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The Effects of Microwave Processing on Fiber-Matrix Adhesion in E-Glass Fiber Composites

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THE EFFECTS OF MICROWAVE PROCESSING ON FIBER-MATRIX ADHESION IN E-GLASS FIBER COMPOSITES

By

Matthew Mark Kendziorski

A THESIS

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

MASTER OF SCIENCE

Department of Chemical Engineering

ABSTRACT

THE EFFECTS OF MICROWAVE PROCESSING ON FIBER-MATRIX ADHESION IN E-GLASS FIBER COMPOSITES

BY

MATTHEW MARK KENDZIORSKI

Microwave curing of single fiber composite specimens was done using a single mode (TE_{11}) cylindrical microwave cavity operating at 2.45 GHz. A microwave curing cycle was developed which would produce epoxy specimens with matching physical properties to those cured with a conventional thermal curing cycle. Interfacial shear strength (IFSS) measurements for both thermal and microwave cured specimens were made for specimens containing bare E-glass, silane sized E-glass, and commercially sized E-glass. Both the single fiber critical length test and the microindentation test as done by the interfacial testing system were used to determine IFSS values. There was an increase in IFSS from thermally cured to microwave cured specimens for all three fiber types. The increase in IFSS for specimens containing the commercially sized E-glass fibers was over two and one half times as large as the increase for specimens containing the silane sized fibers.

To my family, for all their love, support, encouragement, and understanding.

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INTRODUCTION

1.1 Introduction and Literature Review

Curing thermoset polymer composites with conventional methods requires the transfer of heat by conduction from the outer surfaces of the composite to its center. Due to the low thermal conductivity of polymeric materials this can be a slow process. In order to speed the curing process it is common to exceed the desired temperature at the outer surfaces of the composite in order to more quickly cure the matrix material at the center. This results in large temperature gradients over the cross section of the composite and thermal degradation of the polymeric material near the outer surfaces. As a result, the mechanical properties of the composite may be less than optimum.

An alternative to conventional thermal curing is the use of microwave curing. In this method a microwave field is applied to the composite inside a microwave applicator. Heating occurs inside the polymeric material because it contains dipoles such as the hydroxyl (O-H) group. These dipoles rotate in order to follow the oscillation of the microwave electric field. This oscillating motion of the dipoles causes motion of the polymer molecules which results

in the increase in temperature which is necessary for curing. The increased and different oscillation of the polymer molecules in microwave curing may result in differences in the network structure and orientation of the polymer molecules as compared with thermal curing even though the mechanical properties are matched. The possible effects at the fiber-matrix interface are of particular interest.

The phenomena of orientation and restructuring of polymer molecules at the interface together with the formation of an interphase exhibiting properties different from the bulk polymer are of great importance in determining fiber-matrix adhesion.¹ A comparison of specimens cured to the same extent of cure thermally and by microwaves showed that the microwave cured specimens had significantly lower tensile strength and slightly higher Young's modulus.² It has been hypothesized that microwave curing produces a well packed molecular structure with a lower free volume and higher density than thermal curing.² Curing with microwave radiation accelerates the curing reaction during the early stages of the process by inducing rapid cross-linking. However, the molecular network which is created is rigid enough to trap unreacted functional groups, causing a lower degree of cure for microwave cured epoxies.³ With this information, it is possible to infer that microwave and thermal curing will produce specimens with different extents of cure and polymer network structures when the mechanical

properties are matched.

Microwave curing is not only much faster, but also much more uniform than conventional thermal curing. Since heat is produced throughout the bulk of the polymeric material, its low thermal conductivity is not a factor. The rate of microwave heating is dependent on the dielectric loss factor of a material.^{4,5} The rate of power absorption by a material in a microwave field is given by:

$$\langle P \rangle = \frac{1}{2} (E_o)^2 \omega \epsilon''$$

Where $\langle P \rangle$ is the rate of power absorption, E_o is the electric field intensity, ω is the frequency of radiation, and ϵ " is the loss factor. The higher the loss factor of a material, the faster the heating for a given microwave field intensity and frequency of radiation. The hydroxyl group has a particularly high loss factor. A study of the interaction of small molecules important in the curing of epoxies with a microwave field has shown that the hydroxyl group converts microwave energy into heat more effectively than the epoxy group.⁶

Composite mechanical properties are dependent upon the type and level of adhesion at the interface. The mechanical properties of the material in the interphase have been shown to have a significant effect on the interfacial adhesion.^{7,8} The use of reinforcing fibers with a significantly different loss factor than the matrix material can result in different curing conditions in the interphase than in the bulk material. This could result in the interphase material having different mechanical properties than the bulk phase. Previous research has shown that the fiber-matrix adhesion of microwave cured single fiber specimens containing conducting fibers may be superior to that of thermally cured specimens.⁹ Therefore by using a reinforcing fiber with a proper dielectric loss factor, it may be possible to produce a composite with unique mechanical properties.

The use of fiber sizings may have an effect on the resulting mechanical properties of a microwave cured composite when compared with a conventionally thermally cured composite with the same composition. Sizings are typically used on glass fibers to prevent damage during handling, to promote wetting of the fiber surface with the matrix material, and to improve the ultimate bond characteristics. A commercial size can result in an interphase that has a higher modulus, and greater tensile strength, but a lower toughness.¹⁰ Table 1 lists the components of a typical commercial fiber size and their general proportion.¹¹ The list does not include the solvent or carrier used in application of the sizing. Each of the components in a sizing could possibly cause some phenomena in microwave curing which would change the type or level of adhesion as compared with those in thermal curing.

The use of silane in a sizing is very important in determining the level of fiber-matrix adhesion. However, a full understanding of the mechanism of fiber-matrix adhesion

Table 1. Typical components of a glass fiber size.¹¹

Component	Percent
Film-forming resin Coupling agent Lubricant Antistatic agent	$1.0 - 5.0 \\ 0.1 - 0.5 \\ 0.1 - 0.2 \\ 0.1 - 0.2$

through silane coupling agents has not yet been achieved.¹² Silane coupling agents improve glass fiber/epoxy composite properties by increasing the strength of the glass fibers, by promoting matrix adhesion, and by forming polysiloxane/ epoxy interphases with properties superior to the bulk polymer.¹³ A silane sizing can produce an interphase material with a higher modulus, a lower tensile strength, or a lower toughness depending on the chemical functional groups of the silane.¹⁰

The concentration of the silane and the degree of hydrolysis of the silane can determine the rigidity or mobility of the interphase region.¹⁴ Increased crosslinking of the siloxane structure in the interphase region can give increased bond strength.¹⁵ When the silane is hydrolyzed, the possible formation of entanglements may increase the rigidity of the system and decrease the degree of phase separation through the formation of an interpenetrating polymer network (IPN).¹⁴ The IPN can act in conjunction with chemical bonding to yield a stronger bond. The different modulus and toughness of the interphase combined with the increased fiber-matrix adhesion can be used to explain the resulting mechanical properties of composite materials.⁶ Silanes also contain many hydroxyl groups which may be effective in converting energy from a microwave field into thermal energy.

The differences in the dielectric loss factors of the fiber, sizing, and polymer matrix could result in unique

curing conditions in the interphase. A cured composite with unique mechanical properties would be the result. In order to produce microwave cured composites with optimum mechanical properties for a given application, the effects of microwave curing on the fiber/matrix interphase must be explored. This study investigates the effects of microwave curing on fiber/matrix adhesion for glass fibers with and without fiber sizings. The resulting information is used to gain insight into the effects of microwave curing on the fiber/matrix interphase.

