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PHOTOPOLYMERIZABLE LIQUID ENCAPSULANTS FOR MICROELECTRONIC DEVICES

By

Kiran K. Baikerikar

A DISSERTATION

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

DOCTOR OF PHILOSOPHY

Department of Chemical Engineering

2000

ABSTRACT

PHOTOPOLYMERIZABLE LIQUID ENCAPSULANTS FOR MICROELECTRONIC DEVICES

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Plastic encapsulated microelectronic devices consist of an integrated circuit die that is physically attached to a leadframe, electrically interconnected to input-output leads, and molded in a plastic that is in direct contact with the die, leadframe, and interconnects. The plastic is often referred to as the molding compound or encapsulant, and is used to protect the integrated circuit die (silicon chip) from adverse mechanical, chemical, thermal, and electrical environments. Encapsulation of microelectronic devices is typically accomplished using a transfer molding process in which the molding compound is cured by heat. Most transfer molding processes suffer from significant problems arising from the high operating temperatures and high pressures required to fill the mold. These aspects of the current process can lead to thermal stresses, incomplete mold filling, and wire sweep (flow-induced deformation of the wires that interconnect the silicon chip to the leadframe during molding). As the size of the encapsulant and the associated wires shrink to smaller and smaller dimensions, so does the operating window for transfer molding; hence, it is difficult to control wire sweep in the high pin count, fine These problems lead to productivity decreases due to increased pitch packages. packaging-related rejects.

In this research, a new strategy for encapsulating microelectronic devices using photopolymerizable liquid encapsulants (PLEs) has been investigated. These highly filled PLEs consist of an epoxy novolac-based vinyl ester resin (~25 wt.%), fused silica (70-74 wt.%), and small amounts of a photoinitiator, thermal initiator, and silane coupling agent. For these encapsulants, the use of light rather than heat to initiate the polymerization allows precise control over when the reaction starts, and therefore completely decouples the mold filling and the cure. The relatively low viscosity of the PLE allows low operating pressures and minimizes problems associated with wire sweep. Because photoinitiation allows active centers to be formed rapidly at room temperature, the in-mold cure time for the PLEs is no longer than the in-mold cure times of current transfer molding compounds.

In this thesis, an extensive series of studies on the thermal and mechanical properties, as well as the viscosity and adhesion of photopolymerizable liquid encapsulants, are reported in order to demonstrate that a UV-curable formulation can, indeed, have the necessary material properties required for microelectronic encapsulation. Specifically, the viscosity, flexural strength and modulus, coefficient of thermal expansion, glass transition temperature, thermal stress parameter, thermal conductivity, thermal diffusivity, specific heat, and adhesive peel strength of the PLEs have been characterized. In addition, the effects of the illumination time, postcure time, fused silica loading, and the inclusion of a thermal initiator on the thermal and mechanical properties of the FLEs are the same, if not better, than those exhibited by conventional transfer molding compounds and demonstrate the potential of using PLEs for encapsulating microelectronic devices.

ACKNOWLEDGMENTS

I would like to thank, first and foremost, Dr. Alec Scranton for serving as my graduate advisor throughout this project. I have really enjoyed working on this research project and am grateful to Dr. Scranton for giving me the opportunity to work in the areas of photopolymerization and microelectronic encapsulation. I would also like to thank the members of my doctoral committee, Dr. Martin Hawley, Dr. Robert Ofoli, and Dr. Jack Giacin for their guidance and helpful suggestions. I would like to thank Mike Rich for training me in the polymer composites laboratory and for always taking the time to answer any questions that I had about thermal and mechanical testing. In addition, I would like to thank Dr. Richard Schalek for his help and guidance in using the environmental scanning electron microscope.

I would like to thank the current and former graduate students in Dr. Scranton's research group whom I had the pleasure of working with over the years, including Bernhard Drescher, Julie Jessop, Arvind Mathur, Vijaykumar Narayanan, Khanh Nguyen, and Katy Padon. These friends were always quick to help someone out and I appreciate the help that they often gave me.

