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MECHANICAL BEHAVIOR OF EPOXY: PART A: INFLUENCE OF LOCAL STRUCTURE ON VISCOELASTIC AND MOISTURE TRANSPORT PROPERTIES PART B: INFLUENCE OF REINFORCEMENT presented by

Peter John Scheuer

has been accepted towards fulfillment of the requirements for

Master's degree in <u>Materials</u> Science

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MECHANICAL BEHAVIOR OF EPOXY: PART A: INFLUENCE OF LOCAL STRUCTURE ON VISCOELASTIC AND MOISTURE TRANSPORT PROPERTIES PART B: INFLUENCE OF REINFORCEMENT

By

Peter John Scheuer

A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Department of Materials Science and Mechanics

ABSTRACT

MECHANICAL BEHAVIOR OF EPOXY: PART A: INFLUENCE OF LOCAL STRUCTURE ON VISCOELASTIC AND MOISTURE TRANSPORT PROPERTIES PART B: INFLUENCE OF REINFORCEMENT

By

Peter John Scheuer

Viscoelastic and moisture transport properties of modified network epoxy glasses were examined and probed through stress relaxation and gravimetric sorption experiments, respectively. The modified networks contained a monofunctional epoxy which results in "dangling" chains within the network structure. The viscoelastic response of these modified networks to physical aging was affected by the local network mobility. Moisture absorption experiments reveal that the path for diffusion, as a result of the local network structure, plays a significant role in the transport of small molecules into glassy materials. In addition, the feasibility of orienting, via a magnetic field, metallic glass ribbons into complex configurations within an epoxy matrix was investigated. Magnetic field orientation of reinforcements is possible provided precise control of the matrix's viscosity. A low viscosity results in reinforcement sinking, while a high viscosity prevents the reinforcements from moving into desired configurations when exposed to the magnetic field.

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To my future wife...

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PART A: INFLUENCE OF LOCAL STRUCTURE ON VISCOELASTIC AND MOISTURE TRANSPORT PROPERTIES

CHAPTER 1 INTRODUCTION

Epoxies are used in many industrial applications. For example, the aerospace industry primarily uses epoxy in the form of matrices for composite materials and adhesives in structural components. The use of epoxies for such applications requires knowledge of their lifetime performance in extreme service environments. Due to the severity of conditions in extreme environments, the durability of epoxies is critical information in the design and development of aerospace components. The durability of epoxy adhesives and composites is difficult to predict unless a fundamental understanding of how the chemical structure present in epoxies affects the long-term, inservice performance of these materials.

There has been increased interest in the structural and property changes that occur in glassy polymers upon annealing below the glass transition. This "aging" or timedependent behavior is a direct result of the non-equilibrium nature of the glassy state. The importance of this phenomenon in applications stems from the fact that material performance must be predictable in order to insure compliance with design specifications throughout the service life of the fabricated polymer product.

1.1 Polymer Glasses

Amorphous polymers upon isobaric cooling from the melt through the glass transition into the glassy state depart from their thermodynamic equilibrium and exhibit

non-equilibrium characteristics. As the polymer is cooled there occurs a rapid decrease in molecular mobility which results in a sudden increase in the viscosity and modulus as the transition temperature is approached. The polymer molecules are unable to reach their equilibrium conformation and packing, and as the temperature is further decreased the molecules are essentially "frozen" into a non-equilibrium state of higher energy and volume relative to the equilibrium state at the same temperature [1]. Figure 1-1 is a plot of the volume *versus* temperature behavior for a typical glass forming polymer.

The temperature at which the non-equilibrium structure and behavior begins to deviate from the extrapolated equilibrium state is one definition of the glass transition temperature, Tg. The position of the glass transition is dependent upon many factors such as the processing conditions (i.e. rate of cooling) of the polymer. Cooling a polymer melt at a high rate will result in a higher energy and volume non-equilibrium state, as compared to a polymer which has been cooled at a slower rate, because the polymer molecules have even less time to reach their equilibrium conformation. As a result of this relatively elevated non-equilibrium state, the glass transition of the polymer moves to higher temperatures along the equilibrium melting curve (Figure 1-1).

1.2 Physical Aging

The non-equilibrium state of an amorphous polymer appears to be unstable. Volume relaxation studies have revealed that glasses, at temperatures below Tg, undergo slow processes which attempt to establish equilibrium. This gradual approach to equilibrium affects many mechanical and physical properties of the polymer system: (1) an increase in density, tensile and flexural yield stress, and elastic modulus; (2) a

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Figure 1-1. Schematic diagram of volume vs. temperature behavior of a glass forming material isobarically cooled from T1 to T2. Q is the rate of cooling.

decrease in impact strength, fracture energy, ultimate elongation, and creep rate. The time dependent evolution of these properties is referred to as aging [1]. There are two types of aging; "Physical aging" is the change in viscoelastic (mechanical) properties accompanying volume relaxation, and "chemical aging" which is material degradation of the polymer through processes such as thermal breakdown and photo-oxidation. Physical aging, unlike chemical aging, is a thermoreversible process where any previous aging can be erased by re-heating the aged sample to a temperature above Tg [2].

The effects of physical aging on the mechanical properties of glassy materials are commonly examined through viscoelastic experiments. Stress relaxation is a viscoelastic experiment which consists of instantly straining a viscoelastic material and, while maintaining this deformation, measuring the stress as it decays from an initial value. The decaying stress in this type of relaxation experiment is impacted by the internal molecular friction between the polymer molecules [3]. During physical aging the polymer undergoes densification, thus the internal molecular friction is effected. Therefore, stress relaxation experiments can be used to probe the change in viscoelastic properties during aging.

The viscoelastic response of polymers affects polymer morphology and structure [4]. Polymer structure and morphology are important characteristics which contribute to the mechanical properties of polymers. For example, polymer branches and crosslinks are structural components which influence the properties and performance of polymers [5]. Thermoset materials, such as epoxies, are highly cross-linked or networked polymeric systems. Defects in the epoxy network, such as loops and dangling ends, affect the

structure and thus the performance of epoxy polymers. To explore the degradation due to network defects viscoelastic experiments are used.

In addition to affecting the mechanical properties of polymer glasses, physical aging affects the diffusivity and solubility of polymers [2]. The diffusivity and solubility are important properties which have an impact on the performance of polymers in moist environments. Hygrothermal effects on epoxies and epoxy composites have been widely studied. The main hygrothermal effects in epoxy systems are plasticization, swelling, microcracking, and Tg suppression. The effects may be reversible, as in the case of plasticization or swelling, or the effects may be irreversible such as hydrolysis or microcracking. Network defects affect the mechanical properties of thermoset polymers and thus they may also affect the hygrothermal performance of thermoset polymers. Local defects affect specific attributes of a polymer network. For example, the presence of dangling ends leads to a lower cross-link density. On the other hand, chain entanglements lead to higher values of cross-link density [6,7]. In this case, the affect of network defects is a change in the cross-link density, which may affect the sorption behavior of glassy polymers.

Since physical aging is an important phenomenon in the area of polymer glasses and little attention has been paid to its effects on polymer networks; it is the aim of this investigation to further understand and clarify the effects of aging on epoxy networks. Viscoelastic and moisture absorption experiments were conducted in order to determine the effect of local network structures on physically aged epoxy glasses.

CHAPTER 2 MATERIALS AND SAMPLE CHARCTERIZATION

2.1 Materials

2.1.1 Epoxy

Epoxy resins are characterized by a three-member ring known as the epoxide, oxirane, or ethoxyline group, and are represented as:



where R is a resin containing aliphatic, cycloaliphatic, or aromatic backbones. Properties of cured epoxy polymers are influenced by many factors at the molecular level, such as backbone structures of the epoxy resin and curing agent; nature of the cross-linking bond formed by the resin and curing agent; and the density and extent of cross-linking. Due to the ease of processing, epoxy has become an important class of engineering polymers.

2.1.2 Modifiers

In order to facilitate processing and to modify cured network properties, other substances, such as fillers, solvents, diluents, plasticizers, and toughening agents may be included in the compositions. For example, rubber particles are added as toughening agents to improve the fracture toughness of brittle thermoset polymers. A commonly used modifier is diluents. Diluents affect the properties of cured resin systems, and in particular, lower the viscosity in order to facilitate processing. Compounds containing only one epoxy or functional group per molecule are known as monofunctional epoxies and are commonly added to conventional epoxy resin systems as diluents. For example, addition of a monofunctional epoxy to a conventional epoxy resin system reduces the viscosity of the resin which improves the wetting capability of the polymer when used in coating applications. In addition, reinforcements, such as metallic glass ribbons, may be added to a polymer system in order to improve the strength and toughness of polymer matrix composites.

2.1.3 Curing Agents

In order to achieve desired engineering properties various curing agents, which react with the epoxy rings to form insoluble and intractable thermoset polymers, are used. For example, epoxy resin cured with anhydride based curing agents exhibit low viscosity, low exothermic heats of reaction, and little shrinkage when cured at elevated temperatures. The cured system exhibits good mechanical and electrical properties along with good thermal stability which makes this polymer system useful in electrical applications. Polyamide epoxy curing agents are used extensively and are extremely versatile. Polyamides are inexpensive, have little color and can be mixed in any ratio. Epoxies cured with polyamides have good mechanical properties, cure under mild conditions, and are often used in coating applications.