1.2 Background

1.2.1 Thermosetting Resins

Thermosetting resins are liquid materials that are irreversibly converted to solids through polymerization reactions which are brought about by the application of heat. During the polymerization reactions short chain polymer molecules react with a curing agent or other polymer molecules to form a cross-linked molecular network. Epoxy resins are a common type of thermosetting resins. Epoxy resins contain epoxide groups which react through a ringopening mechanism. A common epoxy/curing agent combination is a DGEBA (diglycidyl ether of bisphenol A)/amine system. An example of an amine curing agent is the difunctional curing agent mPDA (meta phenylene diamine). The

functionality of a resin or curing agent is determined by the number of reactive groups per molecule.

Cross-linking in an epoxy/amine system occurs through reaction of the terminal (chain ending) epoxy groups with amine groups, and subsequent reaction of epoxy groups with hydroxyl groups that are formed during the reaction. The progress of the reaction is measured as a percentage of the available epoxide groups which have reacted and is known as the extent of cure. Formation of the molecular network structure may progress differently with different curing techniques due to different molecular motions.

1.2.2 Microwave Curing

Microwave heating is an alternative to conventional thermal heating which can be used to promote polymerization reactions. A microwave is any electromagnetic wave in the frequency range from 1 to 5000 GHz. Energy in these waves alternates between electric and magnetic fields occurring perpendicular to one another. Microwaves may be allowed to propagate freely from a source or may be reflected from a conducting surface. When reflected, some of the energy of the microwave is absorbed by the reflecting surface as heat due to the electrical resistance of the surface. For a conductor, this effect may be very small. Microwaves may be contained in cavities with reflecting walls. When the geometry of such a cavity is properly matched to the

frequency of the wave, a standing wave or mode is generated.

Microwaves are converted into thermal energy by dielectric materials. Such materials contain dipoles which oscillate due to the torque exerted upon them by the microwave electric field. Many thermoset polymer systems have sufficient numbers of polar functional groups with permanent dipole moments for microwave curing. The dipole moments are normally randomly oriented due to thermal Brownian motion. In this state the polarization is zero. Polarization is defined as the net dipole moment per unit volume.

An electric field exerts a torque on the dipole which causes it to align with the field. This increases the polarization. If all the dipoles in a given material are in alignment with an electric field, the polarization is at a maximum value. However, random thermal Brownian motion prevents all of the dipoles from aligning with an electric field and this keeps the polarization below its maximum possible level. When an oscillating molecule collides with another molecule, the energy is converted into thermal energy.

In order for the transfer of energy from the electric field of the microwave to the oscillation of the dipolar molecule to be efficient, the microwave frequency must be matched to the response time of the dipolar molecule. The response time is defined as the time required for the dipoles of a dipolar material to return to their normal

random orientation after an electric field is suddenly turned off. If the microwave frequency is too high, the dipolar molecules will not be able to react to the oscillations of the electric field and the transfer of energy will be insignificant. On the other hand, too low a frequency will result in the dipoles following the electric field but not in the creation of much heat because of the low energy of the intermolecular collisions. The best microwave frequency for heat generation in a given dipolar material is equal to the response time of the material.

At a frequency close to the response time of the dipoles, the dipoles oscillate with the electric field due to the torque exerted upon them by the electric field. When the electric field reaches its maximum intensity, the polarization may still be low but will keep increasing as the electric field intensity decreases. This is due to the fact that the dipoles cannot instantaneously rotate with the electric field because of the fact that they have mass spread over an area and because of intermolecular forces or collisions exerted upon them. The lag between electric field intensity and polarization indicates that energy from the electric field is being transferred into random thermal motion of the molecules in the material, i.e. heat is being generated.

For cylindrical cavities with small perturbations, there are two types of microwave fields, the transverse electric (TE) and the transverse magnetic (TM) fields.¹⁶ In

the TE field, the electric field has only a transverse component to the propagation direction while the magnetic field has both transverse and longitudinal components. In the TM field, the magnetic field has only a transverse component while the electric field has both transverse and longitudinal components. For a cylindrical cavity, the Zaxis must be used as the reference direction.¹⁶

Microwave heating has been used for a significant length of time in many industries because of the high heating rates possible, the capability of heating uniformly, and the low amount of energy consumption as compared to conduction and convection heating. Interest in the use of microwave heating to cure composites has been stimulated in resent years because of the increasing use of polymer composites in both advanced and high volume applications.

1.2.3 Silane Coupling Agents

Silanes have long been used to improve fiber-matrix adhesion in polymer composites with glass fibers. A silane is a silicon compound that contains both organic and inorganic reactivities in one molecule, such as (RO)₃SiCH₂CH₂CH₂-X, where X is an organofunctional group. Because both organic and inorganic reactivities are present, silanes can function as coupling agents which act at the interface between an organic substrate and an inorganic substrate to bond the two dissimilar materials together. An

example of this is using a silane coupling agent to bond an epoxy matrix to a glass fiber. Studies have shown that a chemical reaction can occur between a silane coupling agent and an epoxy resin. A simplified depiction of the bonding mechanism of a silane coupling agent is shown in Figure 1.

Another mechanism through which bonding may occur is known as an interpenetrating polymer network (IPN). By definition, an IPN is a combination of two or more polymers in a network in which one polymer is synthesized and/or cross-linked in the presence of the other. During IPN formation, the matrix diffuses into a condensed silane interphase to form an entangled network.



Figure 1. Formation of a silane layer and bonding mechanism.

EXPERIMENTAL

2.1 Approach

2.1.1 Single Fiber Critical Length Test

Fiber-matrix adhesion in single fiber bare E-glass specimens was determined using the single fiber critical length test. When the magnitude of an increasing tensile load which is being applied to a single fiber dogbone specimen becomes great enough, the fiber begins to fragment. The fragmentation process continues as the tensile load on the specimen is increased until the matrix can no longer transmit enough tensile load to the fiber fragments to induce further fragmentation. A schematic representation of the single-fiber fragmentation process is shown in Figure 2.^{17,18} Figure 3 shows the axial normal stress and interfacial shear stress distribution in a broken fiber fragment.¹⁸ In a theoretically perfect single fiber specimen, all fiber fragments would be of the same length, and this length would be the critical length. After the measurement of the fiber diameter, the interfacial shear strength could be calculated using the equation at the top of page 17:







Figure 2. Schematic representation of the single-fiber fragmentation process.^{17,18}



Axial normal stress and interfacial shear stress distribution in a broken fiber fragment.¹⁸ Figure 3.

where
$$\sigma_f$$
 is the fiber tensile strength at the critical length l_c and d is the fiber diameter.

However the fiber fragments in a real single fiber specimen will be shorter than the critical length and a range of lengths will be present due to random defects in the fiber. The fiber fragment lengths can be fit by the two parameter Weibull distribution.^{19,20} The two parameters of the distribution, α and β , can be determined using the maximum likelihood method (see the computer code in the Appendix). A mean value of interfacial shear strength can be calculated using the two parameters (α and β) as follows:

$$\tau = \frac{\sigma_f}{2\beta} \Gamma\left(1 - \frac{1}{\alpha}\right)$$

where σ_f is the fiber tensile strength at the critical length, Γ is the Gamma function, and α and β are the parameters of the Weibull distribution.