I would also like to thank my loving parents, Dr. Kamalakar and Vijaya Baikerikar, for always encouraging me and giving me their undivided support. My parents always sacrificed for me and instilled in me the power of hard work and dedication. I would not be where I am today without their guidance, and for that, I am eternally grateful. Finally, I would like to express my appreciation for the person that I am most fortunate to share my life with, my wonderful wife, Naina. She has never shied away from offering me encouragement and support when I most needed it. I am lucky to be with her and am forever grateful for her compassion and unconditional love.

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Chapter 1

INTRODUCTION

1.1. OVERVIEW AND IMPORTANCE OF MICROELECTRONIC ENCAPSULATION

The microelectronics, communication, and computer industries have undergone a major shift from highly sophisticated and expensive mainframe systems to small-scale systems, such as personal computers and communication devices. This trend arises from the continuous push for the integration of many functions on a single chip. Very large scale integration (VLSI) and ultra large scale integration (ULSI) ultimately are made possible by the ability to fabricate devices with smaller and smaller feature sizes.

As the feature sizes on a semiconductor chip are reduced, the probability of contamination or damage (by scratching, handling, corrosion, *etc.*) is dramatically increased, and consequently there is a drastic reduction in the yield of the process.¹⁻³ For this reason, silicon chips are encapsulated in a plastic or ceramic package to protect the chip from adverse mechanical, chemical, electrical, and thermal environments. Another consequence of the increasingly large integration of features on a chip is the use of smaller and finer wires to electrically connect the semiconductor chip to the leadframe. During the encapsulation of microelectronic devices by the transfer molding process, these extremely fine wires are subjected to flow stresses from the molding compound and may be deformed or displaced (a phenomenon known as wire sweep). If the deformation of a bonding wire during encapsulation is sufficiently large, it may cause a short circuit (due to adjacent wires touching) or an open circuit (due to wires breaking).⁴ If this happens, the device cannot be repaired and must be discarded. Thus, minimizing wire

sweep during encapsulation is of prime importance, and is becoming more critical due to the use of an increasing number of wires in microelectronic packaging.

The process of chip encapsulation is particularly important since the chip has already undergone numerous processing steps and is just a few steps away from being a finished product (and thus has considerable value that is lost if the encapsulation step fails). With the currently used transfer molding process, it is very difficult to control the problem of wire sweep in a high pin count, fine pitch package. New trends in die design and packaging pose an increasing challenge to the wire sweep problem.^{2,3} Indeed, due to the continuing advances in device capabilities and rapid changes in circuit board assembly methods, the packaging and encapsulation steps are more important than ever before, and may, for the first time, impose limits on the design and performance of the final microelectronic device.⁵

Microelectronic devices are typically encapsulated in a protective thermoset body from which a number of leads extend to allow electrical contact and interconnection between the encapsulated semiconductor device and a printed circuit board. Encapsulation of microelectronic devices has traditionally been accomplished using a transfer molding process. In this process, the thermoset molding compound (typically a solid epoxy preform) is dielectrically preheated and then placed into the pot of the molding tool. A transfer cylinder, or plunger, is used to push the molding compound into the runner system and gates of the mold.⁵ The molding compound then flows over the chips, wirebonds, and leadframes, encapsulating the entire assembly.

Most transfer molding processes suffer from significant problems arising from high operating temperatures (the molding compound is a solid at room temperature) and

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high pressures required to fill the mold (even in the melt state, the molding compound has a high viscosity, and the viscosity increases further with reaction). These aspects of the current process can lead to incomplete mold filling, thermal stresses (since the reaction temperature is much higher than the final use temperature), and wire sweep. Therefore, current transfer molding processes are plagued by two important problems: i) wire sweep due to the high initial melt viscosity, and ii) inadequate time to fill the mold due to rapid cure (concurrent with mold-filling) at the elevated operating temperatures. As the package sizes and the associated wires shrink to smaller and smaller dimensions, so does the operating window for transfer molding; hence, it is difficult to control wire sweep in the high pin count, fine pitch packages. In turn, these problems lead to decreases in productivity for the new fine pitch microelectronic devices due to increased packagingrelated rejects.