Polymer molecules linked together through the use of a curing agent form a network which is, in effect, one giant molecule (Figure 2-1. "Ideal" network structure diagram). Network polymers, at temperatures below the glass transition temperature, are hard intractable solids, but network polymers above the glass transition temperature are rubbery [5]. The characteristics of a network polymer depend on the functionality of the resin, flexibility of the polymer chain, and the type and concentration of the crosslinking

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agent. Polymer chains with high functionality are capable of forming a crosslink through a reaction with curing agents or hardeners which react with the epoxide functional groups on the polymer chain. In order for a network to form, the polymer mixture must contain an average of three or more functional groups. A monofunctional epoxy is incapable of forming a crosslink because it has only one epoxide group which can react with the curing agent. In this manner, addition of a monofunctional epoxy imparts "dangling" chains into the network. These dangling chains are considered local network defect structures. The number of dangling chains present in the network is important because dangling chains do not contribute to the elasticity and, as network defects, may reduce the effectiveness of existing crosslinks (Figure 2-2. Epoxy network modified with a monofunctional epoxy).



Figure 2-1. Schematic diagram of an "ideal" epoxy network.



Figure 2-2. Schematic diagram of an epoxy network modified with a mono-functional epoxy.
2.2 Sample Materials and Preparation

Samples with various network structures were investigated. The epoxide monomers studied were di-functional pure diglycidyl ether of bisphenol-A (DER 332, Dow Chemical, USA) mixed with varying amounts of a low viscosity o-cresyl glycidyl ether monoepoxide (Heloxy 62, Shell Chemical, USA). The epoxide mixtures were crosslinked with either an amine terminated poly (propylene oxide) (Jeffamine D230, trademark of Texaco Chemical Company) or m-Phenylenediamine (mPDA, DuPont, USA). The chemical structures of the components are described in Figure 2-3 through Figure 2-6.



Figure 2-3. Diglycidyl ether of bisphenol A (DER 332)-"Epoxy".

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Figure 2-4. o-Cresol glycidyl ether (Shell Heloxy 62)-"Modifier".



Figure 2-5. Polyoxypropylenediamine (Jeffamine D230)-"Curing Agent".



Figure 2-6. m-Phenylenediamine (mPDA)-"Curing Agent".

2.2.1 DGEBA/Heloxy 62/D230

DGEBA, di-functional epoxide monomer, was preheated at 60°C for 2 hours to melt any crystals present. Stoichiometric portions of the DGEBA epoxide monomer, monofunctional Heloxy 62 modifier and, D230 amine curing agent were weighed and thoroughly mixed together. Table 2-1 lists the mixing ratios used in the preparation of samples to be used for viscoelastic experiments. The mixture was vacuum degassed at room temperature for 30 minutes in order to remove entrapped air, then poured into 1/2" diameter x 7" long glass tubes, which were sealed at one end with silicone plugs, and cured at 100°C for 24 hours. The epoxy rods were allowed to slowly cool down to room temperature. Specimens were then machined, on a lathe, from the cast rods into cylindrical tensile coupons and stored in a desiccator at room temperature until the experiments were performed.

Sample	Total Weight (grams)	Wt. fraction of DGEBA	Wt. fraction of Heloxy 62	Wt. fraction of D230
100%DGEBA/0%Heloxy/D230	22,750	74.73%	0%	25.2 7%
95% DGEBA/5%Heloxy/D230	22,795	70.85%	3.93%	25.22%
90% DGEBA/10%Heloxy/D230	22,840	66.98%	7.83%	25.17%
80% DGEBA/20%Heloxy/D230	22,930	59.31%	15.61%	25.07%

TABLE 2-1. Stoichiometric mixing ratios of epoxy components with D230.

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2.2.2 DGEBA/Heloxy/mPDA

The DGEBA and mPDA curing agent were preheated at 60°C to melt any crystals present in the epoxide and to melt the mPDA, which existed as solid flakes. The DGEBA epoxide monomer, Heloxy 62 modifier, and mPDA curing agent were weighed and quickly mixed together to prevent the mPDA from crystallizing which can occur at room temperature. Table 2-2 presents the mixing ratios used in the preparation of samples to be used for moisture absorption experiments. After thorough mixing, the resin was vacuum degassed at room temperature for 15 minutes to allow air bubbles to escape. The mixture was then poured into a stainless steel mold and cured for 2 hours at 75°C followed by 3 hours at 120°C. Figure 2-7 depicts the curing cycle used in the sample preparation. After curing, the epoxy plaques were removed from the mold while still warm, placed back in the oven and allowed to slowly cool to room temperature. The plaques were then cut into 1.5"x 1.5" squares and stored in a desiccator at room temperature until the experiments were performed. In addition, all samples had an average thickness of 1/32".

Sample	Total Weight (grams)	Wt. fraction of DGEBA	Wt. fraction of Heloxy 62	Wt. fraction of mPDA
100%DGEBA/0%Heloxy/mPDA	19,700	86.29%	0%	13.71%
95% DGEBA/5%Heloxy/mPDA	19,745	81.79%	4.53%	13.67%
90% DGEBA/10%Heloxy/mPDA	19,790	77.31%	9.04%	13.64%
80% DGEBA/20%Heloxy/mPDA	19,880	68.40%	18%	13.58%

TABLE 2-2. Stoichiometric mixing ratios of epoxy components with mPDA.



Figure 2-7. Curing cycle for DGEBA/mPDA sample processing.

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2.3 Sample Characterization

2.3.1 Glass Transition Temperatures

Differential scanning calorimetry, DSC, is a thermal analysis technique which measures the input power differential between a sample cell and reference cell. When the sample undergoes a transition, a characteristic change in power differential is observed. The nature of the change depends on the order of the thermodynamic transition. Melting or crystallization is a first order transition which manifests itself as an endothermic or exothermic peak respectively on the heat flow versus time/temperature curve. The glass transition is a second order transition which results in an endothermic step change of the heat flow baseline.

The glass transition temperature, Tg, for the DGEBA/mPDA glasses containing incremental amounts of Heloxy 62 monoepoxide upto 100 wt% were determined using a TA Instruments Differential Scanning Calorimeter (Modulated DSC). The heating scans were performed at 5°C/min immediately after a cooling run. The glass transition was taken at the inflection point of the step transition curve. Figure 2-8 is a plot of the glass transition temperatures as a function of Heloxy content. As can be seen, as the Heloxy content is increased the glass transition temperature of the polymer decreases, and the experimentally determined transition temperatures are in good agreement with the theoretical values of Tg as determined by the rule of mixtures. Another interesting result was that even though increasing the Heloxy content decreased the Tg, the width of the glass transition zone was not affected.



Figure 2-8. Plot of glass transition temperatures as a function of Heloxy content. Solid line represents the rule of mixtures values. (•) corresponds to experimentally determined Tg values.

2.3.2 Network Formation

In order to determine the network structure present in the epoxy glasses, a set of specimens containing a range of Heloxy from 0 wt% to 100 wt% in increments of 10 wt% were fabricated. A portion of each sample was placed in a vial of solvent at room temperature. Samples containing more than 50 wt% Heloxy dissolved in the solvent which indicates the lack of an infinite network. Samples containing less than 50 wt% Heloxy swelled due to solvent uptake by the network. These results indicate that 50 wt% is the critical concentration necessary to form an infinite network. This value is in agreement with the value for the critical concentration of bonds needed to form an infinite network according to bond percolation theory (Table 2-3).

Lattice	Coordination Number (z)	Percolation Threshold (p _c)	Critical bond number (Z p _c)
Honeycomb	3	0.6527	1.96
Square	4	0.5000	2.00
Triangular	6	0.3473	2.08

Table 2-3. Bond percolation threshold values for 2-D lattice. Adapted from (8).

Bond percolation theory applies to a lattice where a fraction p of the bonds are connected. A function P(p) refers to the probability that a given connected bond is part of an infinite cluster linked by other such bonds. The percolation probability P(p) is equal to zero for $p < p_c$, where p_c is the critical concentration necessary to form an infinite network and is dependent on the lattice type. Above the critical concentration, the percolation probability rises monotonically from zero at p_c to a value approaching unity at p=1. The critical bond number or the number of bonds needed to form a network, is a function of •

the dimensionality, 'd', of the lattice and the coordination number, 'z', and gives a result for p_c to within a few percent of that observed experimentally [8].

$$zp_c \approx d/(d-1)$$
 (2-1)

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Therefore, the network structure present in the Heloxy modified epoxy glasses is a two-dimensional square lattice. Figure 2-2 is a schematic diagram of the epoxy network modified with a monofunctional epoxy.

