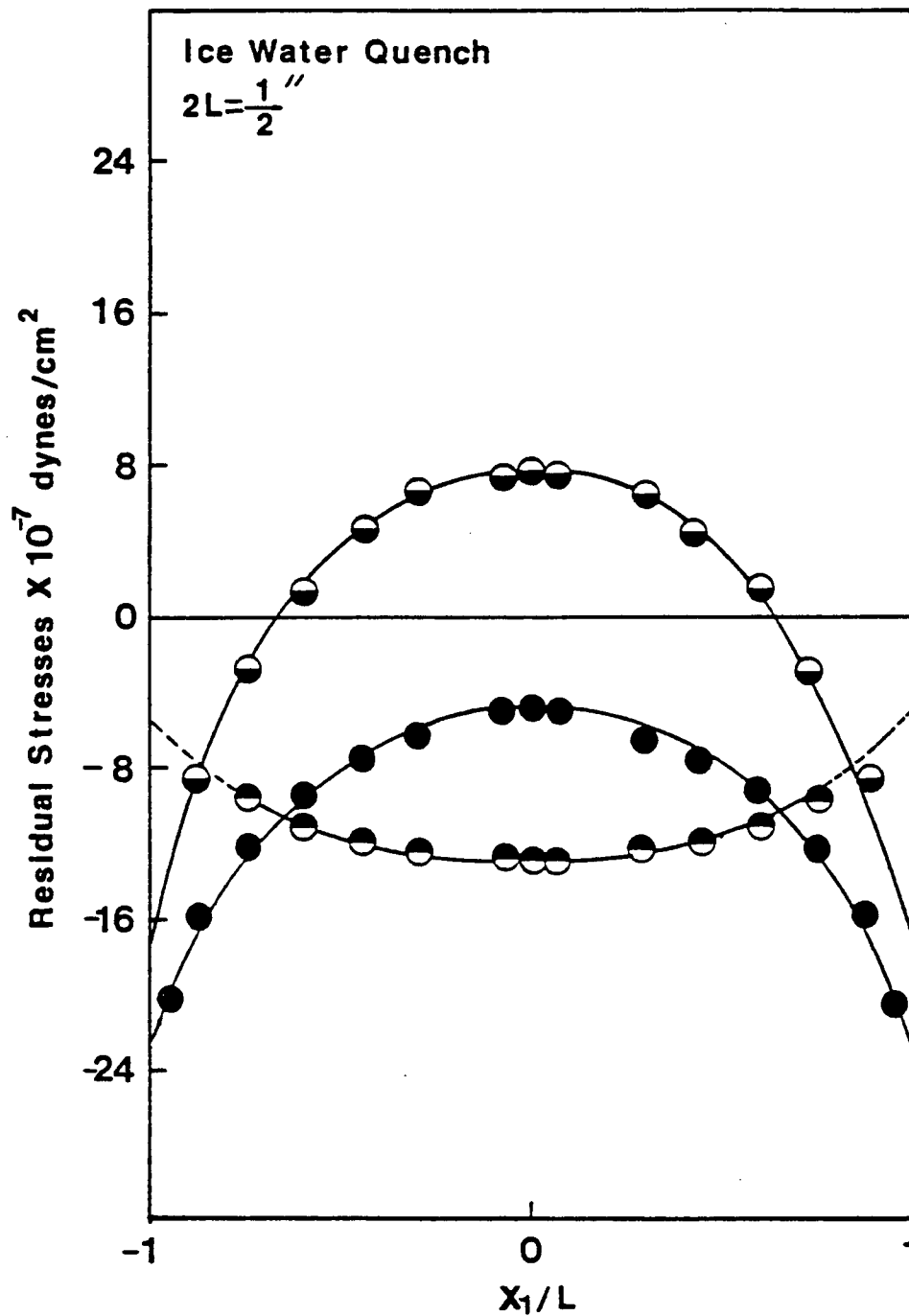


Figure 7.11. Plots of measured residual stress: ● total effect ○ effect due to molecular orientation ● effect due to thermal stress ($\frac{1}{2}$ " slab, ice water quench).

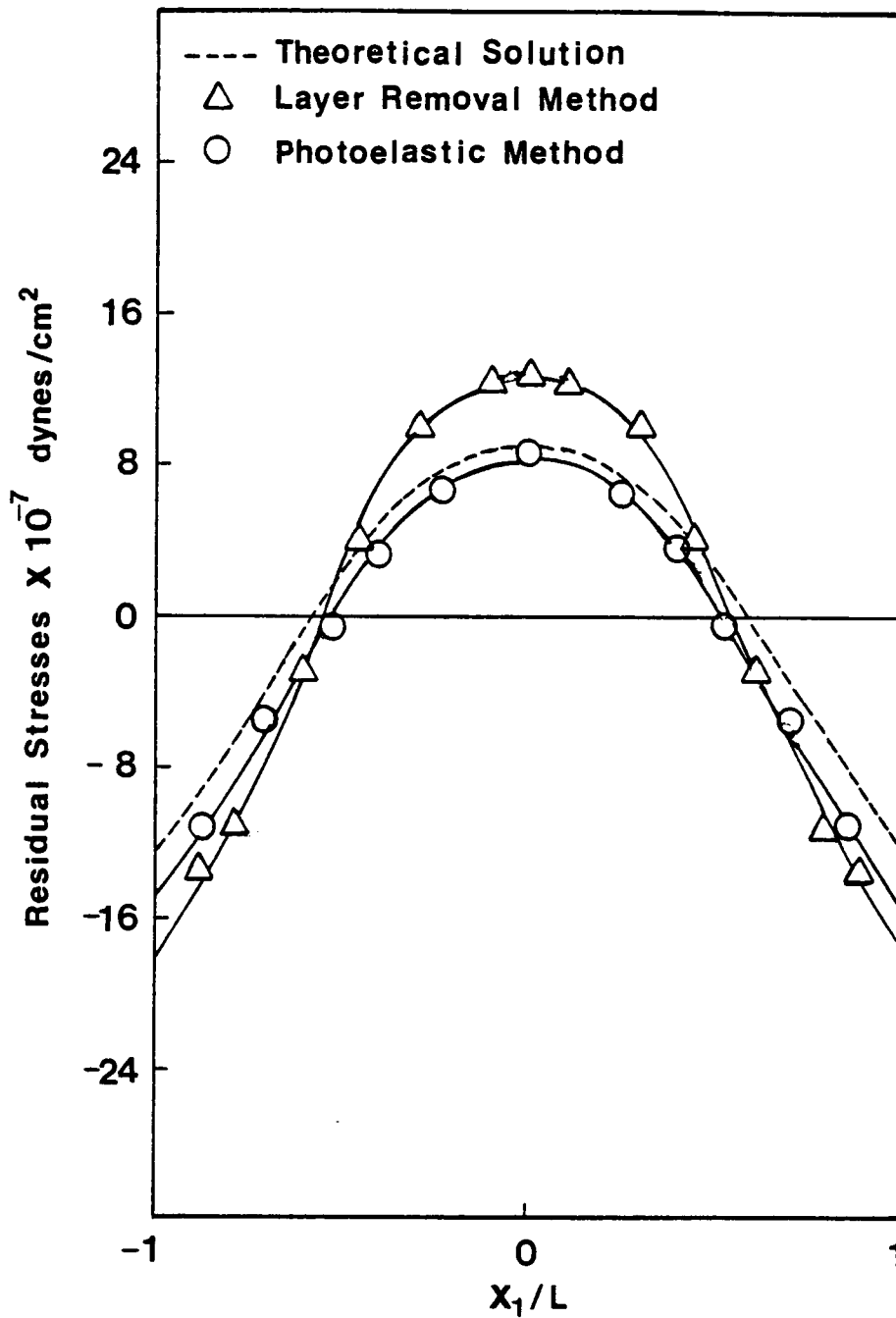


Figure 7.12. Calculated and measured residual stress for a $\frac{1}{4}$ " thick slab under ice water quenching.