1.2. SCOPE AND AIM OF RESEARCH

In this research, we are investigating a new strategy for microelectronic encapsulation using photopolymerizable liquid encapsulants (PLEs). These highly filled PLEs consist of an epoxy novolac-based vinyl ester resin (~25 wt.%), fused silica (70-74 wt.%), and small amounts of a photoinitiator, thermal initiator, and silane coupling agent. For these encapsulants, the use of light rather than heat to initiate the polymerization allows precise control over when the reaction starts, and therefore completely decouples the mold filling and the cure. The relatively low viscosity of the PLE allows low operating pressures and minimizes problems associated with wire sweep. Because photoinitiation allows active centers to be formed rapidly at room temperature, the inmold cure time for the PLEs is no longer than the in-mold cure times of current transfer molding compounds.

In recent years, a number of investigators (including our research group) have demonstrated the feasibility of photopolymerizing thick polymers and composites.^{6,7} In addition, Hanneman *et al.* recently demonstrated the feasibility of using photopolymerizations to produce molded acrylate parts.⁸ These authors molded unfilled poly(methylmethacrylate) and found that they could produce high quality parts more than five millimeters thick. Therefore, the potential exists to develop a photomolding process to encapsulate microelectronic devices. Before this can be accomplished, however, a suitable photopolymerizable formulation must be developed which possesses the appropriate material properties that can effectively protect microelectronic devices. This is the main objective of this research project.

In this thesis, an extensive series of studies on the thermal and mechanical properties, as well as the viscosity and adhesion of photopolymerizable liquid encapsulants, are reported in order to demonstrate that a UV-curable formulation can, indeed, have the necessary material properties required for microelectronic encapsulation. Specifically, we have characterized the viscosity, flexural strength and modulus, coefficient of thermal expansion, glass transition temperature, thermal stress parameter, thermal conductivity, thermal diffusivity, specific heat, and adhesive peel strength of PLEs containing 70.0-74.0 wt.% fused silica. In addition, the effects of the illumination time, postcure time, fused silica loading, and the inclusion of a thermal initiator on the thermal and mechanical properties of the final cured encapsulants have been investigated.

1.3. REFERENCES

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Chapter 2

BACKGROUND

2.1. COMPONENTS OF A MICROELECTRONIC DEVICE

The microelectronic device (also known as the plastic package) consists of: (i) a silicon chip, (ii) a metal support or leadframe, (iii) metal wires that electrically interconnect the chip circuits to the leadframe, (iv) an adhesive to physically attach the chip to the leadframe, and (v) the plastic encapsulation material (molding compound) to protect the chip and the wire interconnects, as shown in Figure 2.1:



Figure 2.1. Schematic of a microelectronic device.

The leadframe is the main supporting structure of the device to which every other element is attached. Etched or stamped from a thin metal strip, the leadframe carries the chip throughout the assembly process and is imbedded in plastic after molding. The functional requirements of the leadframe as described by Robock and Nguyen¹ are: (i) a holding fixture that indexes with tool-transfer mechanisms as the package proceeds

through various assembly operations, (ii) a dam that prevents the encapsulation material from rushing out between leads during the transfer molding operation, (iii) chip attach substrate, (iv) support matrix for the encapsulation material, and (v) electrical and thermal conductor from chip to board. Typically, the leadframe is made of Alloy 42 (58% iron, 42% nickel), Alloy 50 (50% iron, 50% nickel), or a copper alloy (Alloy 194, Alloy 151), and is plated with gold and silver or palladium, either completely or in selected areas over nickel or nickel/cobalt.² Selecting the appropriate leadframe material requires the evaluation of a number of issues. For example, the leadframe material plays a significant role in determining the degree of adhesion between the molding compound and the leadframe, the thermomechanical shrinkage stresses, the heat dissipation capacity of the package, and the buckling of the leadframe after molding. All of these issues have direct implications for packaging yield and reliability.³ Alloy 42 is one of the most commonly used leadframe materials because of its low coefficient of thermal expansion (CTE), as well as its resistance to buckling under the compressive loads applied by the molded body (Manzione, 96). The small mismatch in coefficients of thermal expansion between Alloy 42 (CTE = 4.5 x 10^{-6} °C⁻¹) and the silicon chip (CTE = 2.6 x 10^{-6} °C⁻¹) results in lower thermomechanical shrinkage stresses. In addition, Alloy 42 exhibits a higher degree of adhesion to molding compounds because it does not form a passivating oxide film as easily as the copper alloys.³ However, its main drawback is its low thermal conductivity, which limits the amount of heat dissipated from the chip to the printed circuit board.