CHAPTER 3 LOCAL STRUCTURE EFFECTS ON THE VISCOELASTIC RESPONSE

3.1 Background

3.1.1 Viscoelasticity

A material may exhibit behavior which combines liquidlike and solidlike characteristics. For example, a body, which is not quite solid, does not maintain a constant deformation under constant stress, but slowly continues to deform or creep with time. When a body is constrained at constant deformation, the stress required to hold it diminishes gradually, or relaxes. On the other hand, a body, which is not quite liquid, may, while under constant stress, store some of the energy input instead of dissipating it like a solid. Materials whose behavior exhibits this energy storage and loss are called viscoelastic. In polymeric systems, mechanical behavior is dominated by viscoelastic phenomena because of the molecular mobility associated with polymeric structures. Under a macroscopic deformation, the flexible polymer molecules are able to make complicated molecular adjustments [9]. Molecular structure is one factor which determines the viscoelastic properties of a polymer. Relaxation times are directly related to the structure of the polymer molecules, thus, the mechanical properties of the material will be influenced by aging via changes in relaxation times. An increase in aging time changes all relaxation times by the same factor, thus the shape of creep or stress relaxation curves are not changed [2]. A change in aging time will only affect the position of the curve on the log-time scale, and not its shape. Figure 3-1 is a schematic diagram of stress relaxation curves as a function of log time for isothermally aged polymer glasses. This is an important factor in the applicability of a classical time-aging



Figure 3-1. Response of stress relaxation curves to isothermal aging.

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time superposition. According to the superposition principle it is possible to predict the long-term properties of polymeric materials, for various aging times, using short-term tests.

Creep and stress relaxation experiments are two direct methods to study the viscoelastic properties of polymeric materials. Creep and stress relaxation parameters are generally improved on cross-linking. In addition, the glass-transition temperature, Tg, increases by increasing the cross-link density, which is a measure of the total number of links between chains in a given mass of material. The structure and distance between crosslink junctions are important characteristics in polymeric networks. Lee and McKenna [10] investigated the viscoelastic response of physically aged epoxy networks of different crosslink densities with homogeneous lengths. In that study, altering the molecular weight between crosslinks produced various homogeneous network structures. Utilizing a higher molecular weight curing agent produced a network structure in which the distance between junctions was longer than the distance between junctions produced from a low molecular weight curing agent. In other words, the crosslink density increased with a decrease in crosslink molecular weight. Lee and McKenna also found that when the crosslink density increased, the glass transition temperature, Tg, increased; however, the shape of the viscoelastic spectrum was independent of the crosslink density for the epoxy networks. In addition, it was possible to superimpose the stress relaxation curves at different aging times, temperatures, and crosslink densities to form a single master curve, demonstrating the applicability of a time-aging time-temperature-crosslink density superposition principle to these types of network structures.

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In order to elucidate the effect of the molecular weight distribution between crosslinks on the mechanical and viscoelastic responses of epoxy networks. Wang [11] used a mixture amine terminated curing agents of various molecular weights to form random networks with a crosslink distribution. Two epoxy systems were studied: one contained a single diamine (DGEBA/D230) and the other contained a mixture of two diamines (DGEBA/D230/D400 or D2000). The first epoxy system represents a network structure which is homogeneous due to crosslinks which are equal in molecular weight: i.e. the length of the crosslinks are the same. The second epoxy structure, which contains two diamines of differing molecular weights, forms a heterogeneous network because the diamines have two different molecular weights which causes the crosslinks to have two different lengths. In that study it was found that the glass transition is broadened and the transition temperature decreases with the addition of D400 or D2000. The viscoelastic response curves for different aging times and temperatures were able to be superimposed to form master curves, thus demonstrating the applicability of the classical time-aging time; time-temperature superposition principle. In addition, the viscoelastic spectrum was broadened with an increase in D2000 content and thus the aging process was retarded by the presence of the long D2000 chains.

3.1.2 Memory Effect

In addition to being nonlinear, glassy state relaxations are also nonexponential and exhibit the memory effect, that is, relaxation from a particular state depends not only on what the state is, but also on how that state was reached [12]. Thermal treatments, involving two consecutive temperature jumps of opposite sign, are depicted in Figure 3-2. Kovacs [13] studied the response of the system, at a fixed temperature, to these thermal treatments through their volume recovery behavior. Route A corresponds to a direct quench from a temperature above Tg to a temperature below Tg. Routes B-E correspond to temperature jumps from the same temperature above Tg to various T_1 temperatures below Tg, followed by isothermal recovery. The isothermal recovery times, 't₁', for each route were identical. After 't₁' time for recovery, the specimens were instantaneously reheated to T₂, where the isothermal recovery is observed as a function of elapsed time (tt₁), where 't' is the time at each volume measurement during the experiment. The curves displayed in Figure 3-3 are isothermal volumetric recoveries in which curve A represents a simple approach experiment where the sample is guenched from a temperature above Tg to a temperature below Tg without any additional thermal treatments. Thus, the volume approaches the structural equilibrium values as a monotonically decreasing function and is referred to as a "simple approach" experiment. Curves B through E are the response curves to two consecutive temperature jumps of opposite sign and are examples of the phenomena called memory or crossover effects, which have often been observed experimentally and are attributed to a multiplicity of retardation mechanisms.



TEMPERATURE

Figure 3-2. Thermal treatment involving two consecutive temperature jumps of opposite sign. (A) Sample directly quenched, then aged, (B-E) Samples quenched to various temperatures below Tg; $(T_B > T_C > T_D > T_E)$. All samples were aged for the same time. After aging all samples were reheated to the same temperature. Adapted from [13].



Figure 3-3. Volume recovery as a function of time for the samples conditioned with the thermal treatments provided in Figure 3-2. (A) Direct quench; (B-E) quench-storage-"up-jump". δ measures the volume departure from equilibrium. Adapted from [13].

Certain conditions are necessary for the occurrence of a peak, which may be a maximum or minimum depending on the sign convention used, in the response curves of a recovery experiment. The first condition is that there is a distribution of relaxation times. If there is only one relaxation time or mechanism, the recovery as a function of time will vary monotonically and will not show a maximum. A second condition is that the recovery time, 't₁', should not be too long nor too short; it should be longer than the shortest relaxation time, and shorter than the longest relaxation time. If the recovery time, 't₁', is longer than the longest relaxation time, the material attains equilibrium during the first loading period in a stress relaxation experiment. If 't₁' is shorter than the shortest relaxation time, the material will not have sufficient time to respond to the applied strain during the first stress relaxation period. In other words, the stress relaxation in the first period must be considerable without the material having attained equilibrium.

Alternatively, a peak in the response curve can be explained more directly through the use of a generalized Maxwell model, which is diagramed in Figure 3-4. A generalized Maxwell model consists of an array of individual Maxwell elements connected in parallel. Since the relaxation times of the different elements in the model are not the same, rapid units will reach equilibrium during the first strain loading period, and slow units will not. During the second period, the rapid units which have reached equilibrium, will have to return (i.e. expand); while the slower units will continue to relax in the same direction [2]. Therefore, the system departs from its apparent equilibrium, passes through a maximum or minimum, and then approaches true equilibrium. The peak corresponds to the point at which the short-time contributions exactly compensate the long-time



Figure 3-4. Schematic diagram of a generalized Maxwell model.

contributions. The "memory effect" peak increases in magnitude and occurs at a shorter time for samples isothermally aged at temperatures the further below Tg [13].

The goal of this work was to study the effects of physical aging on the viscoelastic response of an epoxy/diamine network modified with a monofunctional epoxy (Heloxy-62). Addition of the monofunctional epoxy results in the formation of a network that contains dangling chains. These chains are only linked at one end and thus do not contribute to the overall crosslink structure; however, the chains may have an effect on the relaxation response of the modified networks. Small strain relaxation tests in simple extension for various aging times and temperatures were be used to develop a relationship between the viscoelastic response and the epoxy network.

3.2 Viscoelastic Response

3.2.1 Isothermal Aging

The aging behavior was probed using uniaxial extension under stress relaxation conditions. The mechanical tests were performed using a computer controlled servo-hydraulic testing machine (Instron Model 1321) equipped with an oven for temperature control. Cylindrical dumb-bell shaped specimens were first annealed, for 30 minutes, at 20°C above the glass transition temperature of the particular system studied to remove any previous aging, and then quickly placed in the testing machine at a temperature where the amorphous glass specimens began to age. Successive deformations were applied at aging times, t_e, which approximately doubled with each application, [namely $t_e=60$ min, 120 min, 240 min, etc.]. At each interval of deformation, the ratio of the deformation duration time, t_i , to aging time was 0.05. Figure 3-5 is a plot of the applied strain history. For the stress relaxation tests, the applied strain, ε , in these tests was 0.1% and was measured with an Instron extensometer. The stress, $\sigma(t)$, was measured using a 2200lb (900 kg) capacity load cell. Thus the stress relaxation modulus could be calculated from the following relation:

$$E(t) = \sigma(t)/\epsilon$$
 (3-1)

The isothermal stress relaxation curves for the modified epoxy networks are depicted in Figures 3-6 through 3-8.