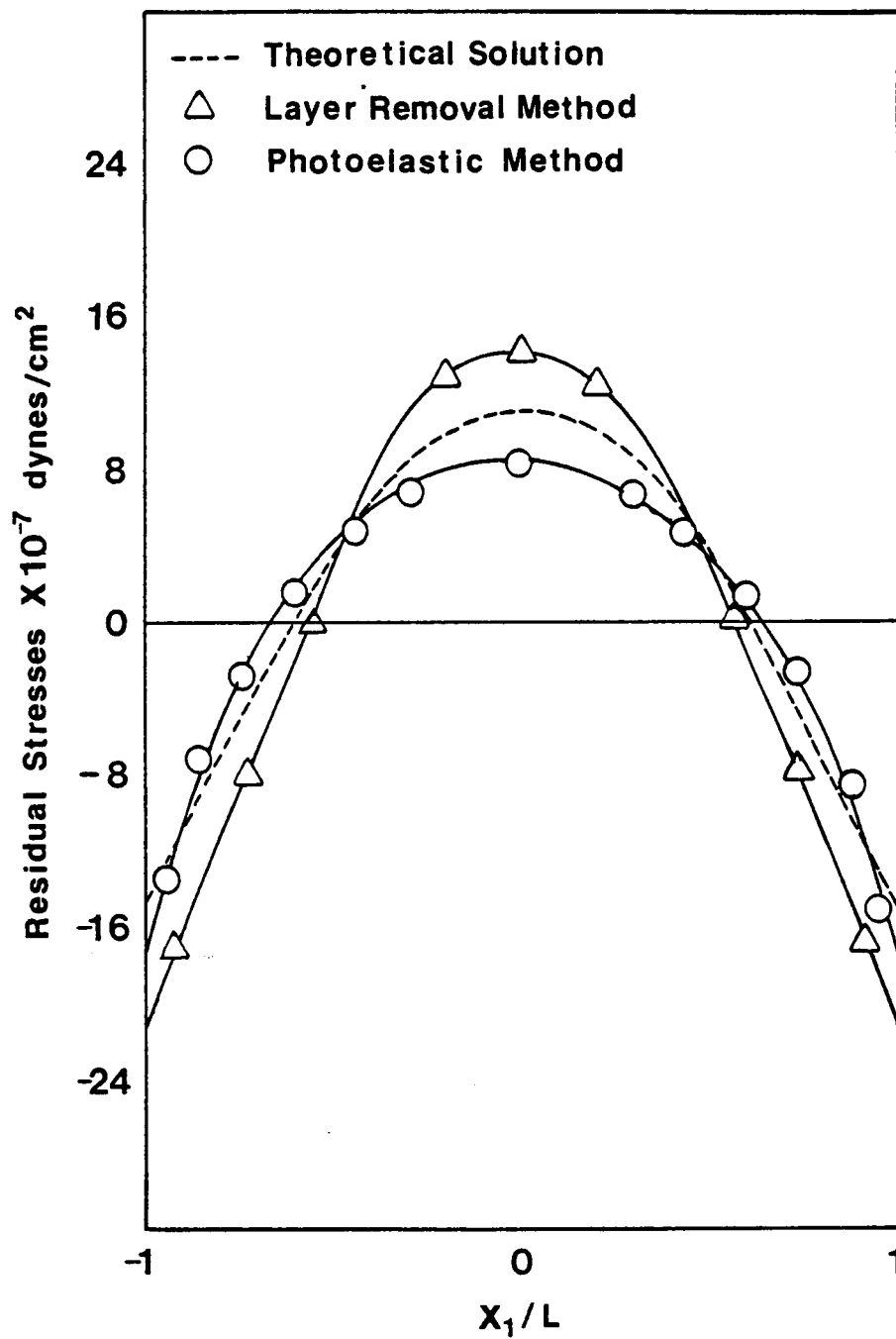


Figure 7.13. Calculated and measured residual stress for a $\frac{1}{2}$ " thick slab under ice water quenching.

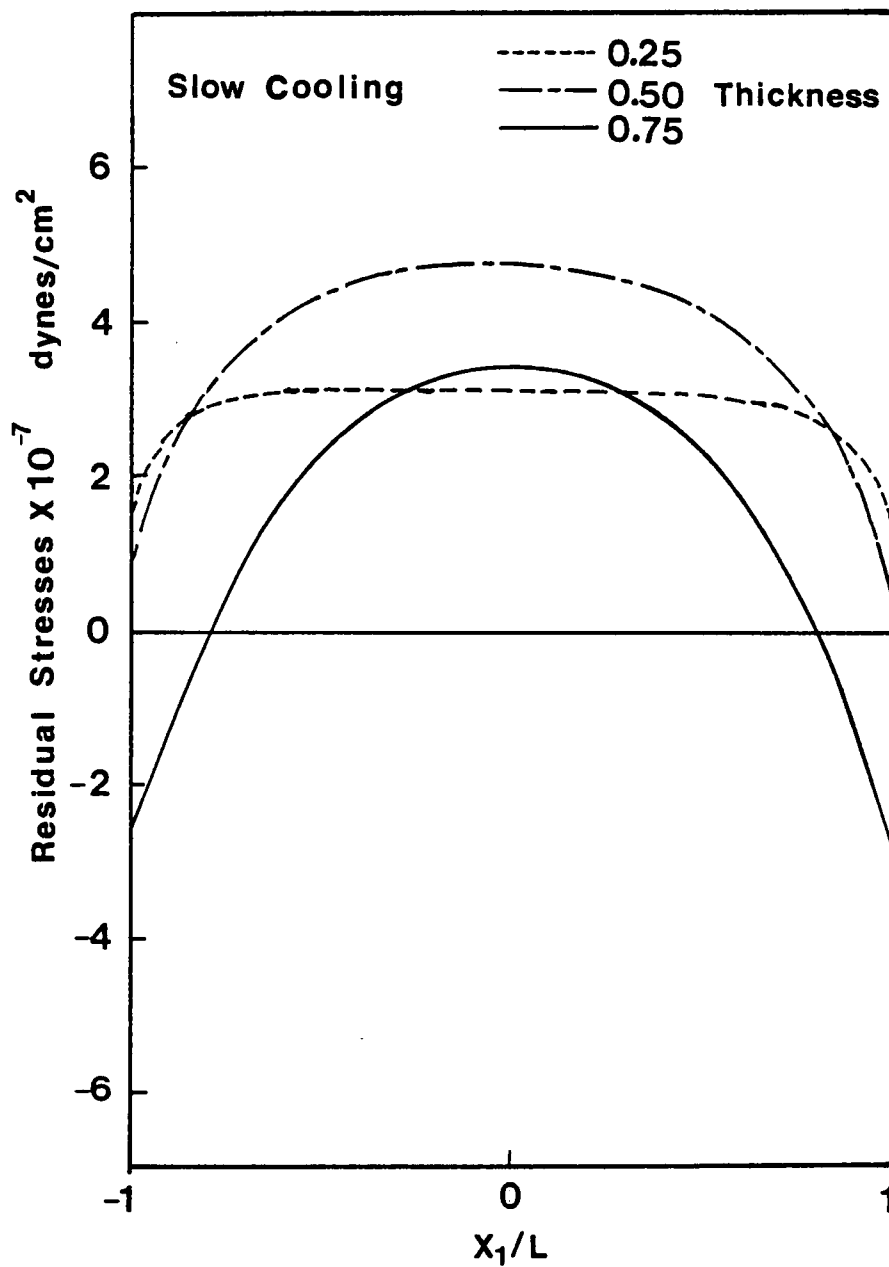


Figure 7.14. Measured residual stress for various thicknesses of slabs under slow cooling.

7.4 Discussion

The theoretical solution based on the simplified assumptions seems a good approximate solution to the residual stress distribution of a glassy epoxy solid under nonhomogeneous cooling process. Although the time-temperature dependence of viscoelasticity is neglected and a low modulus above T_g is assumed, the results still reveal a reasonable agreement between theory and experiments. However, in a very severe quenching such as in liquid nitrogen (-195.8°C), the solution of theory appears to be not adequate to predict the residual stresses, overestimate the effect in contrast to those from experiments. The reason for this is not known.

The peculiar birefringent phenomenon leading to unbalanced stresses as indicated previously has also been observed by Filon and Harris (28) in their study of the effect of cooling glass under pressure. This is similar to the case as Struik (99) claimed that a reacting entropic stress or orientation could occur due to the external pressure in the rubbery state. From photoelastic measurements of the quenched epoxy samples, it is also evident that the entire stress distribution receives contributions not only from the thermal stresses, but also from effects such as orientation and plastic yielding. It is possible that some type of orientation may be set up during the quenching process.

The results obtained from the layer removal method are more or less larger than those from the theoretical and photoelastic methods. It is difficult to argue about these differences. However, it is believed that the average errors of the results due to the machining process and integration are estimated to be roughly 10-15 percent.