Because of their higher coefficients of thermal expansion, copper alloys (CTE = $16 \times 10^{-6} \text{ °C}^{-1}$) will have larger thermomechanical shrinkage stresses. However, they do

have much higher thermal conductivities than other alloys and this is the principal reason for their use. Heat conduction along the leadframe is an important heat dissipation mechanism in microelectronic devices and the higher thermal conductivity of copper alloys makes them an attractive choice for high-power devices.³

The silicon chip is usually mounted to the leadframe with what is known as a die attach adhesive. Previously, solders were used to mechanically attach the chip to the leadframe, but now these are being displaced by conductive polymer adhesives because they are less expensive and their application is more easily automated.³ Presently, solventless conductive epoxies filled with silver flakes are the most widely used die attach adhesive. To electrically connect the bonding pads of the die with the leads of the frame, gold, aluminum, or even copper wires are used. For gold wires, the typical diameters are 0.0025 to 0.0032 cm, while for aluminum, they are up to 0.005 cm.³

2.2. COMPONENTS OF THE ENCAPSULATION MATERIAL

Encapsulation materials are usually proprietary mixtures of at least eight categories of raw materials, including the epoxy resin, curing agent (hardener), accelerator (catalyst), filler, coupling agent, flame retardant, mold release agent, and colorant.^{1,3}

2.2.1. Epoxy Resin

The epoxy resin is commonly a cresol-novolac epoxy and is the base upon which the encapsulation material is built, accounting for 25 to 30 wt.% of the formulation. As Robock and Nguyen¹ explain, "It is the organic binder that, when cured, holds all the constituents together and imparts the inherent characteristics of high T_g : shrinkage on cure, low moisture absorption, and chemical inertness to the plastic package". The excellent high temperature properties of epoxy novolacs are the primary reason they have replaced the bisphenol epoxies, phenolics, and silicones as the major compound used for integrated circuit packaging.

2.2.2. Curing Agent

Curing agents or hardeners such as phenols, amines, and acid anhydrides are used to crosslink the epoxy resins. Depending on the type of resin and hardener in the formulation, the concentration of hardener can range from as low as 1 part of hardener per 100 parts of resin (1 phr) to 100 phr.¹ Currently, phenol novolac and cresol novolac hardeners are the most widely used because of their excellent moldability, electrical properties, and heat and humidity resistance.³

2.2.3. Accelerator

Accelerators act as catalysts to accelerate crosslinking of the epoxy when heat and pressure are applied in the molding process, thus reducing in-mold cure times and improving productivity.^{1,3} They also tend to affect the electrical properties and humidity resistance of the cured molding compound. Accelerators that are usually used include amines, imidazoles, organophosphines, urea derivatives, and Lewis bases and their organic salts.⁴ The problem with accelerators is that their reactions are initiated at comparatively low temperatures, thus deteriorating the moldability or pot life of the molding compound.⁴ Therefore, accelerators that promote rapid curing of resins when heated to a certain temperature, without promoting curing at lower temperatures, are preferred. This is why organophosphine compounds and Lewis base salts are widely used in epoxy molding compounds.