By observing the condition of the fiber and matrix in the region of a fiber break, information about the stress transfer between the fiber and matrix can be obtained. This is done using both regular and polarized light. If the matrix is ductile and there is a high level of adhesion between the fiber and matrix, a matrix crack as shown in Figure 4a will occur.²¹ This crack is circular in shape

 $\tau = \frac{\sigma_f}{2} \left(\frac{d}{l_c} \right)$



Low energy resolved shear stress induced tensile cracks in the matrix

Figure 4. Possible failure modes in the single fiber critical length test: a.) matrix cracking, b.) interfacial failure, c.) failure by shear.²¹ when viewed down the length of the fiber. If there is a low level of adhesion between the fiber and matrix, interfacial failure will occur. This situation is shown in Figure 4b where it can be seen that the fiber and matrix have separated near the fiber break.²¹ When the matrix is brittle and a high level of adhesion exists between the fiber and matrix, matrix failure by shear will result. This situation is shown in Figure 4c.²¹ In this situation a matrix crack at 45° indicates failure by shear. In some cases where the critical length can not be reached before specimen failure, other methods must be used to measure fiber-matrix adhesion.

2.1.2 Interfacial Testing System Test

Adhesion between the fiber and matrix in single fiber specimens containing silane sized E-glass and commercially sized E-glass were ranked using the interfacial testing system (ITS) since the critical length could not be reached in the single fiber test. The specimens used in this test consisted of single fiber dogbone specimens cut in the gauge length and mounted into a polymeric mounting media. Mounting was done so that the fiber axis was perpendicular to the ITS specimen surface.

In the test a microindenter applies an increasing load to the center of a fiber end until the fiber debonds. A depiction of the microdebonding test is shown in Figure 5.



Figure 5. Depiction of microdebonding test. Fiber debonding is said to have occurred when an interfacial crack continuously covers 1/4 to 1/3 (90° to 120°) of the perimeter of the fiber. The value of the load at which this occurs is used to calculate a relative interfacial shear strength. Also necessary for the calculation are the shear modulus of the matrix, the tensile modulus of the fiber, the diameter of the fiber, and the distance of the fiber from its nearest neighbor. The equation used in calculating the IFSS was derived using finite element analysis.^{22,23,24,25} The values obtained using the ITS can be used for comparative purposes. In this study, the adhesion in specimens which were conventionally thermally cured was compared with that for specimens which were microwave cured.

2.1.3 Comparison of Properties

In order to directly compare the adhesion of microwave cured and conventionally thermally cured specimens, it was necessary to achieve the same bulk matrix properties with both curing techniques. In order to do this, the tensile modulus and tensile strength of microwave cured epoxy dogbone specimens were matched to those of conventionally thermally cured epoxy dogbone specimens. Matching the tensile modulus was given a higher priority because of the extreme sensitivity of the tensile strength to slight variations in specimen condition which are unavoidable.

2.2 Materials

2.2.1 Thermosetting Resin and Curing Agent

The materials chosen for this study were selected to allow the determination of interfacial shear strength values as well as detection of phenomena occurring in the interphase. The thermosetting resin chosen was a diglicidyl ether of bisphenol-A (DGEBA) based resin (Dow Chemical, DER 331) cured with the stoichiometric amount of meta-phenylene diamine (mPDA). mPDA was used in the stoichiometric amount of 14.5 parts per hundred. This system was chosen because it has been shown to be very suitable for the single fiber critical length test, because it has sufficient polar groups necessary for microwave curing, and to maintain continuity with previous work. The chemical structure of the DGEBA is:



The structure of the mPDA curing agent is:



The physical properties of DER 331 which has been conventionally thermally cured with a stoichiometric amount of mPDA are listed in Table 2.^{18,26} The dielectric constant at various temperatures and the dissipation factor at various frequencies of conventionally thermally cured DGEBA with mPDA are shown in Figure 6 and Figure 7.²⁷ Typical

Table 2. Physical properties of conventionally cured DER 331 + mPDA.^{18,26}

3.8 (0.65) GPa (Msi) Modulus of Elasticity Tensile Strength 8000 psi Elongation 1.8 % Poisson's Ratio 0.35 1.4 (0.20) GPa (Msi) Shear Modulus 68 (32) 10⁻⁶/°C (10⁻⁶/°F) Coefficient of Thermal Expansion Dielectric Constant, 10³ cps to 10¹⁰ cps Dissipation Factor, 10³ cps to 10¹⁰ cps 3.8 to 2.8 0.002 to 0.025






Figure 7. Dissipation factor vs. temperature of DGEBA cured with a stoichiometric amount of mPDA.²⁷

values of the dielectric constant and loss factor are 3.8 and between 0.01-0.08 respectively. The dielectric properties of the DGEBA and DDS system during microwave curing have been reported by Jow et al. Some of their results are shown in Figure 8.⁴

2.2.2 E-glass Fibers

E-glass fibers were used as the reinforcement in three different conditions: bare; with a pure silane sizing; and with a commercial sizing. The commercial sizing was tested as a representative commercial sizing. Since this sizing was proprietary, its composition is not known. The pure silane sizing was tested because of its importance as a component of commercial sizings in determining fiber-matrix adhesion. Bare E-glass was tested as a base line.

Unsized water-washed E-glass fibers made by PPG were used both as delivered and with a silane coating. The bare E-glass fibers were water washed after production and had no further treatment. The physical properties of the E-glass fibers as delivered are presented in Table 3. There are many hydroxyl groups on the surface of E-glass fibers and the surface adsorbs water. Many oxides are also present on the surface of E-glass fiber. Some of these, such as SiO_2 , Al_2O_3 , and Fe_2O_3 are non-hygroscopic and therefore adsorb water. Water is adsorbed as hydroxyl groups and as water molecules which are hydrogen bonded to the hydroxyl groups.





Table 3. Physical properties of E-glass fibers.

Young's Modulus	76 GPa
Tensile Strength	3.45 GPa
Elongation to Fracture	4.8 %
Coefficient of Thermal Expansion	2.8 10 ⁻⁶ /°F
- Axial Thermal Conductivity - Axial	1.04 W/m°C
Specific Heat	0.197 Cal/g°C
Poisson's Ratio	0.22

.

Other oxides are hygroscopic and become hydrated when water is adsorbed at the surface. The surface of the glass fibers rapidly adsorbs water. The presence of many hydroxyl groups on the surface and the glass fiber's low dielectric dissipation factor may have some counteractive effects in microwave curing. Glass fiber is non-conductive.

2.2.3 Silane Coated E-glass Fibers

The same unsized water-washed E-glass fibers which were used as delivered were also given a silane coating before use. An amino-alkyl functional silane known as Dow Corning Z-6020 was used. The chemical formula of this compound before hydrolysis is:

 $H_2NCH_2CH_2NHCH_2CH_2CH_2Si(OCH_3)_3$

A depiction of the bonding of a polymeric matrix to a glass fiber through a silane is shown in Figure 1. This silane was chosen because of its effectiveness with epoxy systems and because it will contain many hydroxyl groups after hydrolysis which should effectively convert microwave energy into thermal energy. Because the E-glass fiber is coated with an excess of silane, a coating rich in hydroxyl groups is created. This coating will result in an interphase which is rich in hydroxyl groups before the fiber is cured into an epoxy matrix.

2.2.4 Commercially Sized E-Glass Fibers

The commercially sized fibers had a proprietary epoxy compatible sizing. These fibers were supplied by PPG and were 10 mm diameter E-glass fibers with a proprietary sizing. This is an unusually thick sizing. In fact it is possible to see roughness in the surface of the sizing under a microscope. This sizing was chosen in order to determine the effects of microwave curing on a commercial sizing. Since commercial sizings are proprietary, exact compositions are not supplied by the producer. However most commercial sizings for glass fibers are similar in composition.

The key components in a glass fiber size excluding the solvent or carrier used in applying the size are shown in Table 1.¹¹ The size contains processing aids in addition to the coupling agent. The processing aids may have an effect on the interphase properties which are similar to the effect of the coupling agent or very different from the effect of the coupling agent.