The proposed method of two stages measurement of the retardation seems to work reasonably well. However, the method lacks verification. As noted previously, we assume that the contribution of retardation from the residual thermal stresses can be completely released by cutting or slicing through the direction perpendicular to the principal stresses of specimens. However, this is only imagined from the physical evaluation, an adequate experimental proof has not been done.

A low residual stress distribution is also observed within the epoxy even though the sample is cooled slowly from the curing temperature to the room temperature. The thermal effect should not be significant in a very slow cooling. Therefore, it can be said that these stresses should come from the curing process. These curing stresses, which have been claimed by Gillham (36), are a consequence of the exothermic effect. The effect will lead to the inside vitrifying before the outside. Thus the volumetric shrinkage on vitrification will result in the built-in curing stresses.

7.5 Effect of Residual Stresses on Impact Behavior of Epoxies

The influence of the residual stresses on the impact strength of epoxy samples is shown in Figure 7.15. It can be seen that the Izod impact strength increases after the epoxy is quenched. This is due to the suppression of crazing by the residual compressive stresses on the surface. Broutman et al. (96) have claimed a similar effect on the PMMA and PC. From the layer removal experiment and the annealing treatment, a warpage is also perceived which is believed to be due to the relief of the residual stresses. The residual stresses may be expected to affect the physical aging process and account for the dimensional instability as implied from the work of McGrath et al. (70) and Struik (89). However, no experiment has to be done to prove these effects in the current works.

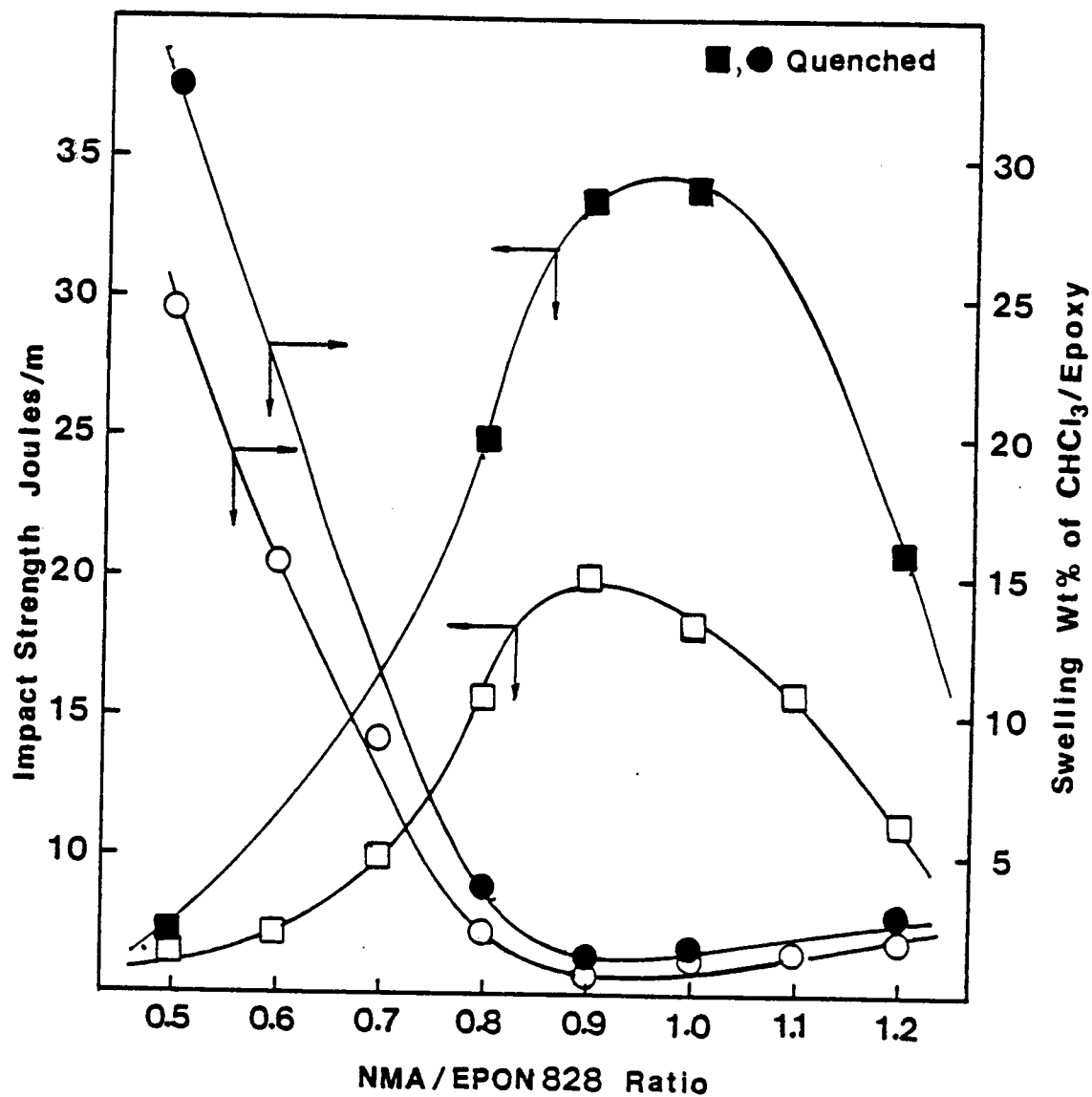


Figure 7.15. Effect of quenched epoxy sample on impact strength for various NMA/EPON 828 ratio.

CHAPTER 8

SUMMARY AND CONCLUSIONS

1. The residual stress distribution in quenched epoxies measured from the layer removal method shows parabolic type curves. The results indicate that the severer the quenching occurs, the steeper is the curve of the residual stress distribution developed.

2. Measurements using the photoelastic method exhibit peculiarly unbalanced residual stress patterns. This can be explained that molecular orientation or plastic yielding deformation are possibly involved during the cooling process. They will also contribute to the retardation measurement in the polariscope. A method to separate these effects from that of the thermal stress was proposed. As a result, the residual stress pattern becomes balanced. The proposed method seems to work well in our measurements, but it has not been verified.

3. A theoretical solution was derived to calculate the residual stress distribution. The results were compared to the measured results from the layer removal method and the photoelastic method. The results from the photoelastic method seems much closer to the theoretical results than those from the layer removal method. It indicates that the photoelastic method is quite suitable to measure

the residual stresses in a slab. Also, this simplified theoretical solution seems applicable.

4. A residual stress pattern with compressive stresses near the surface of specimens increases the impact strength.

5. The curing and properties of the epoxies were investigated. From DSC measurements, the cure reaction mechanism of our epoxy system is consistent with the assumption made that the reaction mechanism is simple second-order kinetics and can be described by an Arrhenius type equation. The activation energies are about 50 Kcal/mole in our NMA/EPON 828/BDMA system.

6. The effect of the stoichiometric ratio of the curing agent to epoxy resins on the crosslinked network of cured epoxies was investigated from studies of the measured swelling ratio and glass transition temperature. The network becomes less crosslinked when the stoichiometric ratio either has an excess of epoxy resin or excess of curing agent. The effect of cure temperature does not show a clear trend.

7. Density decreases with increases of glass transition temperature. This can be explained due to the fact that the non-equilibrium glassy state of cured epoxies occurs. The free volume seems to increase for higher glass transition temperature materials. The density may be a non-equilibrium effect.

8. A distinct globular structure was observed throughout the etched epoxy surface with a size ranging from 0.1 to 0.7 μm . The size of globules varies with the variation of the stoichiometric ratio of curing agents.