2.2.4. Filler

Epoxy resins, curing agents, and accelerators alone cannot be used for packaging microelectronic devices, because these materials do not yield optimal material properties to the final encapsulant. For this reason, inert materials called fillers are used. The inclusion of fillers in the encapsulation material offers a number of benefits, most notably, lower coefficient of thermal expansion, increased thermal conductivity, improved mechanical properties, and prevention of excessive resin bleed at the parting line of the molding tool.³ In order to obtain these advantages, fillers are added in large amounts, anywhere from 70 to 80 wt.%. Fillers that have been used in epoxy molding compounds include fused silica, crystalline silica, aluminum oxide, and aluminum nitride, with fused silica being the most commonly used. The widespread use of fused silica is due to its very low coefficient of thermal expansion (CTE = $0.5-0.6 \times 10^{-6} \text{ °C}^{-1}$) and its low abrasiveness, which provides a reasonable molding tool lifetime.³ However, the primary drawback of fused silica is its low thermal conductivity (1.5 W/m-K) and this is the reason high thermal conductivity fillers such as crystalline silica (3.0 W/m•K), aluminum oxide (42.0 W/m·K), and aluminum nitride (150-220 W/m·K) are finding more use.⁵ High thermal conductivity fillers are required as a cost-effective means of removing heat from plastic packages. Besides selecting the appropriate filler, the proper selection of the filler particle size and distribution also plays a key role in determining the encapsulation material's properties. Typically, fused silica particles are irregularly shaped flakes that range in size from 10 to 25 microns, but the size distribution can be wide with some particles reaching 125 microns.³ This can present a problem because the large particles can become trapped in the gates (a gate admits the molding compound into

the cavity of the device to be molded) which can be as thin as 150 microns or caught between the leads of packages where the interlead spacing is 100 microns.³ Usually, a blend of small particles of different size distributions is used in order to maximize filler loadings, without a substantial increase in viscosity. This is one of the main reasons for the use of spherical particles, which are used in conjunction with flakes.

2.2.5. Coupling Agent

The purpose of coupling agents is to bind the polymer matrix and the inorganic filler in order to improve the physical properties and maximize the filler-to-polymer ratio. Coupling agents used for molding compounds include silanes, aluminum chelates, titanates, and zircoaluminates, with silanes being the most commonly used coupling agent. Silanes are organofunctional compounds that act as molecular bridges at the interface between the polymer matrix and the filler particle surfaces of the composites. They are linear molecules which have a reactive group at one end capable of being incorporated into the matrix of a curing polymer and a silicon-based group at the other end which bonds to inorganic fillers. Benefits of silanes include reduced viscosity of the molding compound, improved processability, better coating adhesion to substrates, improved humidity and heat resistance, and improved mechanical and electrical properties.

2.2.6. Flame Retardant

Epoxy materials are not inherently flame retardant, so flame retardancy is required for epoxy molding compounds to insure safety. Product safety requirements for plastic packages used in electronic equipment specify an Underwriter's Lab flame retardant ratio of 94V-O. This can be achieved only by the addition of flame retardants such as tetrabromobisphenol-A and antimony trioxide to the molding compound.¹

2.2.7. Mold Release Agent

Because of the excellent adhesion of epoxies to all types of surfaces, mold release agents are used to ease the release of the cured encapsulants from compounding and molding equipment. The most commonly used mold release agents for epoxy molding compounds include hydrocarbon waxes, silicones, metallic salts of organic acids, and fluorocarbons. Of these, hydrocarbon waxes, such as carnauba wax, are the most widely used mold release agents for microelectronic encapsulation.²

2.2.8. Coloring Agent

Coloring agents are used primarily for aesthetic purposes, since the filled molding compound without any coloring agent is a translucent yellow.² They are also used to distinguish different device types in packages. Carbon black is the predominant coloring agent for plastic packaging of microelectronic devices, even though it degrades the moisture resistance and slightly increases the electrical conductivity of the molding compound. For this reason, it is used in concentrations less than 0.5%.

2.3. MATERIAL PROPERTIES USED TO EVALUATE ENCAPSULATION MATERIALS

An encapsulant is an electrically insulating, plastic material that protects an electric or electronic component from adverse mechanical, chemical, electrical, and thermal environments. Therefore, materials used for this application must deliver a balanced combination of properties in the areas of viscosity, mechanical strength and toughness, chemical resistance, electric and dielectric insulating performance, thermal

conductivity, adhesion, and thermal and moisture stability in the general temperature range of -65 to 200°C.⁶ Some of the more important material properties used to evaluate encapsulation materials are described in more detail below.