2.3 Application of Silane Sizing To Bare E-Glass

The silane selected was an aminoalkyl-functional silane (Dow Corning, Z-6020). It was chosen because it works well with epoxy and has many dipolar hydroxyl groups which should interact with the microwave field in microwave curing. A 1% by weight silane solution was made by adding the Z-6020 to

purified, slightly acidified deionized water with vigorous mixing. The deionized water was acidified by adding glacial acetic acid until the Ph was in the range of 3.5-6. The surface of the solution was then skimmed off in order to remove an oily layer of un-hydrolyzed silane.

The bare E-glass fibers were cut into small segments. These segments were then strung individually across an aluminum frame and glued to the frame with a hot melt glue gun. The aluminum frame with attached fibers was dipped into the silane solution three times from each end. After removing the frame from the solution the fibers were allowed to air dry for at least 48 hours so that a silane layer could form and properly dry on the surface of the fibers.

2.4 Single Fiber Sample Preparation and Thermal Curing

The molds used for specimen casting were constructed of General Electric RTV-664 silicone. It is possible to cast eight standard ASTM 63.5 mm (2.5 in.) dogbone specimens in each mold. These specimens are 3.175 mm (1/8 in.) wide, 1.59 mm (1/16 in.) deep, and have a 2.54 mm (1 in.) long gauge section. (Figure 9.) The eight cavity silicone mold has dimensions of: 7.62 cm (3 in.) wide by 20.32 cm (8 in.) long by 1.27 cm (1/2 in.) thick. In order to allow a fiber to be aligned and fastened lengthwise into the dogbone, sprue slots with a depth of 0.8 mm (1/32 in.) are molded into both ends of each dogbone cavity.



In the first step of specimen preparation, a single filament of a particular fiber was fastened into the sprue slots using rubber cement. Care was taken when handling the fibers so that they were not damaged by abrasion or by application of too great a tension. After the rubber cement was dry, the fiber, if loose, was tightened by pushing on the rubber cement with forceps. The desired amount of epoxy resin (DER 331) and the stoichiometric amount (14.5 phr) of mPDA were weighed in separate beakers. The beaker containing the epoxy resin was placed into a vacuum oven and heated at 100°C. The resin was then degassed at 29 in. Hg until the formation of vapor bubbles slowed significantly. The oven was returned to ambient pressure and the beaker containing the curing agent along with the silicone mold was placed into the oven at 100°C.

When all the mPDA had melted, the mPDA and epoxy resin were mixed and degassed at 75°C and 29 in. Hg. The mold was then held at an angle and the mixture of epoxy resin and curing agent was poured in one continuous pouring from one end. The mixture of resin and curing agent was poured into the sample molds to a level slightly above the surface of the mold. The cavities were filled in this way to prevent air bubbles from becoming trapped in the mixture. The cavities were filled to a level slightly above the surface of the silicone mold. Any additional mixture of the epoxy resin and curing agent was added in drops into the tab region of the molds so that the possibility of trapping air

bubbles in the mixture in the gauge length was minimized.

The silicone mold containing the eight uncured single fiber dogbone specimens was then placed into an air circulating oven with electronic temperature control. The controller was preprogrammed for a curing cycle of 2 hrs. at 75°C followed by a ramp at 2°C per minute to 125°C, held there for 2 hrs and finally ramped back down to room temperature at 2°C per minute. After completion of the curing cycle the specimens could be removed from the silicone mold and any excess material sanded away. The top surface of the specimens were then sanded smooth using an Abramin rotary polisher in order to obtain uniform specimens. Finally, the specimens were placed into a desiccator and left there until they were tested.

2.5 Single Fiber Sample Preparation for Microwave Curing

For microwave curing, a silicone mold was prepared which contained eight dogbone molds with circular wells in one of the tabs of each. These circular wells were 21.5 mm from the center of the gauge length of the dogbone and were 3 mm deep and 4 mm in diameter. Each of the eight individual standard ASTM dogbone molds was then separated from the others. A small hole was made in the bottom of the mold in the center of the circular well. This was done to allow the insertion of a small piece of quartz capillary (15 mm long with a 2 mm O.D.) which was fused on one end.

Excess silicone around the circumference of the quartz capillary at the bottom of the mold was then cut away with a scalpel. The result was a sealed fit between the silicone mold and the glass capillary. The quartz capillary would be necessary to protect a fluor-optic temperature probe tip that would be placed into the specimen before curing. The capillary was placed so that the fused end was inside the dogbone mold and the tip was flush with the bottom of the normal dogbone mold cavity (the top of the well).

The silicone mold was placed onto a Teflon block which had a hole drilled through it for the quartz capillary. (Figure 10.) A single fiber was then glued into the mold and after the rubber cement had dried the ends of the mold assembly were taped with autoclaving tape so that the silicone mold and Teflon block could be handled as one unit. The mixture of epoxy resin and curing agent was prepared and poured into the molds in the same manner as for thermal curing. The mold assemblies were then placed into a container and covered. The container was placed into a refrigerator-freezer and left there until the samples were cured. A minimum of 1 hr. in the refrigerator was allowed. This was done to minimize any reactions which would otherwise occur.



Top View

Figure 10. Mold assembly for creating microwave cured specimens with control of temperature.

2.6 Microwave Curing

Microwave curing was carried out in a cylindrical brass cavity with a 7 in. I.D. and transverse brass shorting plates at the base and top of the cylinder. (Figure 11.) A cross sectional view is shown in Figure 12.²⁸ The brass base plate is fastened onto the bottom of the cylinder at a fixed position but can easily be removed to load and unload specimens. The position of the top plate or sliding short can be adjusted up or down by turning a gear outside the cavity. In this way the cavity length can be adjusted.

Microwave energy is introduced into the cavity through an adjustable excitation probe (coupling probe). The probe is coaxial with an outer conductor diameter of 1.27 cm and an inner conductor diameter of 0.442 cm. The center of the coax is 3.81 cm above the base plate. The coupling probe can be moved into or out of the cavity by turning a gear outside the cavity. Adjustment of the sliding short and coupling probe are necessary to maintain the TE_{111} microwave mode. A depiction of the TE_{111} mode can be seen in Figure 13.^{29,30}

Microwave power is generated with a magnetron based generator (Opthos MPG-4) having a power output range from 0 to 120 Watts at a fixed frequency of 2.45 GHz. In order to protect the source, a circulator is used to channel any reflected power to a dummy load. The microwave power is transmitted down cables with an impedance of 50 Ohms. A



Figure 11. Cylindrical brass cavity for microwave curing.



(3) end plate, coaxial input diagnostic 10) holes, (11) microcoax electric field probe, (12) threaded bolts. (2) sliding short process material, (6) screened viewing port, port, (8) adjustable coupling probe, (9) brass microcoax probe holder, Cross sectional view of the cylindrical brass cavity. The numbered parts are: (1) conducting cylindrical shell, (4) silver finger stock, (5) process material, (6) screene



Figure 13. Depiction of the ${\rm TE}_{111}$ microwave mode. $^{29,\,30}$

make-before-break switch is used to allow switching the microwave energy between the microwave cavity and a dummy load. This type of switch is used to prevent arcing during the switching process. (Figure 14.) A bi-directional coupler is placed between the switch and the microwave cavity in order to allow readings of the input and reflected power to be taken using power meters.

After the specimens had been refrigerated for at least one hour, a single specimen was taken to the microwave cavity. The base plate was removed from the cavity and a fluor-optic temperature probe tip was inserted through a hole at the proper position in the base plate. The fluoroptic temperature probe tip was then inserted up through the hole in the Teflon block of the specimen assembly into the quartz capillary until the tip of the temperature probe touched the fused end of the capillary. The specimen assembly was placed onto the base plate so that the specimen would be in alignment with the coupling probe and the base plate was reattached to the cavity.