LIST OF REFERENCES

LIST OF REFERENCES

1. Adams, L. H. and E. D. Williamson, J. Franklin Inst., 190, 597 (1920).
2. Adams, L. H. and E. D. Williamson, J. Franklin Inst., 190, 835 (1920).
3. Aggarwala, B. D. and E. Saibel, Phys. Chem. Glasses, 2(5), 137 (1961).
4. Anderson, H. C., J. Appl. Polym. Sci., 6(22), 481 (1962).
5. Andrews, E. H., "Fracture in Polymer," American Elserview (1968).
6. Arnold, R. J., Modern Plastics, 41 149 (1964).
7. Aspbury, P. J. and M. Phillips, "Adhesion 1," K. W. Allen ed. Appl. Sci., Publisher Ltd., London (1977).
8. Bartenev, G. M., "Tempering of Glass," Zh. Tekhn. Fix., 19(12), 1423 (1949).
9. Batzer, H., F. Lohse and R. Schmid, Agrew Makromol. Chem., 29/30, 349 (1973).
10. Bell, J. P., J. Polym. Sci., 14, 1901 (1970).
11. Bobalek, E. G., E. R. Moore, S. S. Levy and C. C. Lee, J. Appl. Polym. Sci., 8, 625 (1964).
12. Bowen, D. O. and R. C. Whiteside, "Epoxy Resins," Advances in Chemistry Series, Am. Chem. Soc., Washington, D. C., 48 (1970).
13. Brinson, H. F., Experimental Mechanics, 8, 561 (1968).
14. Broutman, L. J. and S. M. Krishnaumar, Polym. Eng. Sci., 14, 249 (1974).
15. Burhans, et al. Designing Epoxy Resins Specially for Filament-wound Deep submergence Application, RIP Div. of SPE Chicago (1965).
16. Carslaw, H. S. and J. C. Jeager, "Conduction of Heat in Solids," Clarendon Press, Oxford (1974).
17. Castan, P., Brit. Pat. 518, 057.

18. Cuthrell, R. E., J. Appl. Polym. Sci., 12, 955 (1968).
19. Dannenberg, H., SPE J., 15, 875 (1959).
20. Dannenberg, H. and W. R. Harp, Analy. Chem. 28, 86 (1956).
21. Delmonte, J., J. Appl. Polym. Sci., 2, 108 (1957).
22. Durbetaki, A. J., Analy. Chem. 28, 2000 (1956).
23. Erath, E. H. and M. Robinson, J. Polym. Sci., C(3), 65 (1960).
24. Ernsberger, F. M., "The Glass Industry," Sept., 481 (1966).
25. Fava, R. A., Polymer, 9, 137 (1968).
26. Fellers, J. and A. Golovoy, J. Appl. Polym. Sci., 15, 731 (1971).
27. Feltzin, A., M. K. Barsh, E. J. Peer and I. Petker, Macromol. Sci., A3, 261 (1969).
28. Filon, L. N. G. and F. C. Harris, Roy. Soc. Proc., A103, 561 (1923).
29. Fisch, W. and W. Hoffman, Plastics Technol. August (1961).
30. Flory, P. J., Chem. Rev., 39, 137 (1946); Principles of Polymer Chemistry, Cornell University Press, Ithaca, N. Y. 1953.
31. Flory, P. J. and J. Rehner, J. Chem. Phys., 11 521 (1943).
32. Fox, T. G. and S. Loshaek, J. Polym. Sci., 15 371 (1955).
33. Funke, W., J. Polym. Sci., C(16), 1497 (1967).
34. Gillham, J. K., Polym. Eng. Sci., 19(10), 676 (1979).
35. Gillham, J. K., Technical Report No. 22 (1981).
36. Gillham, J. K., Technical Report No. 18 Sept. (1979).
37. Gilmore, G. D. and R. S. Spencer, Mod. Plast., 28(4) 117 (1951).

38. Gordon, M., T. C. Ward and R. S. Whitney, "Polymer Network," Proc. of ACS Symp. on Highly Cross-linked Polymer Networks, Plenum Press, New York (1971).
39. Gough, L. J. and I. T. Smith, J. Appl. Polym. Sci., 3, 363 (1960).
40. Graenwald, G., Mod. Plastic, 37, 137 (1960).
41. Han, C. D., "Pheology in Polymer Processing," Academic Press, New York, 291 (1976).
42. Heijboer, J., Polym. Eng. Sci., 19, 664 (1979).
43. Herzberg, G., "Infrared and Raman Spectra," 340 Van Nostrand, N. Y. (1945).
44. Igarashi, T., S. Kondo and M. Kurokawa, Polym, 302 (1978).
45. Indenbom, V. L., "Theory of Tempening of Glass," Zh. Tekhn. Fiz., 24(5), 925 (1954).
46. Jenkins, R. and L. Karre, J. Appl. Polym. Sci., 10, 303 (1966).
47. Kaelble, D. H. "Epoxy Resin, Chemistry and Technology," ed. by C. A. May and Y. Tanaka, Marcel Dekker, N. Y. (1973).
48. Kaelble, D. H., J. Appl. Polym. Sci., 9, 1213 (1956).
49. Kelley, et al. "The Relationship of Molecular Structure and Resin Performance for a series of Diglycidyl ethers," ACS Symp., Chicago (1961).
50. Kenyon, A. S. and L. E. Nielsen, J. Macromol. Sci.-Chem., A3(2), 275 (1969).
51. Kim, S. L., J. A. Manson and S. C. Misra, "Epoxy Resin Chemistry," ACS Symp. Series 114, Am. Chem. Soc. Washington, D. C., 183 (1979).
52. Kim, S. L., M. D. Skibo, J. A. Manson, R. W. Hertzberg and J. Aniszewski, Polym. Eng. Sci., 18(14), 1093 (1978).
53. Kitoh, M. and K. Suzuki, Kobunshi Ronbunshu, 33, 19 (1976).
54. Kreibich, V. T. and R. Schmid, J. Polym. Sci. Symposium, (53), 177 (1975).

55. Kuhn, W. and H. Majer, Kvnstatoffe Plastics, 3, 1 (1956).
56. Labana, S. S., S. Newman and A. J. Chomppf, "Polymer Networks," Proc. of ACS Symp., Plenum Press, New York. (1971).
57. Landau, A. J., Am. Chem. Soc. Symp. (1964).
58. Lee, E. H. and T. G. Rogers, J. Appl. Mech. March, 127 (1963).
59. Lee, E. H. and T. G. Rogers, Trans. ASME, Dec. 874 (1965).
60. Lee, E. H., T. G. Rogers and T. C. Woo, J. Am. Chem. Soc., 48, 480 (1965).
61. Lee, H. and K. Neville, "Handbook of Epoxy Resins," McGraw-Hill, New York (1967).
62. Lee, H. T. and D. W. Levi. J. Appl. Polym. Sci., 13, 1703 (1969).
63. Leven, M. M., "Epoxy Resin for Photoelastic Use," Proc. International Symp. on Photoelasticity, M. M. Frocht ed. Pergamon Press, New York, 145 (1961).
64. Lewis, A. F., M. J. Doyle and J. K. Gillham, Polym. Eng. and Sci., 19, 683 (1979).
65. Lewis, A. F. and J. K. Gillham, J. Appl. Polym. Sci., 6, 422 (1962).
66. Lohse, F., R. Schmid, H. Batzen and W. Fisch, Brit. Polym. J., 1, 110 (1969).
67. Maxwell, J. C. "On the Equilibirum of Elastic Solids," Roy. Soc. ed. Trans., 20, 87 (1853).
68. May, C. A. and Y. Tanaka, "Epoxy Resins," Marcel Dekker Inc., New York (1973).
69. Menges, G., A. Dierkes, L. Schmidt and E. Winkel, 38th Annual Technical Conference Report, New York, 300 (1980).
70. McGrath, J. E., A. K. Banthis, Y. Mohajer, M. R. Tant, S. W. Kong and G. L. Wilkes, Technical Report No. 3, March (1981).
71. Miles, B. H., Am. Chem. Soc. Symp. (1964).

72. Misra, S. C., Ph.D. Dissertation, Lehigh University (1978).
73. Misra, S. C., J. A. Manson and L. H. Sperling, "Epoxy Resin Chemistry," ACS Symposium Series 114, 157 (1979).
74. Morgan, R. J. and J. E. O'Neal, J. Macromol. Sci-Phys., B15(1), 139 (1978).
75. Morland, L. W. and E. H. Lee, Trans. Soc. Rheo., 4, 233, (1960).
76. Muki, R. and E. Steinberg, J. Appl. Mech., March 127, (1963).
77. Mussatti, F. G. and C. W. Macoske, Polym. Eng. Sci., 13, 236 (1973).
78. Naganuma, S., J. Sakurai, Y. Takahashi and S. Takahashi, Kobunshi Kagaku, 29, 105 (1972).
79. Narayanaswamy, O. S. and R. Gardon, J. Am. Cerm. Soc., 52, 554 (1969).
80. Narracott, E. S., Brit. Plast., 26, 120 (1953).
81. Neiman, M. B., B. M. Kovarskaya, L. I. Golubenkova, A. S. Strizhkova, I. I. Levantovskaya and M. S. Akutin, J. Polym. Sci., 56, 383 (1962).
82. Nielsen, L. E., J. Macromol. Sci.-Revs. Macromol. Chem., C34, 69 (1969).
83. O'Rourke, R. C. and A. W. Saenz, Quarterly Appl. Math., 8, 303 (1950).
84. Parks, V. J. and A. J. Durelli, Trans. of ASME, Sept., 504 (1965).
85. Parry, H. L. and H. A. Mackay, SPE J. July, 22 (1958).
86. Peyser, P. and W. D. Bascom, J. Appl. Polym. Sci., 21, 2359 (1977).
87. Peyser, P. and W. D. Bascom, "Analytical Chemistry," 3, R. S. Porter and J. F. Johnson eds., Plenum Press, New York, 537 (1974).
88. Potter, W. G., "Epoxide Resins," Plastics Institute, London (1970).