Figure 3-5. Schematic diagram of the applied strain history. Applied strain: $\epsilon=0.1\%$



Figure 3-6. Stress relaxation modulus curves for DGEBA+95 wt% D230+5 wt% Heloxy-62 quenched from 20°C above Tg and aged at 59.7°C. Applied strain is 0.1%. Aging time in hours: (O)0.5 (●)1.0 (□)2.0 (■)4.0 (◊)8.0 (♦)16.0 (◊)32.0 (♦)64.0.



Figure 3-7. Stress relaxation modulus curves for DGEBA+90 wt% D230+10 wt% Heloxy-62 quenched from 20°C above Tg and aged at 54.9°C. Applied strain is 0.1%. Aging time in hours: (O)0.5 (●)1.0 (□)2.0 (■)4.0 (◊)8.0 (♦)16.0 (◊)32.0 (♦)64.0.



Figure 3-8. Stress relaxation modulus curves for DGEBA+80 wt% D230+20 wt% Heloxy-62 quenched from 20°C above Tg and aged at 41.8°C. Applied strain is 0.1%. Aging time in hours: (○)0.5 (●)1.0 (□)2.0 (■)4.0 (◊)8.0 (♦)16.0 (◊)32.0 (♦)64.0.

3.2.2 Memory Effect

The memory effect phenomena was probed in a stress relaxation experiment using the same procedures as for the isothermal aging experiments. However, prior to testing the DGEBA/D230 sample which contained 10 wt% Heloxy was quenched from 80°C (20°C above Tg) to 46.8°C and 38.7°C and annealed at those respective temperatures for 116 hours. Subsequently, the sample was "jumped" to the testing temperature of 59°C where the glass began to age. The stress relaxation experiment was then conducted at various aging times. Figure 3-9 is the isothermal stress relaxation curves for the sample annealed at 46.8°C and then "jumped" to the testing temperature of 59°C.


Figure 3-9. Stress relaxation modulus curves for DGEBA+90 wt%D230+10 wt% Heloxy-62 quenched from 20°C above Tg and aged at 59°C. Prior to the mechanical test, the sample was annealed at 46.8°C for 116 hours. Applied strain is 0.1%. Aging time in hours: (O)0.5 (●)1.0 (□)2.0 (■)4.0 (◊)8.0 (♦)16.0 (▲)32.0 (△)64.0.

3.2.3 Data Analysis Method

Each stress relaxation curve at a given aging time was curve fitted with the Kohlrausch-Williams-Watts [14,15] stretched exponential function:

$$E(t) = E_o \exp[-(t/\tau)^{\beta}]$$
(3-2)

where E_0 is the modulus at t=0, τ is a characteristic relaxation time, and β describes the shape of the relaxation curve and the width of the viscoelastic spectrum. The ability to perform superposition and form a master curve requires that the value of β at various aging times must be the same, i.e. the shape of the relaxation spectrum must be invariant. Thus, horizontal shifts of the relaxation curves, a_{te} , along the time axis can be defined in terms of the KWW function as:

$$a_{te} = \tau(t_e) / \tau (t_e(ref))$$
(3-3)

where the τ (t_e) is the value of τ at the relevant aging time and τ (t_e(ref)) is the value of τ at the reference aging time. The stress relaxation curves for the isothermally aged samples were fitted with equation 3-2 and the KWW parameters are presented in Table 3-1.

The aging process at different temperatures is conveniently characterized by the double-logarithmic shift rate, μ , defined as [2]:

$$\mu = d \log (a_{te})/d \log (te)$$
 (3-4)

Sample	t (hr.)	Eo (GPa)	τ (Sec.)	β
DGEBA+95%D230+5% Heloxy	0.5	2.6183	1903.1	0.3
T _a : 60°C	1	2.6154	3408.6	0.3
	2	2.654	7315.1	0.28
	4	2.698	14978	0.27
	8	2.697	20691	0.28
	16	2.705	41143	0.28
	32	2.748	811 64	0.285
	64	2.755	1.52E+05	0.28
DGEBA+90%D230+10% Heloxy	0.5	2.763	224.3	0.295
T _a : 55°C	1	2.779	492.1	0.292
	2	2.806	903.47	0.285
	4	2.798	1573.7	0.291
	8	2.82	2580.7	0.291
	16	2.841	3918.2	0.29
	32	2.876	6796.6	0.289
	64	2.897	10233	0.285
DGEBA+80%D230+20% Heloxy	0.5	3.13	223.1	0.259
T _a : 41.8°C	1	3.13	274.9	0.274
	2	3.21	430.4	0. 267
	4	3.23	643 .7	0.273
	8	3.28	999.8	0.269
	16	3.3	1471.8	0.265
	32	3.31	2125	0.269
	64	3.31	2972	0.275

Table 3-1. KWW curve fitting parameters. $\varepsilon=0.1\%$; T_a: aging temperature

3.3 Results and Discussion

3.3.1 Isothermal Aging

As seen in Figures 3-6 through 3-8 it is apparent that as the aging time increases, the relaxation modulus shifts to the right along the time axis. Applying time-aging time superposition to such data allows one to determine the shift factor, a_{te} , for these data sets. The KWW parameters given in Table 3-1 indicate that the instantaneous modulus, E_{o} , and the shape parameter, β , do not vary with aging time for a given epoxy network, thus each relaxation curve may be shifted along the time axis to form a single master curve. When the fraction of Heloxy content in the epoxy network increases, the value of β decreases indicating a broadening of the viscoelastic spectrum. In addition, since the values of β are independent of aging time, a classical time-aging time superposition appears to be valid for these epoxy networks. The instantaneous modulus, E_{o} , did not change by increasing the Heloxy 62 content. The monofunctional modifier is only crosslinked at one end; i.e. dangling, thus it does not have an effect on any load bearing properties. Thus the number of dangling chains present does not affect the instantaneous modulus; however it does affect the relaxation behavior of the network.

Figures 3-10 through 3-13 are the double logarithmic plots of the aging time shift factor, a_{te} , versus aging time, t_e , at different values of T-Tg for each modified network. These plots reveal that the value of $log(a_{te})$ increases with increasing aging time at a temperature far below Tg, but shows a more complicated behavior at temperatures closer to Tg. As the temperature increased, the material showed a regime of rapid aging followed by one in which aging virtually ceased. Figures 3-14 through 3-16 reveal that as

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the fraction of Heloxy present in the epoxy network increased the rate of shifting, i.e. the slope, μ , of the plot decreased.

In addition, for systems which were aged into structural equilibrium at 10°C below Tg, the time required to reach structural equilibrium decreased with an increase in the fraction of Heloxy content present in the epoxy network glasses.



Figure 3-10. Double logarithmic plot of aging time shift factor, a_{te} , versus aging time for DGEBA/D230 samples at different aging temperatures. Reference aging time is 28 minutes. Applied strain is 0.25%. Aging temperature in °C: (O)57.6 (x)61.9 (\Box)66.9 (\triangle)71.5 (\bullet)81.8. $\mu \approx 0.9$.



Figure 3-11. Double logarithmic plot of aging time shift factor, a_{ke}, versus aging time for DGEBA/D230/5 wt% Heloxy samples at different aging temperatures. Reference aging time is 30 minutes. Applied strain is 0.1%. Aging temperature in °C: (0)59.7 (●)65.3 (□)70.4.



Figure 3-12. Double logarithmic plot of aging time shift factor, ate, versus aging time for DGEBA/D230/10 wt% Heloxy samples at different aging temperatures. Reference aging time is 30 minutes. Applied strain is 0.1%. Aging temperature in °C: (O)50.3 (●)55.1 (□)60.2.



Figure 3-13. Double logarithmic plot of aging time shift factor, ate, versus aging time for DGEBA/D230/20 wt% Heloxy samples at different aging temperatures. Reference aging time is 30 minutes. Applied strain is 0.1%. Aging temperature in °C: (O)37.1 (●)42.4 (□)46.3.



Figure 3-14. Double logarithmic plot of aging time shift factor, a_{tc} , versus aging time for DGEBA/D230/5 wt% Heloxy samples at an aging temperatures of 65.3°C. μ =0.83.



Figure 3-15. Double logarithmic plot of aging time shift factor, a_{te} , versus aging time for DGEBA/D230/10 wt% Heloxy samples at an aging temperatures of 54.9°C. μ =0.77.



Figure 3-16. Double logarithmic plot of aging time shift factor, a_{to} , versus aging time for DGEBA/D230/20 wt% Heloxy samples at an aging temperatures of 41.8°C. μ =0.56.

3.3.2 Memory Effect

Figure 3-17 is a plot of the characteristic relaxation time versus aging time for an epoxy sample containing 10 wt% Heloxy. The curves are similar, though inverted, to the volume relaxation curves in Figure 3-3 developed by Kovacs where in he defined the volume departure as a positive quantity. During the step up-jump in temperature, the characteristic relaxation time crosses over the actual equilibrium, exhibits a minimum, and then asymptotically approaches the simple approach curve indicated by the bold circles in Figure 3-17. The position of the minimum on the graph is dependent on the thermal history applied to the sample. The minimum moves to shorter aging and characteristic relaxation times as the sample is quenched deeper into the glassy region. The results, in agreement with Kovacs' volume recovery experiments, indicate that it is possible to use the characteristic relaxation time to monitor the kinetics of the glass forming process.