The microwave power (2.45 GHz) was then turned on and set at a power level of 9.5 Watts. In order to find the TE_{111} mode, the sliding short was moved to an approximate height where the mode was known to occur. Both the height of the sliding short and the length of the coupling probe were then adjusted simultaneously until the reflected power reached a minimum. A power supply controlling the switch was turned on, causing the microwave switch to reroute the



Figure 14. Circuit Diagram of Microwave Curing System with Computer Control of Specimen Temperature. microwave power to a dummy load. The preceding steps were done as quickly as possible in order to minimize the amount of heating in the specimen. The curing cycle was then ready to begin.

The curing process was controlled using a personal computer with dedicated control software written at Michigan State University.³¹ This software continuously monitors the temperature as measured by a fluor-optic temperature sensing system (Luxtron Model 750) as well as input and reflected power as measured by separate power meters. Control of the switch is based on specimen temperature. If the specimen tab temperature exceeds the prespecified limit of 170°C (140°C gauge section temperature), an electrical signal is sent from the computer to a relay which causes a power supply to come on. This results in the switch sending the microwave power to a dummy load. If the specimen temperature is below the temperature limit, no signal is sent from the computer and the microwave power is sent to the microwave cavity.

The control program is used to start the curing cycle from the computer keyboard. When this is done, an electrical signal being sent from the computer to the relay stops and the microwave power is rerouted from a dummy load to the microwave cavity. At this point the specimen begins heating as the energy from the microwave electric field is transferred into thermal motion of the molecules in the epoxy resin. The silicone mold also contributes to the

heating process by turning some of the microwave energy into thermal energy. As the specimen heats, the dielectric properties of the curing epoxy change which results in the loss of the TE_{111} mode. This is observed as an increase in the reflected power from the cavity. The mode is restored by simultaneous adjustment of the height of the sliding short and the length of the coupling probe until the reflected power is again minimized. This process continues throughout the curing cycle.

When the gauge section temperature of the specimen reaches 140°C, the microwave power is switched to a dummy load. The temperature of the specimen may continue to rise for a few seconds due to exothermic reactions which are occurring in the curing epoxy and a small time lag for heat conduction to the fluoroptic sensor. However the temperature soon begins to fall as heat is convected away and no microwave energy is present to cause the generation of heat. When the gauge section temperature drops below the limit of 140°C, the microwave power is switched back to the microwave cavity so that sample heating can resume. Aqain there is a lag in the response of the specimen temperature. This time the lag is due to the fact that heat must also be supplied to the mold assembly which has also cooled and again a small amount of time is required for heat conduction to the fluoroptic sensor. When the sample temperature increases back to the preset limit, the microwave power is again switched back to the dummy load and the process begins

again.

This process of switching the microwave power between the microwave cavity and a dummy load is continued throughout the rest of the curing cycle so that the specimen gauge section temperature is maintained as close to 140°C as possible. When the curing is complete at 12.5 minutes the power is automatically switched to a dummy load and no more data is taken by the control software. The microwave generator can then be turned off and the fully cured specimen can be removed from the microwave cavity. Any extra material is removed from the specimen, and it is polished and placed in a desiccator until it is tested. The cycle chosen has been optimized for properties and not speed.

2.7 Single Fiber Critical Length Test

This test was used for determining the interfacial shear strength in specimens containing bare E-glass fibers which were both thermally and microwave cured. Specimens were examined under a microscope for any defects such as bubbles or foreign particles in the epoxy, flaws in the fiber, or multiple fibers. Any specimen containing such defects was not tested. Specimens which passed visual inspection were then fastened into a tensile testing fixture which was mounted on a microscope (Olympus BH-2). At this point a dial on the tensile testing fixture was

adjusted to remove any looseness between the specimen and the clamps on the fixture. A dial gauge which was used to give a relative measure of the amount of strain on the specimen was set to zero.

The strain on the specimen was increased slowly while viewing the fiber under the microscope. When fiber breaks were noticed, the number of breaks and the corresponding reading on the dial gauge were noted. The strain was then increased in small increments, and the number of fiber breaks noted after each incremental increase. This process continued until the number of fiber breaks remained the same after three successive incremental increases in the strain on the specimen. Photomicrographs were taken of the fiber failure mechanism and the birefringence pattern before the strain on the sample was decreased back to zero.

The lengths of the fragments were measured using a filar eyepiece on the microscope and an actuator attached to the tensile testing fixture. With this setup, the length of each fiber fragment could be measured by moving the fixture with the actuator from fiber break to fiber break as seen through the microscope. The distance between fiber breaks was noted from a readout on the actuator controller.

The fiber diameters were also measured under the microscope. A video camera attached to the microscope was used to send the image of the fiber to a video monitor which had been configured for measuring fiber diameters. The fiber diameter was then measured at three different

locations along its length and the three values were averaged to obtain an overall fiber diameter. The data gained could then be used to determine the interfacial shear strength after the fiber fragment length measurements were fit to a Weibull distribution. A Weibull distribution was used to account for imperfections in the fiber.

2.8 Interfacial Testing System (ITS) Test

This test was used for determining the relative interfacial shear strength in specimens which were both thermally and microwave cured containing silane coated Eglass or commercially sized E-glass fibers. The ITS test was used for specimens containing these fibers because specimen failure occurred before the critical length was reached in the single fiber critical length test. In other words, the fiber-matrix IFSS was greater than the tensile strength of the specimen. In preparation for this test, single fiber specimens were cut twice in the gauge length of the specimen to form three segments. These segments were cut carefully with a diamond saw to be sure that no heat buildup occurred which could affect the properties of the interphase. The end of each segment which had been in the gauge length was sanded smooth. This was the end which would eventually be tested. The segments were then cleaned of any debris or surface deposits.

The segments were mounted in room temperature curing

polyester mounting media using the following procedure. One open end of a small phenolic ring (1 in. ID) was taped over with autoclaving tape. The specimen segments were then taken one at a time and placed sanded end down onto the sticky surface of the tape inside the ring. After filling the outer 1/4 in. of the ring with sample segments, the ring was filled with a polyester resin and hardener and allowed to cure.

Once the polyester had hardened, the ITS specimens were polished. The first five polishing steps were done on a Struers Abramin polisher followed by two steps on a Leco rotary polisher. The final step was done on a Beuhler Vibromet I vibrating lap polisher. The polishing procedure which was used is shown in Table 4. The polished specimens were then put into a desiccator and left there until they were tested.

The interfacial testing system (ITS) (Figure 15.) used to measure the interfacial shear stress at fiber debond in composite samples is configured as follows. A Mitutoyo Metallographic FS100 microscope with a stage which has been modified to contain three Klinger linear motion stages. The linear motion stages provide X, Y, and Z translation with a 1 μ m resolution in the X and Y directions and 0.04 μ m resolution in the Z direction. A Sartorius L610 weighing mechanism is mounted on top of the linear motion stages and a specimen holder is mounted on top of the weighing mechanism.

Table 4. ITS specimen polishing proceedure.

Abrasive	Lubricant	Duration (min)
240 grit silicon carbide	Water	Until flat
320 grit silicon carbide	Water	0.5
1000 mesh silicon carbide	Water	2
2400 mesh silicon carbide	Water	3
3200 mesh silicon carbide	Water	4
1 μ m aluminum oxide	Water	4
0.5 μ m aluminum oxide	Water	4
1 μ m diamond	Oil	240



Figure 15. Interfacial testing system. A diamond tipped micro-indenter is mounted on a collar on the objective lens of the microscope. The profile of the indenter is a 90° cone with an included tip radius of 10 μ m. A Zenith 386 20 MHz microcomputer is interfaced to the stage motion controllers and the weighing mechanism so that the system can be controlled through computer software. A video camera which is attached to the microscope and a monitor are used to observe and select fibers.