89. Prime, R. B., "Analytical Calorimetry," 2, 201, Plenum Press, New York (1970).
90. Racich, J. L. and J. A. Koutsky, "Chemistry and Properties Crosslinked Polymers," ed. by S. S. Labana, Academic Press, New York (1977).
91. Rachich, J. L. and J. A. Koutsky, J. Appl. Polym. Sci., 20, 2111 (1976).
92. Reinking, et al., "Polyhydroxyethers," Part I, ACS Symposium, Los Angeles, 1963.
93. Schneider, N. S., J. F. Sprouse, G. L. Hagnaner and J. K. Gillham, Polym. Eng. Sci., 19, 304 (1979).
94. Selby, K. and L. E. Miller, J. Mat. Sci., 10, 12 (1975).
95. Shechter, L. And J. Wynstra, Ind. Eng. Chem., 48, 86 (1956).
96. So, Paul and L. J. Broutman, Polym. Eng. Sci., 16, 785 (1976).
97. Solomon, D. H., B. C. Loft and J. D. Swift, J. Appl. Polym. Sci., 11, 1593 (1967).
98. Sternberg, E., Proc. 3rd U. S. National Cong. of Appl. Mech. ASME, New York, 673 (1958).
99. Struik, L. C. E., Polym. Eng. Sci., 18, 799 (1978).
100. Tanaka, Y. and H. Kakiuchi, J. Appl. Polym. Sci., 7, 1063 (1963).
101. Tanaka, Y. and H. Kakiuchi. J. Polym Sci., A2, 3405 (1964).
102. Tanaka, Y. and J. Kakiuchi, J. Macromol. Chem., 1, 307 (1966).
103. Treuting, R. G. and W. T. Read, J. Appl. Phys., 22, 130 (1951).
104. Treuting, R. G., J. J. Lynch, H. B. Wishart, P. H. Richards, "Residual Stress Measurements," ASM Published, Cleveland (1952).
105. Whiting, D. A. and D. E. Kline, J. Polym. Sci., Symp. 52, 1043 (1974).
106. Wilchinsky, Z. W., J. Appl. Polym. Sci., 7, 980 (1963).

107. Wynstra, "Some Correlation Between Mechanical Properties and Structure of Epoxy Resin Coating," Union Carbide Plastic Co., Report (1960).
108. Shell Chemical Co., "EPON Resin for Casting," (1967).

APPENDIX

APPENDIX

THEORETICAL SOLUTION OF RESIDUAL STRESSES DISTRIBUTION

If considering a problem of determining the stress distribution in a flat slab cooled symmetrically on both faces from above the critical temperature to the temperature of the surrounding cooling medium, the coordinate system is shown in Figure A.1. The theory of the stresses generation in this problem has been derived by Lee et al. (61). They assumed that the material behaves thermoeologically simple shear response to the temperature change, which was defined as the material corresponds to a shift without changing shape of relaxation modulus function under the influence of temperature (75). To deal with varying temperatures, thus it is convenient to define a reduced time ξ which incorporates the varying time scale factor $\psi(T)$, it is written as

$$\xi(\chi, t) = \int_0^t \psi[T(\chi, t')] dt' \quad [A.1]$$

so that in terms of ξ the viscoelastic stress-strain relation at varying temperatures has the same form as the isothermal law at the reference temperature T_r . Thus the viscoelastic stress-strain law for nonhomogeneous temperature fields can be expressed as

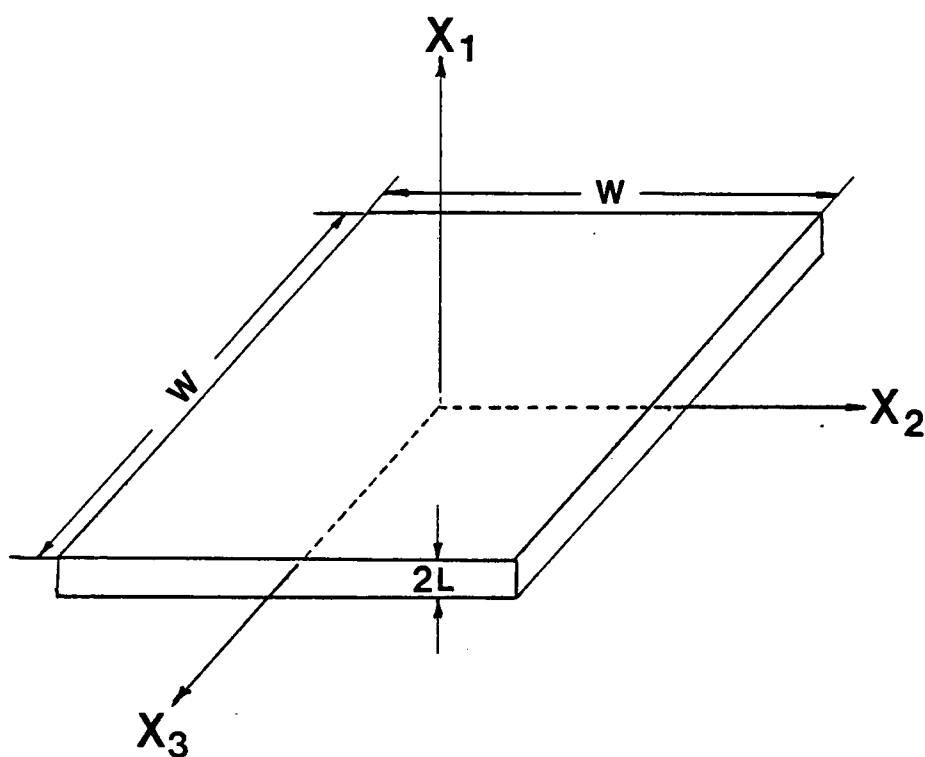


Figure A.1. Schematic diagram of coordinate system of a slab.

$$S_{ij} = \int_0^{\xi} 2G(\xi - \xi') \frac{\partial l_{ij}}{\partial \xi'} d\xi', \quad [A.2]$$

where S_{ij} and l_{ij} are deviator components of stress and strain, respectively. They are given as

$$S_{ij} = \sigma_{ij} - 1/3 \sigma_{kk} \delta_{ij} \quad [A.3]$$

$$\text{and } l_{ij} = \epsilon_{ij} - 1/3 \epsilon_{kk} \delta_{ij} \quad [A.4]$$

It is also assumed that the dilatational response at varying temperatures is elastic. This leads to

$$\tilde{\sigma}_{kk} = 3K[\tilde{\epsilon}_{kk} - 3 a\Delta T] \quad [A.5]$$

where

$$\tilde{\sigma}_{kk} = \sigma_{11} + \sigma_{22} + \sigma_{33}, \quad \tilde{\epsilon}_{kk} = \epsilon_{11} + \epsilon_{22} + \epsilon_{33}$$

and K is the bulk modulus, a the thermal expansion coefficient and ΔT equal to $T(X,t) - T(X,0)$. If in the absence of body forces and neglect the inertia forces for a small deformation, the equation of motion can be reduced to the equilibrium equation, that is

$$\frac{\partial}{\partial X_j} \sigma_{ij} = 0, \quad \sigma_{ij} = \sigma_{ji} \quad [A.6]$$

Since the cooling is symmetry and a zero surface traction assumed, it demands that shear stresses

$$\sigma_{12} = \sigma_{23} = \sigma_{31} = 0 \quad [A.7]$$

and the principal stresses thus coincide in the rectangular coordinate system defining the slab. This leads to the results that stresses are simply dependent on the direction X_1 only, if locations apart from a possible edge effect are considered. In case the thickness of the slab is small compared with lateral dimensions, the stresses $\sigma_{11}(X,t)$ appear to be zero. Since no external forces apply on the edge of the plate, this will lead to a condition for internal static equilibrium for any cross section

$$\iint \sigma_{22} dX_3 dX_1 \quad \text{and} \quad \iint \sigma_{33} dX_1 dX_2 = 0 \quad [A.8]$$

Solving these equations, Lee et al. have given the solution of the equations for thermal stresses during cooling which is written as

$$\sigma_{22}(X_1, t) = 3 \int_0^t R(\xi - \xi') \frac{\partial}{\partial t'} \epsilon_{22}(t') - a[T(X_1, t') - T(X_1, 0)] dt' \quad [A.9]$$

where $R(\xi)$ is an auxilliary function defined by Muki and Sternberg which satisfies the Volterra-type integral

equation given as

$$\frac{4}{3K} \int_0^\xi G(\xi - \xi') \frac{\partial R(\xi)}{\partial \xi'} d\xi' + R(\xi') = 2G(\xi) \quad [A.10]$$

where $G(\xi)$ is the relaxation modulus function. The expression for σ_{33} is the same as Equation [A.9] since $\sigma_{22} = \sigma_{33}$.