Figure 3-17. Characteristic relaxation time, τ, versus aging time for DGEBA+90 wt% D230+10 wt% Heloxy-62 at a testing temperature of 59°C. Applied strain is 0.1%. (O) Sample was quenched directly from 80°C to 59°C; (●) Sample was quenched from 80°C to 46.8 °C and annealed for 116 hours, then jumped to 59°C; (□) Sample was quenched from 80°C to 38.7°C and annealed for 116 hours, then jumped to 59°C.

CHAPTER 4 MOISTURE ABSORPTION

4.1 Background

Epoxy resins are often utilized as glassy composite matrices in the aerospace and automotive industries. In polymer based composites, the long-term stability of the matrix is an important aspect of the performance. Since these materials are used in different temperature and humidity conditions, knowledge concerning the polymers' water sorption and transport behavior in response to glassy structural changes is needed in order to predict short-term as well as long-term performance in service. Many investigations have been conducted in an attempt to develop a fundamental understanding of how moisture transport is affected by epoxy network structures [16,17]. Most of the sorption kinetic studies have focused on the effect of varying the amine (curing agent) content or changing the curing conditions [16-18]. Carfagna [19] investigated the effect of prepolymer composition on the water sorption behavior of amine hardened epoxy resins. Synthesizing epoxies and hardeners with off-stoichiometric ratios will produce either excess epoxides or excess hardeners in the system. If epoxide is present in excess, the secondary hydroxyl groups, could add to the remaining epoxide rings until the glass transition temperature of the forming network exceeds the curing temperature and the reaction becomes diffusion-controlled [20]. When the resin is crosslinked with an excess of hardener there is an increase in the number of hydrogen bonding sites due to the presence of unreacted amines. Carfagna concluded that resin systems with an excess of hardener absorbed more water (i.e. higher water equilibrium level) due to the increase in hydrogen bonding sites which attract and accommodate water molecules [19].

The other technique utilized in the investigation of sorption kinetics is to alter the curing conditions [21,22]. The morphology and chemistry of a polymer system is dependent upon the degree of crosslinking in the resin. Since crosslinking is a thermally activated process, curing at higher temperatures is expected to increase the crosslink density and number of hydroxyl groups in the polymer. Moy and Karasz [23] studied the importance of these effects by examining the water sorption behavior as a function of the extent of curing time. These researchers found that the equilibrium sorption of water in the resin was markedly affected by the curing conditions.

In addition, most of the studies have discussed network structure effects due to a change of the curing agent and their amount. Altering the curing agent, however, alters the resin polarity. Thus, moisture transport may be affected by the "chemistry" of the resin. In view of this, it becomes difficult to predict the moisture absorption behavior or to isolate the contribution of each effect [16]. In an attempt to isolate the structural effects only, the epoxy networks produced for this study will be altered while maintaining nearly the same polymer polarity or moisture affinity. The aim of this study is to investigate the effect of aging on the transport properties of epoxy modified network structures.

4.2 Water Transport in Epoxy Resins

The transport of water in glassy epoxy resins is generally studied by the sorption method in which a polymer sheet is suddenly exposed to water or water vapor and the change in weight of the sample is measured as a function of time. Analytical means in determining the values of the moisture content as a function of time may be obtained when the following conditions are met [24]:

- The temperature inside the material approaches equilibrium faster than the moisture concentration; thus the energy and mass transfer equations are decoupled.
- Moisture diffusion can be described by a concentration-dependent form of Fick's law.
- 3) The thermal conductivity and mass diffusivity depend only on temperature and are independent of the moisture concentration or stress levels inside the material.

If the surface concentration of water on the epoxy sheet is constant at all times and the mass transport process is completely diffusion controlled, then the absorption process under isothermal conditions is said to be "Fickian".

Brewis [25] investigated water sorption kinetics of Diglycidyl ether of bisphenol A cured with various hardeners. Ghorbel and Valentin [26] studied the hygrothermal effects of pure and glass fiber reinforced polyester and vinylester resins. In both investigations, the initial moisture uptake as a function of the square root of time were linear implying Fickian diffusion.

Due to the complexity of the absorption mechanism, sorption of liquids and vapors in glassy polymers is not always described by classic Fick's laws. Apicella has reported anomalous sorption behaviors for numerous polymer diluent systems [27]. For example, moisture absorption at high temperatures and relative humidities can cause voids and/or microcracks in the polymer which, if extensively present, cause a non-Fickian sorption process. The formed voids/cracks facilitate diffusion by creating new channels for water penetration and storage and as a result the absorption process is nonlinear (i.e. non-

Fickian)[16]. Glassy polymers respond slowly to changing conditions and most of the anomalous effects are directly related to this slow response. For example, changing the polymer structure influences the solubility and diffusional mobility. This leads to diffusion coefficients which can depend on the previous time-temperature history and rates of change of the system [28]. Therefore, Fickian and/or non-Fickian transport may occur depending on the cured polymer properties, thermal and time exposure history of the polymer, and environmental conditions. Some studies have shown that, for the same epoxy resin, physical damage occurs while other studies have not observed any damage. Such varied results have added to the confusion regarding the already complex nature of the sorption process in polymers.

The diffusion of penetrant molecules into polymers depends on two factors, namely, the availability of appropriate molecular size holes in the polymer network and the attraction forces between the penetrant molecules and the polymer. The presence of holes is determined by the polymer structure and morphology reflected in its degree of crystallinity, crosslink density, and molecular chain stiffness. Thus the first factor affecting diffusion processes is essentially a structural one and is typically referred to as the "volumetric" approach. The "volumetric" or "free volume" approach presumes that water diffuses into the epoxy resin and resides in the free volume in an unbound state, where it is relatively free to travel through the free volume voids [29]. Free volume is defined as the difference between the measured volume of a polymer and the occupied volume which is the volume occupied by the actual mass of the molecule plus the volume a molecule occupies as a result of thermally dependent harmonic vibrations. The free

volume manifests itself as "holes" or "voids" caused by packing irregularities in the occupied volume.

Diamant [16] investigated the effect of network structure on moisture absorption of a diglycidyl ether of bisphenol A resin systems cured with a stoichiometric amount of mphenylenediamine/aniline mixtures. The effect of replacing amounts of the original diamine hardener with aniline was to increase the molecular weight of the chain between adjacent crosslinks and thus decrease the crosslink density. The moisture absorption experiments revealed that resin systems with higher chain molecular weights between crosslink points exhibited lower diffusion parameters. In addition, all samples obeyed Fickian diffusion laws.

The second factor affecting diffusion processes concerns the chemical nature of the penetrant versus that of the polymer and is referred to as the "interaction" approach. This approach states that water molecules are neither distributed randomly in the network nor concentrated in morphological defects, but rather linked by strong hydrogen bonds to some hydrophilic loci, mainly hydroxyls or amines [17]. For example, the relatively high water absorption capacity of epoxy resins results from the presence of hydroxyl groups (-OH) in the epoxy chains which attract the polar water molecules.

Choi [30] studied network systems, which contained either di-functional, trifunctional, or tetra-functional epoxide monomers, cured with an amine terminated PPO. Results from the moisture absorption experiment reveal that the diffusion process of the crosslinked epoxy of higher functionality is hindered by its higher crosslink density. In addition, the epoxy resin containing the highest number of hydroxyl groups per mole created more hydroxyl sites, which attract and accommodate water, resulting in a higher moisture weight gain for the tri-functional epoxy network.

4.3 Gravimetric Moisture Absorption

4.3.1 Diffusion

As shown in Figure 4-1 and developed by Shen and Springer [31], a plate of thickness, 'h', exposed on two sides to the same moisture environment is considered to be infinite in the y- and z- directions such that the moisture content and temperature inside the plate varies only along the x-direction (one-dimensional). Initially the temperature T_i and the moisture concentration C_i inside the sample are zero. Subsequently, the sample is exposed to a moisture environment where the temperature T_a and moisture concentration C_a are constant. The objective is to determine the moisture content, 'M', of the sample as a function of time, 't', in the moist environment. If the diffusion coefficient is constant, and there is a concentration gradient only along the x-axis, the problem can be described by Fick's second law of diffusion as follows:

$$\frac{\partial C(x,t)}{\partial t} = D_x \frac{\partial^2 C(x,t)}{\partial x^2}$$
(4-1)
C=Ci 0
C=Ca x=0; x=h t>0

where D_x is the diffusion coefficient of the material in a direction normal to the surface. The solution of Eq. 4-1 for the given boundary conditions is given by Jost [32].