An actual test is performed as follows. Initially the sample is scanned by alternately adjusting the X and Y stage controllers and viewing the specimen surface on the monitor. After a fiber end is located, the fiber diameter is measured by stepping either the X or Y stage controller across the fiber and counting the 1 μ m steps. This is viewed as the fiber moving under a locating point on the monitor. After the fiber diameter is noted, the fiber is moved so that the locating point is above the matrix to the lower left of the fiber. The coordinates of the X and Y stage controllers are then set to zero. The coordinate of the Z axis is also adjusted if necessary so that the indenter will be an acceptable distance from the specimen surface when the test begins.

The X and Y stage controllers are adjusted until the center of the fiber is under the locating point on the monitor. This position is the point where the indenter will eventually make contact with the specimen. The coordinates of this point are recorded directly to the computer. At

this time, data identifying the fiber and test are entered into the computer. This data includes the fiber type and sizing, fiber diameter, fiber tensile modulus, shear modulus of the matrix, and distance of the fiber from its nearest neighboring fiber.

The test is started from the computer keyboard. First the stage is moved by the X and Y stage controllers until the fiber end is directly under the indenter tip. The Z stage controller then moves the specimen surface to a distance approximately 4 μ m from the indenter tip. At this point the Z-stage approach rate is slowed to 6 steps per second with a step size of 0.04 μ m per step. When the indenter tip contacts the surface of the fiber, the computer software begins to take data. The readout on the weighing device is monitored so that the loading process can be stopped safely below the start of debonding of the fiber. This is determined from previous tests. When loading is stopped, the Z axis and then the X and Y axes are returned to their initial positions so that the fiber end is under the locating point on the monitor. The location of the indent as well as the condition of the fiber-matrix interface are noted. If necessary, corrections to the X and/or Y axis positions are made so that the indenter tip will contact the fiber surface at the center of the fiber.

The test is continued in increments of approximately 2 grams of increase in load. Between each increase in load, the fiber-matrix interface is observed. Eventually when the

load becomes great enough, an interfacial crack begins to form. This is seen as a darkening at the fiber-matrix interface. The test is continued and when the interfacial crack continuously covers 1/4 to 1/3 the circumference (90 -120°), the fiber is said to have debonded from the matrix. The interfacial shear stress at debond is calculated using the load at which the fiber debonded along with the fiber and matrix data which was entered.

2.9 SEM Sample Preparation and Analysis of Fracture Surfaces

Electron micrographs of the whole fracture surfaces and fiber fracture surfaces were taken for specimens containing each fiber type which were microwave cured and conventionally thermally cured. The fracture surfaces of the specimens were coated with a gold film using a Polaron sputter coating system. A 200 Å thick film was deposited on the fracture surfaces to prepare them for viewing in the scanning electron microscope (SEM). A JEOL SEM was used to examine and take micrographs of the fracture surfaces.

RESULTS AND DISCUSSION

3.1 Determination of Microwave Curing Cycle

A microwave curing cycle was determined which would result in specimens with approximately the same mechanical properties as those of thermally cured specimens. This was done by varying the microwave curing time at a microwave power of 9.5 Watts and a frequency of 2.45 GHz. The tensile modulus and tensile strength of the microwave cured specimens were then compared to the same properties of conventionally thermally cured specimens which had been cured for 2 hrs. @ 75°C followed by 2 hrs. @ 125°C. Fibermatrix interfacial shear strength has been shown to be dependent on the modulus of the matrix.⁸ Matching the tensile modulus was given a higher priority than matching the tensile strength since tensile strength is highly sensitive to the slight variations in specimen condition which are unavoidable. Table 5 contains the mechanical properties used in this comparison.

The microwave curing cycle chosen was 12.5 minutes at 9.5 Watts and a frequency of 2.45 GHz with temperature control monitored by a fluoroptic sensor. This curing cycle was determined to result in specimens with the best

Table 5. Mechanical properties of epoxy for thermal curing cycle and various microwave curing cycles. (All values in MPa)

	Tensile Strength Mean (S.D.)	Tensile Modulus Mean (S.D.)
Thermal Curing 2 hrs @ 75°C + 2 hrs @ 125°C	86.5 (0.3)	1530 (15)
Microwave Curing 10 min 12.5 min 15 min 17.5 min 20 min	(2.45 GHz and 9.5 W - M 72.2 (14.8) 82.9 (8.4) 86.4 (1.8) 84.3 (2.3) 84.0 (5.7)	ax. Temp. 140°C) 1480 (57) 1470 (68) 1450 (100) 1410 (42) 1400 (39)

These values are used only for comparison in this study.

approximation to the tensile modulus and tensile strength of thermally cured specimens while not risking undercuring the corners of the specimens. Faster curing cycles are possible but their development was not the focus of this work.

The temperature profile for the gauge section of a specimen which is being microwave cured is shown in Figure 16. The dielectric properties of the curing specimen change throughout the curing process. Initially the heating rate is high because the dipoles are free to rotate with the electric field due to the fact that mainly monomer and curing agent are present. At approximately 120°C, the exothermic polymerization reactions begin. This results in an even higher heating rate as there are now two sources of heat generation inside the specimen.

When the temperature reaches the control point, temperature control begins. The microwave power is then switched between the microwave cavity and a dummy load in order to maintain a constant gauge section temperature of 140°C. Without temperature control, the gauge section temperature would continue to increase to nearly 200°C. This would result in the curing reactions taking place too quickly and in thermal degradation of the epoxy which would translate into less desirable mechanical properties. Therefore, temperature control is necessary to prevent this from occurring. Because of the differences in the heating process between microwave curing and conventional thermal curing, the tensile modulus of the specimens processed using



Figure 16. Temperature profile for gauge section in microwave curing.

both methods were matched.

3.2 Bare E-Glass Fiber

The interfacial shear strength (IFSS) data for single fiber specimens containing E-glass fibers are presented in Table 6. The IFSS data were obtained from single fiber critical length tests. The data show that the IFSS of microwave cured specimens is approximately 12% greater than the IFSS of conventionally thermally cured specimens (63.3 MPa v. 56.5 MPa). There is a 99% confidence level that this difference is significant. However there was interfacial debonding along the fiber-matrix interface. This indicates that there was a moderate level of fiber-matrix adhesion.

The failure mechanisms for specimens containing bare Eglass fibers which were cured with both methods are shown in Figure 17. The micrographs show that the failure mechanism for thermally cured specimens is fiber-matrix debonding. This indicates a moderate level of fiber-matrix adhesion. For microwave cured specimens, a combination of fiber-matrix debonding and matrix failure occurs. Matrix failure occurs in the form of a matrix crack perpendicular to the fiber axis. The fact that matrix failure occurred indicates that there was a higher level of fiber-matrix adhesion for the microwave cured specimens or that the polymer in the interphase cured by microwaves is more brittle than for thermally cured specimens. These results support the IFSS
Table 6.				
Bare E-Glass				
Single	Fiber	Critical	Length	Test.

	Thermal Cure	Microwave Cure
Total Fragments	398	458
Fiber Tensile Strength (MPa)	2340	2340
Mean IFSS (MPa)	56.5	63.3
S. D. (MPa)	3.3	1.2
<pre>% Increase in IFSS fi</pre>	rom Thermal to Microwa	ve Curing = 12.0
Confidence Level that 99%	Difference in IFSS i	s Significant =

b.) Microwave Curing

Figure 17. Transmitted light micrographs of failure mechanisms for specimens containing a bare E-glass fiber. ł



data obtained.