As mentioned previously, a sophisticated numerical solution is needed to calculate the residual stresses by using the measured relaxation modulus. Thus a simplified approach is used, which is based on the assumptions that the low modulus behavior in the rubbery state at temperatures above the softening point contributes negligible effects on the residual stresses and the material behaves like a Maxwell elastic solid in the glassy state. To apply this to Equation [A.9], the shear modulus of the Maxwell solid can be written as

$$G(t) = \frac{E}{2(1+\nu)} \exp\left(-\frac{t}{\tau}\right) \quad [A.11]$$

By taking the Laplace transformation with respect to t , the Equation [A.11] becomes

$$G^*(\rho) = \frac{E\tau}{2(1+\nu)(\rho\tau + 1)} \quad [A.12]$$

It is noted that the relaxation modulus function should satisfy Equation [A.10]. Thus by taking the Laplace Transformation for this equation, gives

$$\frac{4}{3K}G^*(\rho)\rho R^*(\rho) + R^*(\rho) = 2G^*(\rho) \quad [A.13]$$

and it may be rearranged to get

$$R^*(\rho) = \frac{2G^*(\rho)}{\frac{4}{3K}\rho G^*(\rho) + 1} \quad [A.14]$$

By substituting $G^*(\rho)$ into Equation [A.13], it becomes

$$R^*(\rho) = \frac{E}{3(1-\nu)} \left(\frac{1}{\rho + \delta/\tau} \right) \quad [A.15]$$

where

$$\delta = \frac{1 + \nu}{3(1 - \nu)}$$

The inverse of the Laplace Transformation of $R^*(\rho)$ is

$$R(t) = \frac{E}{3(1-\nu)} \exp \left[-\frac{\delta t}{\tau} \right] \quad [A.16]$$

Since at each specified position of slab, as soon as it passes the vitrification time t_1 , it will vitrify and behave like an elastic solid. Thus we can divide stresses into two parts at time t_1 , it gives

$$\sigma_{22}(X_1, t) = \sigma_{22}(X_1, t_1) + \sigma_{e22}(X_1, t_1, t) \quad [A.17]$$

where $\sigma_{e22}(X_1, t_1, t)$ expresses the change of elastic stresses from time t_1 to time t . As the time goes to infinity, the stresses persist within the body which is the so-called residual stresses, and is given as

$$\sigma_{22}(X_1, \infty) = \sigma_{22}(X_1, t_1) + \sigma_{e22}(X_1, t_1, \infty) \quad [A.18]$$

It is known that no residual stress exists for a thermo-elastic solid. Then we obtain that

$$\sigma_{e22}(X_1, \infty) = \sigma_{e22}(X_1, t_1) + \sigma_{e22}(X_1, t_1, \infty) = 0 \quad [A.19]$$

This leads to

$$\sigma_e(X_1, t_1, \infty) = -\sigma_e(X_1, t_1) \quad [A.20]$$

By substituting Equation [A.20] into [A.18], the residual stresses equation is given as

$$\sigma_{22}(X_1, \infty) = \sigma_{22}(X_1, t_1) - \sigma_{e22}(X_1, t_1) \quad [A.21]$$

Since at the time before the material solidifies, the affect of its low modulus in the rubbery state on the residual stresses is negligible. This will lead to

$$\sigma_{22}(X_1, t_1) = 0 \quad [A.22]$$

and at the time after it becomes solidified, the relaxation time constant τ is infinity, so that

$$R(t) = R(0) = \frac{E}{3(1 - \nu)} \quad A.23$$

and

$$\sigma_{e22}(X_1, t_1) = \frac{E}{(1 - \nu)} [\epsilon_{e22}(t_1) - a[T(X_1, t_1) - T(X_1, 0)]] \quad [A.24]$$

where $\epsilon_{e22}(t_1)$ is the average strain for the instantaneous elastic response of the solid, which can be obtained from the boundary condition of Equation [A.8]. Since the stresses is a function of X_1 only, the equation becomes

$$\int_0^L \sigma_e(X_1, t_1) dX_1 = \int_0^L \frac{E}{(1 - \nu)} [\epsilon_{e22}(t_1) - a[T(X_1, t_1) - T(X_1, 0)]] dX_1 = 0 \quad [A.25]$$

Since $\epsilon_{e22}(t)$ is independent of X_1 , so that

$$\epsilon_{e22}(t_1) = \frac{1}{L} \int_0^L a[T(X_1, t_1) - T(X_1, 0)] dX_1 \quad [A.26]$$

Substituting $\epsilon_e(t_1)$ into Equation [A.24], this gives

$$\sigma_{e22}(X_1, t_1) = \frac{E}{(1-\nu)} \left[\frac{1}{L} \int_0^L a[T(X_1, t_1) - T(X_1, 0)]dX_1 \right. \\ \left. - a[T(X_1, t_1) - T(X_1, 0)] \right] \quad [A.27]$$

Finally, the residual stresses equation can be written as

$$\sigma_{22}(X_1, \infty) = \frac{-E}{(1-\nu)} \left[\frac{1}{L} \int_0^L a[T(X_1, t_1) - T(X_1, 0)]dX_1 \right. \\ \left. - a[T(X_1, t_1) - T(X_1, 0)] \right] \quad [A.28]$$

```

C      PURPOSE:
C      THE PROGRAM IS USED TO OBTAIN THE TEMPERATURE
C      PROFILE IN A SLAB UNDER A QUENCHING PROCESS. THE PROFILE
C      VARIES WITH VARIOUS HEAT TRANSFER COEFFICIENT ASSOCIATED
C      WITH THE COOLING RATE.
C
COMMON /PRAM/L,K,CP,DEN,TEMBAR(100)
REAL*8 TEMP(100),L,K,HTC,PI(6),AUGEXP,TIBR(10)
REAL*8 DEN,TEMBAR,TEM,AUGCOS,COSN,PICON,EXPN
C      DATA (PI(I),I=1,6)/0.8596,3.4251,6.437,9.53,12.65,15.77/
C      DATA (PI(I),I=1,6)/1.0693,3.635,6.573,9.63,12.72,15.83/
C      DATA (PI(I),I=1,6)/1.2306,3.875,6.762,9.77,12.83,15.93/
C      DATA (PI(I),I=1,6)/1.3453,4.1022,6.982,9.96,12.99,16.06/
      DATA (PI(I),I=1,6)/1.3929,4.2145,7.11,10.08,13.10,16.16/
      DATA L/0.3175/,K/4.5E-4/,CP/0.25/,DEN/1.20/
C      DATA HTC/0.0013875/
C      DATA HTC/0.002778/
C      DATA HTC/0.005/
C      DATA HTC/0.008333/
      DATA HTC/0.01094/
      DATA (TIBR(I),I=1,7)/0.005,0.015,0.05,0.1,0.25,0.5,1.0/
      BATA=HTC*L/K
      WRITE(3,600) BATA
      DO 5 M=1,7
      ZZBAR=0.00
      DO 7 J=1,41
      TEM=0.0
      DO 10 N=1,6
      AUGCOS=PI(N)*ZZBAR
      COSN=DCOS(AUGCOS)
      PICON=(BATA**2+PI(N)**2+BATA)*DCOS(PI(N))
      AUGEXP=-(PI(N)**2)*TIBR(M)
      EXPN=DEXP(AUGEXP)
      TEM=TEM+2*BATA*COSN*EXPN/PICON
10    CONTINUE
      WRITE(3,500) TEM,ZZBAR
      ZZBAR=ZZBAR+0.025
7      CONTINUE
5      CONTINUE
      STOP
600    FORMAT(1H1,10X,'AT NUSSELT NUMBER',F10.6,/)
500    FORMAT(10X,E15.6,10X,E15.6)
      END

```

PURPOSE:

THE PROGRAM IS USED TO FIND THE SOLIDIFYING TIME OF EACH LEVELS OF SLAB DURING A NONHOMOGENEOUS COOLING PROCESS.