2.3.1. Viscosity

The microelectronic encapsulation process requires a low viscosity of the molding compound so it can flow into the mold with minimum deformation of the leadframe and wirebonds.² During the encapsulation of microelectronic devices by the transfer molding process, these extremely fine wires are subjected to flow stresses from the molding compound and may be deformed or displaced (a phenomenon known as wire sweep). If the deformation of a bonding wire during encapsulation is sufficiently large, it may cause a short circuit (due to adjacent wires touching) or an open circuit (due to wires breaking).⁷ If this happens, the device cannot be repaired and must be discarded. Thus, reducing the viscosity of the encapsulation material in order to reduce wire sweep is of prime importance, and is becoming more critical due to the use of an increasing number of wires in microelectronic packaging.

2.3.2. Flexural Modulus

An important mechanical property for microelectronic encapsulants is the flexural modulus, which characterizes the stiffness of a material under an applied load.⁸ The optimal value of the flexural modulus provides a balance between two conflicting requirements. A high value of the flexural modulus is desired to maximize the protection of the chip from an applied load; however, lower values of the flexural modulus lead to lower thermal stresses. Recommended flexural modulus values for microelectronic encapsulants are around 1000 kg/mm².³

2.3.3. Coefficient of Thermal Expansion

The linear coefficient of thermal expansion (CTE) is defined as the ratio of the change in the length of the sample to the change in temperature per unit initial length.⁹ This parameter is very important in semiconductor encapsulation because a significant CTE mismatch between the encapsulant, leadframe, and the silicon chip can lead to the build up of internal stresses in the semiconductor device, and could lead to cracking of the chip or encapsulant. Current encapsulants exhibit α_1 values (CTE below glass transition) in the range of 16-25 μ m/m°C.

2.3.4. Glass Transition Temperature

The glass transition temperature is defined as the temperature (or more precisely, the temperature region) at which a vitreous material changes from a hard and relatively brittle condition to a viscous or rubbery condition.² Above this temperature region, the mechanical, dielectric, and thermal properties change dramatically. Indeed, below the glass transition temperature, the coefficient of thermal expansion is low and nearly constant, but above the glass transition temperature, the coefficient of thermal expansion is very high. As a result, encapsulants must have high glass transition temperatures. Commercial encapsulants typically exhibit glass transition temperatures in the range of 140 to 180°C.

2.3.5. Thermal Conductivity

Since the microelectronic device generates a significant amount of heat during use, the thermal conductivity of an encapsulating compound plays an important role in the thermal management of the device. Indeed, the thermal conductivity determines the amount of heat that can be removed from the device and thus affects operating temperatures of electronic components. As semiconductor devices increase in transistor densities, the heat dissipation requirements also increase, resulting in the need for packaging materials with enhanced thermal conductivity.

2.3.6. Adhesion

The adhesion of an epoxy molding compound to the leadframe is a critical parameter for encapsulated microelectronic devices. The on-going trends of increasing silicon chip size and thinner packages, as well as the push towards surface mount operations, have increased the importance of proper adhesion between the molding compound and leadframe.^{10,11} Specifically, improved adhesion between the molding compound and the leadframe leads to enhanced reliability and resistance to package and chip cracking. In addition, inadequate adhesion leads to popcorn problems in surface mount devices, as well as delamination and subsequent thermomechanical failure.^{2,11} Furthermore, a high degree of adhesion limits moisture-induced corrosion by preventing penetration of water along the leadframe.¹²

2.4. SEMICONDUCTOR MANUFACTURING PROCESS

In order to gain a better appreciation for plastic packaging and its role in the microelectronics industry, it is imperative to review the steps in the assembly of microelectronic devices. The sequence of steps is first listed here in Table 2.1. and then described below.³

1. Wafer Separation	7. Postcure
2. Die Attach	8. Trim-and-Form
3. Die Interconnection	9. Solder Dipping/Solder Plating
4. Molding	10. Burn-in
5. Deflashing	11. Testing
6. Code Marking	

Table 2.1. Sequence of steps in the assembly of microelectronic devices

2.4.1. Wafer Separation and Die Attach

The first step involves sawing the silicon wafers into individual chips using a diamond-tipped saw blade. The sawed wafers are then placed on the paddle of the leadframe, which has already been applied with the die attach adhesive. The adhesive not only physically attaches the chip to the leadframe, but also, because it is conductive, allows electrical contacts to be made to the back of the chip. To cure the adhesive, the leadframes are passed through an oven.