Figure 4-1. Conditioning environment

$$\frac{C(x,t)-C_{i}}{C_{M}-C_{i}} = 1 - \frac{4}{\pi} \sum_{j=0}^{\infty} \frac{1}{(2j+1)} \sin \frac{(2j+1)\pi x}{h} \exp[-\frac{(2j+1)^{2} - 2}{h^{2}}]$$
(4-2)

Where C_M is the maximum moisture concentration. The total weight of moisture in the material can be obtained by integrating over the sample's thickness:

$$M(t) = \int_{0}^{h} C(x,t) dx$$
(4-3)

The result of this integration is

$$G = \frac{M - M_i}{M_m - M_i} = \frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{j=0}^{\infty} \frac{\exp[-(2j+1)^2 \pi^2 (\frac{Dt}{h^2})]}{(2j+1)^2}$$
(4-4)

where 'G' is a time dependent parameter of the ratio of moisture content at time, 'M_t', to the equilibrium moisture content ' M_{∞} '. ' M_i ' is the initial weight of the moisture in the material and ' M_m ' is the weight of moisture in the material when the sample is completely saturated. In addition $M - M_i$ equals ' M_i ' which is the moisture content in the material at time t =t and $M_m - M_i$ equals ' M_{∞} ' which is the saturated moisture content of the sample at time t = ∞ .

Equation 4-4 may be approximated by the expression

$$G = 1 - \exp[-7.3(\frac{Dt}{h^2})^{0.75}]$$
 (4-5)

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Comparison of Eq. 4-4 and Eq. 4-5 is shown in Figure 4-2. Since the approximation curve is in good agreement with the theoretical curve, the equilibrium moisture content and diffusivity can be obtained by using non-linear least-square curve fitting.



Figure 4-2. Variation of G with log time. Solid line is based on Eq. 4-4 representing the exact solution and the dashed line is based on Eq. 4-5 representing the approximate solution.

Epoxy samples containing various amounts of Heloxy 62 and cured with mPDA were lightly sanded with a 240 grit sandpaper in order to remove any release agent, which may have leeched to the samples. All of the specimens were then heated to 20°C above their respective glass transition temperature in order to remove any residual moisture and to erase any aging which occurred during storage. A set of specimens from each system was then physically aged, while the remaining samples were not conditioned prior to testing. The aging process consisted of placing the samples between two metal plates which, were in temperature equilibrium inside an oven set at a specific aging temperature. The samples were allowed to isothermally age for 5 days. Subsequent to the aging process, the "as-cured" samples and the "aged" samples were weighed on an analytical balance with 0.1mg resolution in order to establish a pre-conditioned (i.e. dry) weight. The specimens were immersed in distilled water chambers which were maintained at a constant temperature of 60°C with 0.1°C accuracy. Samples exposed to the moisture environment were periodically removed from the bath, gently wiped dry to remove excess surface water, and weighed. Measurements were made every half-hour during the early stages of the experiment so as to obtain a sufficient amount of data points during the initial linear portion of the uptake curve. As the experiment progressed measurements were made periodically until a steady state condition was reached. Three specimens from each system were used and the average %weight gain at each measurement time was calculated.

4.3.3 Analysis

The samples used were thin enough, with the ratio of edge area to total surface area small enough, so as to ignore edge effects, facilitating the validity of the one dimensional diffusion model developed previously. Gravimetric liquid sorption analysis was used to determine the moisture content of the samples as a function of time. Assuming that the sample's weight gain was due to moisture uptake, percent moisture content, can be obtained from Eq. 4-6

$$M = \frac{W - W_i}{W_i} \times 100$$
(4-6)

where M is the percent weight gain (%), W is the weight of the moist sample at time t, and W_i is the initial weight of the dry sample. Moisture absorption profiles are plotted in Figures 4-3 through 4-6 as a function of % weight gain versus time (seconds). Equation 4-5 and non-linear least-square curve fitting was used to fit the experimental data and obtain values for M_{∞} for the Heloxy modified samples.

4.4 Results and Discussion

4.4.1 Cross-link Density Effects

Figure 4-3 is a plot of the moisture absorption profiles for unaged samples containing 0 wt%, 5 wt%, 10 wt%, and 20 wt% Heloxy. As evidenced from the curves, addition of the monofunctional epoxy caused a reduction in the maximum moisture content of the samples. The diffusion of small molecules, such as water, into glassy materials is argued to be dependent on the "free volume" of the glassy structure. The results presented in Figure 4-3 and the values of M_{∞} displayed in Table 4-1 indicate that the available path for diffusion plays a more significant role than the amount of free

wt%	As-cured	Aged	%
Heloxy	M∞	M∞	Difference
0	3.36	3.29	0.07
10	2.82	2.53	0.29
20	2.69	2.03	0.66

Table 4-1. Equilibrium moisture values of Epoxy modified networks.

volume available. Samples containing Heloxy have a lower crosslink density do to network chain scissions. Moy and Karasz [23] investigated the effect of crosslink density on the transport of moisture in glassy materials. These researchers found that a decrease in the rate of absorption and equilibrium moisture content occurred when the curing temperature was increased. Since crosslinking is a thermally-activated process, curing at a higher temperature is expected to increase the cross-link density. This suggests that samples with a lower crosslink density should have a comparatively higher rate of moisture absorption. Thus, in this investigation it was expected that the samples containing Heloxy would absorb more moisture than the samples containing no Heloxy. The results, however, did not show this, but instead the samples containing Heloxy absorbed less moisture. Therefore, these results indicate that morphological features control the transport of moisture in these epoxy systems. It is believed that moisture transport is obstructed because of the mobility of the dangling chains present in the network. In addition, the moisture absorption profiles for the samples containing 10 wt% and 20 wt% Heloxy are nearly identical. This suggests that the reduction in transport properties is independent of the amount of Heloxy present above some critical amount.

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Figure 4-3. Moisture absorption behavior of unaged DGEBA/mPDA samples containing: $(\diamondsuit)0$ wt% Heloxy; $(\Box)5$ wt% Heloxy ($\bigcirc)10$ wt% Heloxy; and $(\bigtriangleup)20$ wt% Heloxy. Bath temperature is 60°C.

4.4.2 Aging Effects

Figures 4-4 through 4-6 compare the absorption profiles of "ideal" and Heloxy modified networks in aged and as-cured epoxy glasses. The aging behavior of the glasses was probed at the same temperature relative to the particular sample's glass transition temperature. The aging temperature used was Tg-13°C.

Figure 4-4 is a plot of the moisture absorption profile for aged and as-cured samples containing no Heloxy. It can be seen that there is virtually no effect on the moisture transport properties of samples which did no contain Heloxy. Since the network present in this sample is considered to be "ideal", it is assumed that there are relatively few network defects. Therefore it is believed the volume and enthalpy recovery response associated with physical aging in glassy materials occurred homogeneously in the sample. The small water molecules were not affected by this uniform relaxation and thus there was no affect on the transport properties.

Figures 4-5 and 4-6 are plots of the moisture absorption profiles for aged and ascured samples containing Heloxy. The effect of aging on networks which contain dangling chains is evident. For networks with large amounts of scissions, the path of diffusion is obstructed during the isothermal aging process. These results suggest that the isothermal aging process results in a heterogeneous relaxation of these modified network glasses. The aging process affected the samples containing 20 wt% Heloxy more significantly than those containing 10 wt% because of the stability of the network. The networks containing more dangling chains or chain scissions are less stable and collapse more readily when subjected to an isothermal volume recovery process such as physical aging.



Figure 4-4. Moisture absorption behavior of aged and unaged DGEBA/mPDA samples containing 0 wt% Heloxy. Bath temperature is 60°C. Samples directly quenched into the water bath from above Tg are represented by (■) symbols. Samples aged at a temperature of Tg-13°C for 120 hours are represented by (O) symbols.

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Figure 4-5. Moisture absorption behavior of aged and unaged DGEBA/mPDA samples containing 10 wt% Heloxy. Bath temperature is 60°C. Samples directly quenched into the water bath from above Tg are represented by (■) symbols. Samples aged at a temperature of Tg-13°C for 120 hours are represented by (○) symbols.



Figure 4-6. Moisture absorption behavior of aged and unaged DGEBA/mPDA samples containing 20 wt% Heloxy. Bath temperature is 60°C. Samples directly quenched into the water bath from above Tg are represented by (■) symbols. Samples aged at a temperature of Tg-13°C for 120 hours are represented by (O) symbols.

CHAPTER 5 SUMMARY

Polymer glasses utilized at temperatures below their glass transition are susceptible to a process known as physical aging. With the growing importance of long-term durability of polymeric materials, it is particularly important to determine the effects physical aging will have on glassy polymers subjected to various mechanical and environmental conditions. Therefore, the goal of this study was to determine the effects of physical aging on modified network glasses.

5.1 Local Structure Effects on Viscoelasticity

Stress relaxation experiments were conducted on epoxy glasses which were modified with a monofunctional epoxy in order to determine the effect of these modifications on physical aged networks. The following results were achieved:

- \Box Classical time-aging time superposition was observed as a result of the relaxation modulus, E_o, and shape parameter, β , being independent of aging time.
- \Box The value of the shape parameter, β , decreased as the fraction of monofunctional epoxy, Heloxy 62, in the epoxy network increased.
- The slope, 'u', of the Log(aging time shift factor) versus Log (aging time) decreased with an increase in the Heloxy content. Thus, the aging process was slowed down due to the presence of the "dangling chains".