PARAMETERS:

L ---- HALF THICKNESS OF SLAB
 K ---- THERMAL CONDUCTIVITY
 CP --- HEAT CAPACITY
 DEN -- DENSITY
 ZBAR-- DIMENSIONLESS DISTANCE
 TTIBR- DIMENSIONLESS TIME
 TEMBAR DIMENSIONLESS TEMPERATURE
 LSK -- DIMENSIONLESS THERMAL DIFFUSIVITY
 INCL-- INCREMENT OF STEPWISE
 TEM -- DIMENSIONLESS TEMPERATURE RETURN FROM THE SUBROUTINE THEAT
 HTC -- HEAT TRANSFER COEFFICIENT
 BATA-- NUSSELT NUMBER
 ROT -- THE SOLIDIFYING TIME FOUND FOR EACH LEVEL

SUBPROGRAM:

ROTBAR: THE SUBROUTINE RETURN THE SOLIDIFYING TIME OF EVERY LEVEL IN THE SLAB.
 THEAT : THE SUBROUTINE RETURN THE DIMENSIONLESS TEMPERATURE WHICH SUBSTITUTE INTO THE ROTBAR TO FIND THE ROOTS.

MAIN PROGRAM

```
COMMON /TEST/L,K,DEN
REAL*8 L,K,DEN,CP,ZBAR,Z(100),RT(100),ROT(100)
REAL*8 TTIBR
OPEN(UNIT=20,FILE='OUP6.D')
DATA L/0.3175/,K/4.5E-4/,CP/0.25/,DEN/1.20/
ZBAR=0.00
DO 10 I=1,73
Z(I)=ZBAR*L
TTIBR=0.00
CALL ROTBAR(TTIBR,ZBAR,ROT(I),RT(I))
IF(ZBAR.GE.0.8) GO TO 30
ZBAR=ZBAR+0.025
GO TO 10
30 ZBAR=ZBAR+0.005
10 CONTINUE
WRITE(20,15)
15 FORMAT(10X,'Z(I)',13X,'ROOT',10X,'REAL SOLID. TIME',/)
WRITE(20,20) (Z(I),ROT(I),RT(I),I=1,73)
20 FORMAT(5X,F10.6,5X,E15.6,5X,E15.6)
CLOSE(UNIT=20,FILE='OUP6.D')
STOP
END
```

```

C
C
C
SUBROUTINE ROTBAR

SUBROUTINE ROTBAR(TIBR,ZBAR,ROOT,RT)
COMMON /TEST/L,K,DEN
REAL*8 L,K,INCL,LSK,F1,F2,F,TIBR1,TIBR2,T,TIBRAV,RT,ROOT
REAL*8 TEM
REAL*8 CP,TEMBAR,ZBAR,TIBR,TG,T1,TO
DATA CP/0.25/,TG/135.0/,TO/180.0/,T1/0.00/
LSK=CP*DEN*(L**2)/K
TEMBAR=(TG-T1)/(TO-T1)
INCL=0.01
TIBR1=TIBR
CALL THEAT(TIBR1,ZBAR,TEM)
F1=TEMBAR-TEM
40  TIBR=TIBR+INCL
    TIBR2=TIBR
    CALL THEAT(TIBR2,ZBAR,TEM)
    F2=TEMBAR-TEM
    IF(F1*F2)10,20,30
30  IF(TIBR2.GT.100) RETURN
    TIBR1=TIBR2
    F1=F2
    GO TO 40
20  IF(F1.EQ.0.00)GO TO 50
    RT=TIBR2*LSK
    ROOT=TIBR2
    RETURN
50  RT=TIBR1*LSK
    ROOT=TIBR1
    RETURN
10  IF(ABS(ABS(F1)-ABS(F2)).GE.1.0E-7) GO TO 60
    TIBRAV=(TIBR1+TIBR2)/2
    RT=TIBRAV*LSK
    ROOT=TIBRAV
    RETURN
60  T=(TIBR1+TIBR2)/2
    CALL THEAT(T,ZBAR,TEM)
    F=TEMBAR-TEM
    IF(F*F1)70,20,90
70  F2=F
    TIBR2=T
    GO TO 10
90  F1=F
    TIBR1=T
    GO TO 10
    RETURN
END

C
C
C
SUBROUTINE THEAT

SUBROUTINE THEAT(TIBR,ZBAR,TEM)

```

```

COMMON /TEST/L,K,DEM
REAL*8 L,K,HTC,COSN,PICON,EXPN,TEM,AUGCOS,AUGEXP
REAL*8 PINN,BATA,PI(6)
REAL*8 TIBR,ZBAR
C DATA HTC/0.0013875/
C DATA HTC/0.002778/
DATA HTC/0.005/
C DATA HTC/0.008333/
C DATA HTC/0.01094/
C DATA (PI(I),I=1,6)/0.8596,3.4251,6.437,9.53,12.65,15.77/
C DATA (PI(I),I=1,6)/1.0698,3.635,6.573,9.63,12.72,15.77/
DATA (PI(I),I=1,6)/1.2306,3.875,6.762,9.77,12.83,15.93/
C DATA (PI(I),I=1,6)/1.3453,4.1022,6.982,9.96,12.99,16.06/
C DATA (PI(I),I=1,6)/1.3929,4.2145,7.11,10.08,13.10,16.16/
BATA=HTC*L/K
TEM=0.0
DO 10 NN=1,6
AUGCOS=PI(NN)*ZBAR
COSN=DCOS(AUGCOS)
PINN=PI(NN)
PICON=(BATA**2+PINN**2+BATA)*DCOS(PINN)
AUGEXP=-(PI(NN)**2)*TIBR
EXPN=DEXP(AUGEXP)
10 TEM=TEM+2*BATA*COSN*EXPN/PICON
RETURN
END

```

PURPOSE:

THE PROGRAM IS USED TO COMPUTE THE RESIDUAL STRESS DISTRIBUTION IN A SLAB UNDER A NONHOMOGENEOUS COOLING PROCESS.

PARAMETERS:

MOST OF PARAMETERE ARE DEFINED THE SAME AS THOSE OF BEING DEFINED IN THE PREVIOUS PROGRAM EXCEPT THOSE OF:

PO ----- POISSON'S RATIO
 ALFA ---- THERMAL EXPANSION COEFFICIENT
 E ----- YOUNG'S MODULUS OF ELASTICITY
 AREA ---- AREA UNDER A SPECIFIED TEMPERATURE PROFILE.
 RS ----- SOLUTION OF RESIDUAL STRESS
 TO ----- INITIAL OVEN TEMPERATURE
 T1 ----- SURROUNDING TEMPERATURE OF COOLING MEDIUM.
 TG ----- GLASS TRANSITION TEMPERATURE OF MATERIALS.

SUBPROGRAM:

TEMPRF: SUBROUTINE WHICH RETURN THE TEMPERATURE PROFILE AT EVERY SPECIFIED TIME.

TESTRS: SUBROUTINE WHICH RETURN THE SOLUTION OF RESIDUAL STRESS.