2.4.2. Die Interconnection

To electrically interconnect the silicon chip and the leadframe (die interconnection), two methods are used: wire bonding and tape automated bonding (TAB). In plastic encapsulated microdevices, wirebonding is the dominant interconnection technology, and therefore it will receive primary attention.² In wire bonding, gold or aluminum wires are used to electrically interconnect the bonding pads of the chip with the leads of the frame. This is done with automated machinery which flame softens the tip of the wire and then mashes it against the bonding pad of the chip. The wire is then looped out and formed into a wedge bond on the leadframe finger.³ The bond length and the loop shape are chosen so as to minimize wire displacement, with bond lengths ranging from 0.15 to 0.30 cm and loop heights about 0.075 cm above the

plane of the device.³ Longer wire spans (due to placing a small chip on a large leadframe paddle) tend to be avoided because of the greater chance of wire deformation during molding.

2.4.3. Transfer Molding

After the die attach and interconnection steps, the chip, wirebond, leadframe assembly is ready for transfer molding, the most popular encapsulation method for essentially all plastic packages in integrated circuit technology.² Equipment for transfer molding includes a transfer molding press with the appropriate molding tool, a dielectric preheater, a cure oven, and frame and cassette loaders. In this process, the cassettes of leadframes are loaded into the mold and then the mold is closed and clamping pressure is applied. The epoxy molding compound, in the form of a solid preform, is dielectrically preheated (to 90-95°C) and then placed into the pot of the molding tool. A transfer cylinder, or plunger, is used to apply the transfer pressure and force the molding compound through the runners and gates of the mold and into the cavities. The molding compound then flows over the chips, wirebonds, and leadframes, encapsulating the semiconductor device. After 2 to 3 minutes at approximately 175°C, the epoxy molding compound is cured to a sufficient degree of conversion (typically 60 to 90%) in the mold. The mold is then opened and the molded devices are ejected and ready for the next processing steps.

2.4.4. Deflashing and Code Marking

During transfer molding, excess epoxy molding compound can inadvertently flow through the mold parting line and onto the leads of the device. This excess material (known as flash) can cause problems in the downstream operations of lead trimming, forming, and solder dipping and/or plating, if not taken care of.² Therefore, this material is removed by a process known as deflashing, in which a mixture of pressurized air and an abrasive are used to mechanically remove the material from the surface of the leadframe. After deflashing, information is printed on the top surface of the package in an operation known as code marking. This marking is typically done using laser writing or polymer-based inks and includes information such as the device code, the manufacturer, and the date of manufacture for product identification and traceability.

2.4.5. Postcure

The plastic packages are now postcured and placed in large batches in ovens for 4 to 8 hours at 170-180°C in order obtain conversions near 100%, and thus fully develop the mechanical and thermal properties of the cured encapsulant. Postcure is necessary because the molding compound does not achieve complete conversion in the 2 to 3 minute cycle time (conversions typically range from 60-90%) and it is inefficient to wait for full conversion in the mold.

2.4.6. Trim-and-Form

In the lead trimming and forming operations, the peripheral leadframe metal that joins all the leads is cut and the leads are bent (formed) to define specific lead shapes. Using a punch press in which a trim-and-form tool is mounted, the tool sequentially steps through the cutting and forming of the lead fingers.

2.4.7. Solder Dipping/Solder Plating

Since most integrated circuit devices are ultimately soldered to a circuit board, solder dipping and plating are used to ease solder attachment. Solder dipping simply

involves dipping the leads into molten solder, while solder plating uses plating chemicals. Typically, a thin coat of solder less than 0.0005 inch is applied.³

2.4.8. Burn-in

Burn-in is a process step where the devices are screened for premature failure at high temperature and high electrical loading.³ Burn-in is accomplished by mounting the devices on special circuit boards that apply the electrical loading, and these boards are then plugged into large oven chambers that maintain a constant high temperature. A commonly used burn-in cycle consists of a voltage loading 1-2 volts above the nominal 5 volt operating range typical for most devices at a temperature of 120°C for 9-24 hours.³