The electron micrographs of a fiber break shown in Figure 18 were taken using a scanning electron microscope (SEM). The micrographs clearly show that fiber-matrix debonding occurred. For the thermally cured specimen, the fiber protrudes from the matrix failure surface. The fiber failure surface of the microwave cured specimen, however, is recessed below the matrix failure surface. Both failure surfaces are equally probable and are characteristic of fiber fracture followed by interfacial failure. The electron micrograph for the thermally cured specimen shows that very little matrix material adhered to the surface of the fiber shaft. The information obtained using the SEM shows that there was a moderate level of fiber-matrix adhesion for specimens cured using both techniques.

A possible reason for this could be that microwave curing is a much faster process and causes different molecular motions than thermal curing. The different molecular motions in microwave curing are caused by the dipoles continually trying to follow the oscillating electric field. The result of this may be the formation of an interphase with polymer molecules having different network structures and properties. In fact, previous work has shown that a higher T_g occurs in microwave processed epoxy samples.²⁹ Also, surface dipoles (-OH) on the glass fiber could preferentially react with the matrix material in microwave curing. This would cause a different level of

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b.) Microwave Curing

Figure 18. Scanning electron micrographs of a fiber failure surface for specimens containing a bare E-glass fiber.





interaction between the fiber and the polymer molecules at the interface.

3.3 Commercially Sized E-Glass

Commercially sized E-glass fibers were tested to determine the effect of microwave curing on polar groups contained in the sizing. Polar groups are known to occur in significant numbers in the silane component of commercial sizings. As a result, determining the effect of microwave curing on this component of the commercial size was of particular interest. The typical composition of a glass fiber size is shown in Table 1.¹¹ Table 7 contains IFSS data for single fiber specimens containing commercially sized E-glass fibers. These data were obtained using the interfacial testing system. The data show that the IFSS values for microwave cured specimens (85.0 MPa) are about 27% higher than those for thermally cured specimens (66.8 MPa). There is a 98% confidence level that the difference is significant.

Figure 19 shows the fiber failure mechanism of the specimens containing these fibers which were microwave cured. Specimen failure occurred before a micrograph could be taken for the thermally cured specimens. Failure is a combination of matrix cracking and matrix failure by shear. Matrix failure by shear can be seen as a matrix crack at 45° to the fiber axis. This combination indicates that the

	Thermal Cure	Microwave Cure	
# of Tests	10	10	
Mean IFSS (MPa)	66.8	85.0	
S. D. (MPa)	12.1	20.6	
<pre>% Increase in IFSS from Thermal to Microwave Curing = 27.4 Confidence Level that Difference in IFSS is Significant = 98 % Tensile Modulus of E-Glass Fiber = 72400 MPa</pre>			
Shear Modulus of Epos	xy = 1200.3 MPa	o mea	

Tab.	le 7.	
Commercially	sized	E-Glass
ITS	Test.	



Figure 19. Transmitted light micrograph of failure mechanism for microwave cured specimens containing a commercially sized Eglass fiber. interphase is more brittle and higher in modulus than for specimens containing the bare E-glass fibers. It also indicates that there is a much higher level of fiber-matrix adhesion for the commercially sized fibers than for the bare fibers. This supports the IFSS data obtained.

The fracture surfaces of specimens containing a single commercially sized E-glass fiber which were cured using both methods are shown in Figure 20. The fracture surface of the microwave cured specimens has a different appearance than that of thermally cured specimens. In fact, the radius of the mirror zone of the fracture surface of the microwave cured specimens is nearly twice the radius of that in thermally cured specimens.

Scanning electron micrographs of the fiber failure surfaces for specimens cured using both techniques are shown in Figure 21. The fiber failure surface is featureless and approximately flush with the matrix failure surface for the thermally cured specimen. The fiber failure surface for the microwave cured specimen has undergone extensive deformation compared to the thermally cured specimen. Neither specimen displays any significant fiber-matrix debonding as compared to specimens containing bare E-glass fibers.

Microwave curing has again resulted in a higher level of adhesion than thermal curing. In this case, an increased absorption of energy in the interphase due to the increased number of polar groups in the sizing over that in the bulk matrix may be partially responsible for the increase in

b.) Microwave Curing

Figure 20. Reflected light micrographs of fracture surfaces for specimens containing a commercially sized E-glass fiber.



i L

b.) Microwave Curing

Figure 21. Scanning electron micrographs of the fiber failure surface for specimens containing a commercially sized E-glass fiber.



IFSS. This occurs specifically in the interphase because the high concentration of polar molecules would be expected to be much more lossy than the bulk matrix and therefore absorb energy to a greater degree. A typical commercial glass fiber sizing contains 0.1-0.5 percent of a silane sizing. These are believed to be the source of the higher heating rate in the sizing. Differences in network structure of the material near the interface as well as the creation of a stress free interphase may also be part of the cause.

3.4 Silane Sized E-Glass

Pure silane sized E-glass specimens were tested to separate out the effects of microwave curing on the silane from those on the rest of the components in the commercial sizing. These tests were performed in order to determine if the increase in IFSS in the microwave cured specimens containing commercially sized E-glass over those which were thermally cured was attributable to the presence of the silane in the sizing. The IFSS data obtained for specimens containing silane sized E-glass fibers are shown in Table 8. The data show a 10% increase in IFSS for the microwave cured specimens (100.8 MPa) over those which were thermally cured (91.7 MPa). The difference in IFSS values between the microwave cured specimens and the thermally cured specimens is significant with a confidence level of 91%.

3	Tabl	.e 8		
Silane	siz	ed	E-gl	ass
I	TS 1	Tes	t.	

	Thermal Cure	Microwave Cure
# of Tests	10	9
Mean IFSS (MPa)	91.7	100.8
S. D. (MPa)	14.68	12.8
<pre>% Increase in IFSS from Confidence Level that I 91 %</pre>	n Thermal to Microw Difference in IFSS	ave Curing = 10.0 is Significant =
Tensile Modulus of E-G Shear Modulus of Epoxy	lass Fiber = 7241 = 1200.3 MPa	4 MPa

The fiber failure mechanism for a microwave cured specimen containing a silane sized fiber is shown in Figure 22. Specimen failure occurred before a micrograph could be taken for the thermally cured specimens. This shows that fiber fracture is a combination of matrix cracking and matrix failure by shear as in the commercially sized fibers. The matrix crack in the silane sized fiber is smaller than for the commercially sized fiber. This is because specimens containing the silane sized fibers tended to fail on the first fiber break so the fiber failure mechanism shown for the silane sized fiber is at a lower tension than those for the commercially sized fiber.

The fracture surfaces of a specimen containing a silane sized E-glass fiber which was thermally cured is shown in Figure 23. The fracture surfaces of thermally cured specimens are similar in nature to those of the commercially sized specimens with either curing method. The scanning electron micrographs for specimens cured using both methods are shown in Figure 24. The fiber failure surface for the thermally cured specimen is approximately flush with the matrix failure surface. The fiber failure surface for the microwave cured specimen is elevated above the matrix failure surface. A considerable amount of matrix material remained adhering to the surface of the fiber shaft in the microwave cured specimen. The micrographs for specimens cured using both techniques show that a high level of adhesion existed between the fiber and matrix.



Figure 22. Transmitted light micrograph of fiber failure mechanism for microwave cured specimens containing a silane sized E-glass fiber.