MAIN PROGRAM

```

COMMON /PRAM/L,K,CP,DEN,TEMBAR(100),BATA
REAL*8 L,K,INCL,ZBAR(100),TIBR(100),ZI(100),TEMBAR
REAL*8 RESTRS(100),RT(100),TEM,ZZBAR,TTIBR,CP,DEN
REAL*8 RS(100),BATA
DATA L/0.3175/,K/4.5E-4/,CP/0.25/,DEN/1.20/
DATA TO/180.0/,T1/0.00/
OPEN(UNIT=20,FILE='RS1.D')
WRITE(20,10) TO,T1,L
10  FORMAT(12X,'AT INITIAL TEMPERATURE',F8.3,/,12X,
1    'AND QUENCHING TEMPERATURE',F8.3,/,12X,
2    'THICKNESS OF SPECIMEN',F8.3)
WRITE(20,11) BATA
11  FORMAT(12X,'NUSSLELT NUMBER BATA IS',F10.5,/)
WRITE(20,25)
25  FORMAT(14X,'ZI(I)',14X,'ZBAR(I)',10X,'RS(I)',/)
READ(8,*)(ZI(II),TIBR(II),RT(II),II=1,73)
DO 20 I=1,73
  TTIBR=TIBR(I)
  ZBAR(I)=ZI(I)/L
  ZZBAR=ZBAR(1)
DO 30 J=1,41

```

```

CALL TEMPRF(TTIBR,ZZBAR,TEM)
TEMBAR(J)=TEM
INCL=0.0250
ZZBAR=ZZBAR+INCL
30  CONTINUE
CALL TESTRS(RS(I))
20  CONTINUE
WRITE(20,40)(ZI(I),ZBAR(I),RS(I),I=1,73)
40  FORMAT(10X,F10.6,10X,F10.6,6X,E15.6)
CLOSE(UNIT=20,FILE='RS1.D')
STOP
END

C
C  SUBROUTINE TEMPRF
C
SUBROUTINE TEMPRF(TTIBR,ZZBAR,TEM)
COMMON /PRAM/L,K,CP,DEN,TEMBAR(100),BATA
REAL*8 TEMP(100),L,K,HTC,PI(6),AUGEXP,BATA
REAL*8 DEN,TEMBAR,TEM,AUGCOS,COSN,PICON,EXPN
C  DATA (PI(I),I=1,6)/0.8596,3.4251,6.437,9.53,12.65,15.77/
C  DATA (PI(I),I=1,6)/1.0698,3.635,6.573,9.63,12.72,15.83/
C  DATA (PI(I),I=1,6)/1.2306,3.875,6.762,9.77,12.83,15.93/
C  DATA (PI(I),I=1,6)/1.3453,4.1022,6.982,9.96,12.99,16.06/
C  DATA (PI(I),I=1,6)/1.3929,4.2145,7.11,10.08,13.10,16.16/
C  DATA L/0.3175/,K/4.5E-4/,CP/0.25/,DEN/1.20/
C  DATA HTC/0.0013875/
C  DATA HTC/0.002778/
C  DATA HTC/0.005/
C  DATA HTC/0.008333/
C  DATA HTC/0.01094/
BATA=HTC*L/K
C  WRITE(5,700) TTIBR
TEM=0.0
DO 10 N=1,6
AUGCOS=PI(N)*ZZBAR
COSN=DCOS(AUGCOS)
PICON=(BATA**2+PI(N)**2+BATA)*DCOS(PI(N))
AUGEXP=-(PI(N)**2)*TTIBR
EXPN=DEXP(AUGEXP)
TEM=TEM+2*BATA*COSN*EXPN/PICON
10  CONTINUE
RETURN
END

C
C  SUBROUTINE TESTRS
C
SUBROUTINE TESTRS(RS)
COMMON /PRAM/L,K,CP,DEN,TEMBAR(100),BATA
REAL*8 L,K,H,TEMP(100),BATA
REAL*8 CP,DEN,TEMBAR,SUM,STRAIN,AREA

```

```
GO TO 20
30 SUM=SUM+2*TEMP(J)
20 CONTINUE
TEMP(41)=TEMPAR(41)*(TO-T1)+T1
SUM=SUM+TEMP(41)
AREA=(H/3.0)*SUM
STRAIN=(ALFA/L)*(AREA-L*TO)
REP=-E/(1-PO)
RS=REP*(STRAIN-ALFA*(TG-TO))
RETURN
END
```

AT INITIAL TEMPERATURE 180.000
 AND QUENCHING TEMPERATURE 0.000
 THICKNESS OF SPECIMEN 0.317
 NUSSELT NUMBER DATA IS 1.960

ZI(I)	ZBAR(I)	RS(I)
0.000000	0.000000	0.703164E+08
0.007937	0.024998	0.702004E+08
0.015875	0.050000	0.698511E+08
0.023812	0.074998	0.692684E+08
0.031750	0.100000	0.684499E+08
0.039687	0.124998	0.673927E+08
0.047625	0.150000	0.660936E+08
0.055562	0.174998	0.645473E+08
0.063500	0.200000	0.627507E+08
0.071437	0.224998	0.606958E+08
0.079375	0.250000	0.583776E+08
0.087312	0.274998	0.557878E+08
0.095250	0.300000	0.529189E+08
0.103187	0.324998	0.497621E+08
0.111125	0.350000	0.463089E+08
0.119062	0.374998	0.425502E+08
0.127000	0.400000	0.384772E+08
0.134937	0.424998	0.340820E+08
0.142875	0.450000	0.293584E+08
0.150812	0.474998	0.243031E+08
0.158750	0.500000	0.189162E+08
0.166687	0.524998	0.132028E+08
0.174625	0.550000	0.717504E+07
0.182562	0.574998	0.854403E+06
0.190500	0.600000	-0.572943E+07
0.198438	0.625002	-0.125360E+08
0.206375	0.650000	-0.195178E+08
0.214313	0.675002	-0.266210E+08
0.222250	0.700000	-0.337918E+08
0.230188	0.725002	-0.409783E+08
0.238125	0.750000	-0.481388E+08
0.246063	0.775002	-0.552396E+08
0.254000	0.800000	-0.622567E+08
0.261938	0.825002	-0.691726E+08
0.269875	0.850000	-0.759738E+08
0.277813	0.875002	-0.826498E+08
0.285750	0.900000	-0.891884E+08
0.293688	0.925002	-0.955772E+08
0.301625	0.950000	-0.101803E+09
0.309563	0.975002	-0.107850E+09
0.317500	1.000000	-0.113705E+09

AT INITIAL TEMPERATURE 180.000
 AND QUENCHING TEMPERATURE 0.000
 THICKNESS OF SPECIMEN 0.317
 NUSSELT NUMBER DATA IS 3.5278

ZI(I)	ZEAR(I)	RS(I)
0.000000	0.000000	0.908262E+08
0.007937	0.024998	0.906813E+08
0.015875	0.050000	0.902472E+08
0.023812	0.074998	0.895207E+08
0.031750	0.100000	0.884996E+08
0.039687	0.124998	0.871792E+08
0.047625	0.150000	0.855536E+08
0.055562	0.174998	0.836171E+08
0.063500	0.200000	0.813601E+08
0.071437	0.224998	0.787752E+08
0.079375	0.250000	0.758513E+08
0.087312	0.274998	0.725778E+08
0.095250	0.300000	0.689432E+08
0.103187	0.324998	0.649362E+08
0.111125	0.350000	0.605461E+08
0.119062	0.374998	0.557639E+08
0.127000	0.400000	0.505837E+08
0.134937	0.424998	0.450042E+08
0.142875	0.450000	0.390302E+08
0.150812	0.474998	0.326767E+08
0.158750	0.500000	0.259678E+08
0.166687	0.524998	0.189412E+08
0.174625	0.550000	0.116458E+08
0.182562	0.574998	0.413990E+07
0.190500	0.600000	-0.351322E+07
0.198438	0.625002	-0.112531E+08
0.206375	0.650000	-0.190244E+08
0.214313	0.675002	-0.267840E+08
0.222250	0.700000	-0.345002E+08
0.230188	0.725002	-0.421490E+08
0.238125	0.750000	-0.497165E+08
0.246063	0.775002	-0.571942E+08
0.254000	0.800000	-0.645656E+08
0.261938	0.825002	-0.718211E+08
0.269875	0.850000	-0.789462E+08
0.277813	0.875002	-0.859247E+08
0.285750	0.900000	-0.927361E+08
0.293688	0.925002	-0.993559E+08
0.301625	0.950000	-0.105759E+09
0.309563	0.975002	-0.111939E+09
0.317500	1.000000	-0.117974E+09

VITA

Yuh-Chen Shen was born in Tainan, Taiwan, The Republic of China, on April 16, 1951. His parents moved to Taipei when he was a child, where he attended elementary and secondary schools. He graduated from the Beng-Chai High School in 1970. He graduated from the Tatung Institute of Technology in June, 1974, and received his Bachelor of Science degree with a major in Chemical Engineering.

After serving two years as an R. O. C. army officer, he returned to work for the Tatung Institute of Technology as a research assistant. In the fall of 1978, he came to the United States to enter the Graduate School of The University of Tennessee, Knoxville. He received his Master of Science degree with a major in Polymer Engineering in June, 1981.

He is a member of the Society of Plastic Engineering.

He is married to the former Li-Yin Lin. They have a daughter, Chia-Hui Shen.