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- □ For systems which were aged into structural equilibrium at 10°C below their glass transition, the time required to reach equilibrium decreased as the fraction of Heloxy 62 was increased.
- The characteristic relaxation time demonstrates the "memory effect" after two consecutive temperature jumps of opposite sign.

5.2 Local Structure Effects on Moisture Absorption

Moisture absorption experiments were conducted in order to determine the role of network structure on the transport properties of aged epoxy glasses:

- The rate of moisture absorption in unaged epoxy glasses decreased as the amount of Heloxy present in the network increased. A critical weight fraction of Heloxy was achieved, above which the reduction of transport properties became independent of the amount of Heloxy present.
- Physical aging had no affect, as compared to unaged specimens, on the rate of absorption of samples without Heloxy. However, aged samples containing Heloxy showed a decrease in moisture transport properties. These decreases became magnified as the fraction of Heloxy content increased.
- Therefore, the diffusion of small molecules into glassy materials is argued to be dependent on the available paths for diffusion.

PART B: INFLUENCE OF METALLIC GLASS RIBBON REINFORCEMENTS

CHAPTER 6 INTRODUCTION

Initial studies have been carried out on the use of metallic glasses as a reinforcing phase for ceramic and thermoplastic polymers. These studies have indicated the tremendous potential of such composites for structural, aerospace, electrical and medical applications [33,34]. Metallic glass ribbons are potential reinforcements because of the unique properties which they possess. These properties include an ultra high tensile strength (upto 4000 MPa), high surface to volume ratio [35], favorable surface morphology [36], and good ductility and corrosion resistance [35]. In addition, metallic glass ribbons have soft magnetic properties which provides the possibility of orienting them into specific configurations, during composite fabrication, with the use of either a magnetic or electric field. It is the intent of this study to determine the feasibility of orienting metallic glass ribbon reinforcements with an external magnetic field during composite fabrication so as to enhance the physical and mechanical properties of complex-shaped polymer matrix composites along critical directions.

The initial studies conducted on the use of metallic glass ribbons as reinforcements in thermoplastic polymer matrix composites have shown that such composites possess relatively weak interfacial strengths [37]. The weak interface is the result of poor adhesion or bonding between the matrix and metallic glass ribbons reinforcements. Another aim of this study is to determine the bonding characteristics of a thermoset polymer, namely epoxy, reinforced with metallic glass ribbons.

6.1 Materials Background

Commercially available metallic glasses are a relatively new class of reinforcements that provide unique advantages over conventional fiber reinforcements. Metallic glass ribbons are potential reinforcements because of the unique properties which they possess. These properties include an ultra high tensile strength, high surface-to-volume ratio, favorable surface morphology, good ductility and corrosion resistance. Some physical properties of a typical metallic glass ribbon are presented in Table 6-1.

Table 6-1. Physical properties of a common metallic glass ribbon.

Material	Chemical Composition	Crystallization Temperature	Elastic Modulus	Yield Strength	Density
Metglas	Fe-78%				
2605s-2®*	B-13%	550°C	85 GPa	1200 MPa	7180 Kg/m ³
	Si-9%				

*Metglas® is a registered trademark of Allied Signal Inc. for amorphous metallic alloys and brazing alloys

Of all of the properties of metallic glasses, it is their soft magnetic properties that have led to the most significant applications. The microstructural homogeneity of the glasses and the absence of magnetocrystalline anisotropy produces glasses which have a high relative permeability and a narrow hysteresis loop [38] facilitating easy magnetization of and requiring only a small external magnetic field to move the ribbon pieces. The magnetic properties of the metallic glass ribbons used in this study are presented in Table 6-2.

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Material	Coercive Force Hc (Oersteds)	Remanent Induction Br (Gausses)	Relative Permeability (µmax)	Resistivity Ohm/cm x 10 ⁻⁶
Metglas 2605s-2	.03	15,000	300,000	130

Table 6-2. Magnetic properties of metallic glass ribbons.

Metallic glasses are produced by rapidly quenching metallic melts. Cooling rates of the order of 105 to 106 Ks⁻¹ are required in order to avoid crystallization. Because of the requirement for rapid liquid quenching, metallic glass samples are available only in thin cross sections (sheets or ribbons) which have a thickness of 25-100 μ m, and a width of 1-15 mm. The cross-sectional geometry is an important characteristic of metallic glasses. Ribbon shaped reinforcements offer improved off-axis composite properties because ribbons, unlike fibers, possess the ribbon width as an additional geometrical parameter [39]. This produces a large interfacial surface area which aids in effective load transfer from the matrix to the reinforcing phase. Therefore, attractive physical properties, in addition to the unique geometry of metallic glasses, have led to use of metallic glass ribbons as reinforcements in composites.

So far studies have been carried out on the use of metallic glasses as a reinforcing phase for ceramic and polymer matrices. These studies have indicated the tremendous potential of such composites for structural, aerospace, electrical and medical applications [33,34].

Metallic-glass ribbons have been found to be successful as reinforcements in ceramics, especially for glassy matrices. In particular, even at a very low volume fraction

of reinforcement, metallic glass ribbons significantly improved the elastic properties, fracture strength and fracture toughness of brittle glass-ceramic matrices [40].

Metallic glasses have been studied as reinforcements for brittle polymer matrices by Hornbogan *et al* [41]. The investigation showed that small volume fractions of metallic glass ribbons have a considerable beneficial effect on the strength of a brittle glassy resin.

CHAPTER 7 BONDING CHARACTERISTICS

7.1 Background

In general, an interface is a critical point in a composite system. Therefore, adhesion or bonding between the matrix and ribbon is an important issue in composite fabrication. No matter what matrix material is chosen, good adhesion between the matrix and reinforcing ribbon is one of the most important factors which determines the mechanical and physical properties of a composite [35]. Various polymer matrices reinforced with metallic glass ribbons have been fabricated in order to investigate the interfacial characteristics of metallic glass ribbon reinforced polymer matrix composites.

Studies carried out on thermoplastic polymer matrix composites reinforced with metallic glass ribbons have shown that they possess relatively weak interfacial shear strengths [37]. The weak interface can be attributed to poor adhesion, or bonding, between the thermoplastic polymer matrix and the metallic glass ribbon reinforcements. A thermoplastic matrix reinforced with a ductile material has a weak mechanical bond and the ductile matrix flows more easily than the reinforcement. For a thermoplastic polymer composite reinforced with continuous ribbons this results in the reinforcements failing first since the ribbons are unable to keep up with the stretching of the matrix. However, for discontinuous ribbon reinforced composite systems, the matrix fails in regions where there is no reinforcement. Due to poor adhesion between the matrix and reinforcement the highly stressed matrix can not effectively transfer its load across the interface to the stronger reinforcing phase.

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This low interfacial shear strength leads to failure behaviors in which a crack, initiated in the matrix, propagates to the interface and causes debonding between the matrix and ribbons. The crack then propagates around the ribbon at the matrix/ribbon interface and when it reaches the same plane on which it arrived it continues on along that plane into the matrix. If the crack propagates to the other end of the sample any further loading will cause a phenomenon known as 'pull-out'. Because the bonds between the matrix phase and reinforcing phase have been broken, the only force holding the matrix and reinforcing phase together is friction. If the loading has sufficient energy to overcome these frictional forces the matrix will be pulled away from the ribbons. However, if there is excellent bonding between the matrix and reinforcement a higher interfacial shear strength is necessary in order to cause debonding.

A brittle matrix composite, such as thermoset polymer composites, reinforced with a ductile material will not fail in the same manners as ductile matrix composites reinforced with a ductile material. For continuous metallic glass ribbon reinforced composite systems the matrix will fail first because it will not be able to stretch as much as the reinforcements. A portion of this study is going to focus on the bonding characteristics of a thermoset polymer matrix composite reinforced with a ductile material. Specifically, an epoxy matrix reinforced with discontinuous metallic glass ribbons will be examined in order to characterize the fracture behavior of these composite systems.