Figure 23. Reflected light micrograph of the fracture surface for a conventionally cured specimen containing a silane sized Eglass fiber.

b.) Microwave Curing

Figure 24. Scanning electron micrographs of fiber failure surfaces for specimens containing a silane sized E-glass fiber.





Although the specimens containing silane sized E-glass fibers had higher IFSS values, the relative increase from thermal to microwave curing was not as great as for the specimens containing commercially sized fibers. The increase in IFSS values for specimens containing the commercially sized fibers is over two and one half times as large as that for the specimens containing silane sized fibers. There are two possible effects which may be causing this. First, some component(s) of the commercial size may be interacting with the microwave field in a way that is more effectively increasing the fiber-matrix bonding over that of thermally cured specimens than the silane alone. This interaction may result in a greater rate of heat generation in the interphase, or in a different network structure of the polymer molecules in the interphase. The addition of Z-6020 silane to an epoxy matrix material has been shown to result in an increase in tensile modulus and a decrease in tensile strength.¹⁰ Any of these could result in an increase in IFSS.

Another possible effect is that the thickness of the commercial sizing may simply increase the significance of the effect of the silane it contains. Either an increase in the number of silane molecules or an increase in the dispersion of those molecules could be the cause. In either case, microwave curing has again resulted in an increase in IFSS over that obtained with conventional thermal curing.

3.5 Comparison of IFSS Values

Figure 25 shows normalized comparisons of IFSS values for the microwave cured specimens with values for the thermally cured specimens used as a baseline. The IFSS increased in going from thermal to microwave curing for all three fiber systems. The increase in going from thermal processing to microwave processing was largest (27%) for the commercially sized fiber system. The bare and silane sized fibers had 12% and 10% increases respectively.

Figure 26 shows the absolute value of IFSS for all three fiber systems and both processing methods. The values for the bare E-glass system and the two types of sized Eglass systems can not be compared since different methods were used to determine IFSS. Comparison between specimens containing the pure silane sized fibers and those containing the commercially sized fibers shows that the absolute values of IFSS for the silane sized system are higher. The IFSS values for the thermal and microwave processed pure silane sized system are 92 MPa and 101 MPa respectively while those for the commercially sized system are 67 MPa and 85 MPa respectively. However, it should be noted that the absolute magnitude of the changes in IFSS from thermal to microwave processing is greatest in the commercially sized system at 18 MPa while that for the silane sized system is 9 MPa.









CONCLUSIONS

- The interfacial shear strength of microwave cured specimens for each of the three E-glass fiber systems tested was higher than the IFSS of thermally cured specimens containing the same fiber type.
- The increase in IFSS for specimens containing bare Eglass which were microwave cured over those which were thermally cured may be due to the creation of a different network structure of polymer molecules at the surface of the glass fiber caused by the interaction of hydroxyl (-OH) groups with the matrix in microwave processing.
- Both the commercially sized and the pure silane sized Eglass fibers are, because of the presence of polar molecules, susceptible to the additional effect of an increased absorption of energy. The result of this increased absorption of energy would be a higher local temperature at the fiber sizing interphase during microwave curing. This increased temperature at the fiber sizing interphase has been shown to result in a higher modulus interphase which will translate into higher IFSS values.

• Specimens containing the commercially sized fibers displayed over two and one half times as large an increase in IFSS in going from thermal curing to microwave curing than those containing the pure silane sized fibers. This may be due to components of the commercial sizing interacting more effectively with the microwave field than the silane alone which results in higher IFSS values. The interaction with the microwave field may cause the generation of more heat in the interphase and therefore the creation of a higher modulus interphase. Alternatively, the interaction with the microwave field could have resulted in a different network structure of the polymer molecules near the interface. The much greater thickness of the commercial sizing (~1000Å vs ~5Å) may result in a magnified effect for the commercial sizing.

RECOMMENDATIONS

Additional research should be performed that would give further insight into the effects of microwave processing on fiber-matrix adhesion. First, the loss factor of several of the materials used in these experiments should be measured in order to determine how they affect the heating process in microwave curing. These materials include: the aminofunctional silane used in its polysiloxane form, the pure silane sized E-glass fibers, and the commercially sized E-glass fibers. These materials could be diluted in epoxy and the loss factor measured as a function of temperature for temperatures around 140°C.

Second, IFSS measurements should be made for several types of single fiber specimens which had been thermally cured using a curing cycle of 2 hours at 75°C followed by 2 hours at 140°C. These would include specimens containing bare E-glass fibers, pure silane sized E-glass fibers, and commercially sized E-glass fibers. 140°C is the temperature at which curing took place for the gauge sections of the microwave cured specimens. These IFSS measurements would eliminate questions about the effects of curing at a slightly elevated temperature in microwave curing.

Finally, the properties of epoxy which had been

conventionally thermally cured for 20 minutes at 140°C should be measured. This would approximate the temperature cycle in microwave curing. From these properties, it could be determined which property changes were due to the differences in the temperature cycles and which were due to different curing phenomena present in microwave curing. APPENDIX

```
С
                                         С
  PROGRAM TO CALCULATE WEIBULL PARAMETERS
                                         С
С
С
                                         С
DIMENSION X(800), XLOG(800)
       OPEN(UNIT=5, NAME='DATA.DAT', STATUS='old')
       TYPE*, 'INPUT NUMBER OF DATA POINTS'
       ACCEPT*, N
С
       TYPE*, 'INPUT DATA POINTS'
С
       ACCEPT*, (X(I), I=1, N)
       READ(5, *) (X(I), I=1, N)
C1000
       FORMAT(*)
       DO 10 I=1,N
       XLOG(I) = ALOG(X(I))
10
       CONTINUE
       SUM1=0.0
       DO 20 I=1,N
       SUM1=SUM1+XLOG(I)
20
       CONTINUE
       SUM1=SUM1/N
С
       NEWTON-RAPHSON METHOD FOR FINDING THE ROOT OF AN EQUATION
С
С
       A(I+1)=A(I) -F(A(I))/F'(A(I))
С
       A=0.1
       DO 60 ITERM=1,100
       SUM2=0.0
       SUM3=0.0
       SUM4=0.0
       DO 50 I=1,N
С
С
       SUM2=SUM2+ X(I)**A
С
       SUM3=SUM3+ (X(I)**A)*ALOG(X(I))
       SUM4=SUM4+ (X(I)**A)*(ALOG(X(I))**2)
С
С
       GOLA=XLOG(I)
       PXE=EXP(A*GOLA)
       SUM2=SUM2+PXE
       SUM3=SUM3+PXE*GOLA
       SUM4=SUM4+PXE*GOLA*GOLA
50
       CONTINUE
С
С
       CALCULATEF(A(I))
С
       F=SUM3/SUM2-1./A-SUM1
С
С
       CLCULATE F'(A(I))
С
       FP=(SUM4*SUM2-SUM3*SUM3)/(SUM2*SUM2)+1./(A*A)
```

С С NEW GUESS С AN=A-F/FP IF(ABS(A-AN).LT.1.0E-4) GOTO 70 A=AN CONTINUE 60 TYPE*, 'NO CONVERGENCE' С WRITE(6,2000) C2000 FORMAT ('NO CONVERGENCE') 70 CONTINUE С С CALCULATE OUTPUTS С BETA=0.0 DO 80' I=1,N BETA=BETA+EXP(AN*XLOG(I)) 80 CONTINUE BETA=(BETA/N)**(1./AN)TYPE*, 'ALPHA=', AN, 'BETA=', BETA WRITE(6,3000)AN, BETA С C3000 FORMAT(1X, 'ALPHA=', F10.3, 'BETA=', F10.3) STOP END

LIST OF REFERENCES

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