7.2 Sample Preparation

The composite system examined in this study consisted of a thermoset polymer matrix, specifically Epon 828 epoxy resin (Bisphenol A/Epichlorohydrin based) cured with a stoichiometric amount of Jeffamine D400, and amorphous metallic glass ribbons as the reinforcement. Metglas 2605S-2 was the specific metallic glass reinforcement used. A closed glass mold was used to cast reinforced plastic composite sheets with the following dimensions 16.5 cm x 3.5 cm x .4 cm (Figure 7-1). The Epon 828 epoxy resin was heated in an oven for 2 hours at approximately 60°C in order to decrease the viscosity so as to allow for uniform and thorough mixing with the curing agent. The epoxy resin and curing agent were weighed separately in aluminum weighing dishes, then mixed by hand until uniform. The mixture was then degassed at room temperature for 20 minutes in a vacuum chamber. In the meantime, the Metglas ribbon, which came on a spool from the manufacturer, was carefully cut into small pieces of various sizes. A portion of the degassed mixture was then poured into the mold and allowed to settle. Some ribbons were then added to the mold which was partially filled with the epoxy/curing agent mixture. This process was repeated until the mold was completely filled. After sealing the mold it was placed in an oven set at 100°C and rotated frequently in order to minimize ribbon sinking and clumping. After approximately 30 minutes the gel point of the polymer mixture had been reached and the ribbons were, in a sense, "frozen" in position; thus, no further turning of the mold was required. The sample was then allowed to fully cure at this temperature for 24 hours. The cast composite sheets were cut, with a diamond saw, into rectangular pieces in order to make compact tension



Figure 7-1. Schematic diagram of the mold set-up for preparation of composite plaques.

specimens (Figure 7-2). A notch was cut, in line with at least one metallic glass ribbon, into the edge of the rectangular pieces. Next, two holes were drilled on either side of the notch. The holes were loading points where upon application of the load the crack would propagate in the direction of the ribbons. A tabletop Instron, model 4302, with a crosshead speed set at its minimum value of 0.5 mm/min was used to test the specimens. Polarized sheets placed in front and back of the sample and a light source positioned behind the Instron were used in order to obtain the isochromatic stress birefringence patterns of these specimens. In addition, a video camera secured to a tripod was positioned in front of the Instron to videotape the compact tension tests. The fractured specimens were then gold coated so that specimen charging would not occur when viewing the fracture surfaces with a scanning electron microscope (SEM).



(A)



- Figure 7-2. Schematic diagram of (A) cast composite sheet, and (B) compact tension specimen.







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7.3 Results and Discussion

Figures 7-3 through 7-5 presents a schematic diagram and the scanning electron micrographs of the fracture surface of a thermoset polymer reinforced composite specimen. One noticeable feature in all of the pictures is that the fracture occurred in the matrix. The fact that the approaching crack did not propagate through the ribbons can be attributed to the superior strength and good ductility of metallic glasses. Typically, metallic glasses have ultimate tensile strengths on the order of 4000 MPa [35]. The ductility of the metallic glass ribbons retards the crack front's propagation, causing crack deflection around the ribbon reinforcement. In the compact tension sample, from the precrack up to the far end of the ribbon's width the surface is smooth due to stable and continuous crack growth. From the end of the metallic glass ribbon through the remaining matrix, the surface is rough because the crack has propagated around the ribbon and does not meet on the same plane. In addition, failure in the matrix is an indication of strong interfacial adhesion between the epoxy and metallic glass ribbons. Weak bonding at the interface would be revealed by different fracture surface features, due to crack propagation through to the interface causing failure along this weak interface path.

Another feature indicating strong interfacial adhesion is observed in the micrographs of Figures 7-6 through 7-7. These SEM micrographs show a magnified section of ribbon which is well-bonded to the matrix. Near the ends of the ribbon, the ribbon attempted to pull away from the matrix but the bonding between the polymer matrix and metallic glass ribbon was strong enough to prevent complete separation of the matrix from the ribbon. The result of this strong interface is a fibril polymer structure formed in those regions where the ribbon and matrix tried to separate.



Figure 7-3. Fracture surface of compact tension composite sample.



Figure 7-4. SEM micrograph of the fracture surface of metallic glass ribbon reinforced epoxy



Figure 7-5. Fracture surface indicating failure in the epoxy matrix.



Figure 7-6. SEM micrograph indicating ribbon bonding to the matrix.



Figure 7-7. SEM micrograph of a ribbon bonded to the epoxy matrix.

CHAPTER 8 FEASIBILITY OF MAGNETICALLY ALIGNING REINFORCEMENTS

8.1 Background

Polymer composites reinforced with metallic ribbons offer very attractive properties. They increase the strength and stiffness over pure polymer structures. The ribbons are the main load-bearing components and the polymer acts as a binder, transferring the load to the ribbons. Ribbon reinforcements are normally distributed with a random orientation. This is acceptable from a macroscopic viewpoint. However, it would be beneficial to be able to orient the ribbons in such a way as to counteract the forces which could possibly cause the failure of a particular component. For example, a rivet is susceptible to shear failure. Therefore, reinforcement, via ribbon alignment, along these critical shear directions could remarkably strengthen those weak areas. The potential use of polymers reinforced with metallic glass ribbons in strengthening applications lies in the ability to disperse the ribbons uniformly and in positioning the ribbons along critical directions.

8.2 Sample Preparation

The same epoxy/curing agent system used for the compact tension specimens was used as the matrix material for the aligned composite samples. A stoichiometric amount of Jeffamine D400 was added to Epon 828 and thoroughly stirred. The mixture was vacuum degassed at room temperature for 20 minutes in order to remove the air bubbles. Metglas 2605s-2 metallic glass ribbon was purchased from Allied Signal and was used as the reinforcing material. The Metglas ribbon came on a spool from the manufacturer and

was carefully cut to size. The ribbons ranged in size from 6.99 to 14.30 mm. in length and 7.01 to 10.40 mm. in width and all ribbons had an average thickness of 25µm. A low volume fraction of reinforcements (less than 5%) was used. The ribbons were cleaned with acetone, dried and added to the liquid epoxy mixture. A magnetic field, generated by permanent magnets, was applied across the mold by placing the magnets at various positions along the perimeter of the mold. A heat lamp, and in some instances a hot plate, was used to cure the sample. A thermocouple attached to the surface of the mold was used to monitor the temperature during curing.

8.3 Results and Discussion

Two problems were encountered during sample fabrication. The first problem is related to the viscosity of the epoxy mixture prior to curing. The viscosity of the matrix has to be sufficiently high enough to overcome gravitational forces acting on the ribbons. When the ribbons were added directly after mixing, the viscosity of the epoxy was very low and the ribbons settled to the bottom of the mold. In addition, when the ribbons were added after the epoxy mixture had cured to a more viscous state, strong drag forces restricted the ribbons motion.

Various curing cycles were utilized in an attempt to control the viscosity of the epoxy matrix. For example, one cycle consisted of allowing the polymer to cure under a heat lamp for approximately 1 hour. This preliminary cure was an attempt to increase the viscosity of the polymer so that gravitational forces would not affect the positioning of the ribbons. This allowed the ribbons to be placed into approximately ideal positions with minor magnetic orientation adjustments still feasible.

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To date, the best solution to the ribbon settling problem was to incorporate a twostep curing cycle into the composite fabrication process. In this procedure, the mold was partially filled with the uncured matrix material and then cured between 1 and 1.5 hours at 100°C. After partially curing the sample, the remaining uncured mixture and metallic ribbons were added on top of the partially cured resin. This allowed the ribbons to be moved through the use of permanent magnets which were positioned around the mold. Since the partially cured resin had become rubbery, the ribbons only sank approximately half-way through the thickness of the sample.

Despite the problems experienced in this portion of the investigation it has been determined that it is possible to orient metallic glass ribbons. Complex shaped ribbon configurations may be possible provided that the viscosity of the matrix is sufficiently high to prevent both magnetic attraction and settling of the ribbons. The viscosity needs to be low enough, however, to be able to move the ribbons into the desired configurations. Future investigations which need to be conducted include, producing a controllable magnetic alignment field so as to allow for better control over the presiding forces. In addition, analytical models of the viscous elastic drag forces and external magnetic forces should be constructed in order to aid in the alignment of metallic glass ribbons into complex patterns.

CHAPTER 9 SUMMARY

Metallic glass ribbons have unique properties which makes them potential reinforcements for polymer matrices. The ribbon's width is an additional parameter providing a greater surface area to volume ratio aiding in effective load transfer from the matrix to the reinforcing phase. This will hold true if there is adequate adhesion or bonding between the two phases. Compact tension tests were conducted in order to test the bonding characteristics of metallic glass ribbons in an epoxy matrix. The results achieved are:

□ Compact tension tests revealed that an approaching crack did not propagate through the ribbon due to the ribbons' superior strength and good ductility.

- Failure in the matrix indicates strong interfacial bonding between the metallic glass ribbons and the epoxy matrix.
- SEM photographs reveal a polymeric fibril structure, between the ribbon and matrix, where the ribbon unsuccessfully tried to pull away from the matrix.

In addition to the unique mechanical properties metallic glasses possess, they also have useful magnetic properties which has lead to interesting applications. The feasibility of utilizing these magnetic properties was investigated. An external magnetic field was used during composite fabrication so as to align the metallic glass reinforcements along critical directions in order to enhance the physical and mechanical properties of the polymer composites. The following results were achieved:

Metallic glass ribbons become magnetized when exposed to an external magnetic field and as a result, ribbon clumping occurred.

The ribbons settled to the bottom of the sample because the viscosity of the epoxy was too low prior to curing. The viscosity of the matrix has to be high enough to counteract the gravitational forces acting on the ribbons so as to achieve the required distribution of reinforcement in an epoxy matrix.
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