2.4.9. Testing

Testing is a final means of evaluating devices, as well as, a means for process analysis and improvement. A full function test on 100% of the packaged devices is standard in the microelectronics industry. Techniques used for testing include x-ray analysis, de-encapsulation, microscopy, scanning laser acoustic microscopy, differential scanning calorimetry, and sectioning.³

2.5. ENCAPSULATION OF MICROELECTRONIC DEVICES BY TRANSFER MOLDING

As was mentioned earlier, transfer molding is the predominant method for encapsulating integrated circuits.⁸ Therefore, further details about this process will be described here. Transfer molding is defined as a method for molding thermosetting materials in which the material is subjected to heat and pressure and then forced into a closed mold cavity by this same pressure and held there under additional heat and pressure until cure is complete.⁸ Transfer molding equipment for microelectronic devices
consists of a hydraulic press equipped with platens, one of which contains a chamber known as the pot, in which the molding compound is placed and liquefied by a combination of pressure and heat. A plunger transfers the molten material at pressures typically around 1000 psi into the cavities of the mold via a series of channels (known as runners), as shown in Figure 2.2. Transfer times are usually between 15 and 20 seconds, although it is not uncommon for some compounds and molds to go outside these limits.⁸ The molding compound then flows over the chip-wirebond-leadframe assembly (located in the cavities), encapsulating the microelectronic device. At the end of the transfer stroke, the two mold halves remain clamped for a short time to allow the resin to react further. Mold temperatures are normally 170-175°C. Once the molding compound has reached an ejectable hardness (typically after two to three minutes), the encapsulated devices are removed from the mold and postcured to fully develop the material properties of the encapsulant.



Figure 2.2. Transfer molding process for encapsulating microelectronic devices.¹³

2.6. DISADVANTAGES OF TRANSFER MOLDING

Although transfer molding is the predominant means of encapsulating silicon chips, it does suffer from a number of problems. Three problems commonly encountered during transfer molding are: i) incomplete mold filling; ii) leadframe movement during cavity filling; and iii) wire sweep, which is displacement or deformation of the wires that provide electrical connection between the chip and the leadframe. Each of these molding problems is directly related to the processing conditions and the rheological characteristics of the molding compound used for encapsulation.¹⁴ Of significant interest is wire sweep, which is the largest and predominant cause of defects in the encapsulation of microelectronic devices.¹

Most of the limitations of transfer molding in high volume production arise from the fact that the resin system begins to react before and as it enters the mold due to high operating temperatures. As a result, the resin becomes very viscous, necessitating the use for high operating pressures during transfer molding. All of these factors contribute to the wire sweep problem. As the package sizes and the associated wires shrink to smaller and smaller dimensions, so does the operating window for transfer molding; hence, it is difficult to control wire sweep in the high pin count, fine pitch packages. In turn, these problems lead to productivity decreases due to increased packaging-related rejects. Moreover, the capital costs associated with transfer molding are quite high.

Photopolymerizable liquid encapsulants (PLEs) for microelectronic devices may offer important advantages over traditional transfer molding compounds (which are solid at room temperature), including alleviation of the three problems mentioned above. In

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order to fully appreciate the benefits that a photopolymerizable encapsulant can offer, it is important to first review the area of photopolymerizations.

2.7. OVERVIEW OF PHOTOPOLYMERIZATIONS

As the name implies, photopolymerizations are polymerization reactions that are initiated by light. Photoinitiation is achieved by the addition of a photoinitiator (and perhaps a photosensitizer) which produces active centers upon absorption of light of the appropriate wavelength. Once the active centers are produced, the polymerization proceeds by propagation of the active center with successive monomer units, just like in traditional thermal polymerizations.

Photopolymerizations offer a number of advantages that make them attractive for a variety of applications. For example, photopolymerizable formulations are typically solvent-free, thereby minimizing volatile organic emissions. Moreover, since active centers may be produced rapidly and efficiently using photochemical processes, photopolymerizations provide high production rates, and are very energy efficient compared to thermal systems, in which the entire reaction system is raised to an elevated temperature. Finally, photopolymerizations provide a great deal of control over the initiation reaction: spatial control, since the light may be directed to locations of interest in the system; and temporal control, since the light may be readily shuttered on or off. These advantages have led to the widespread use of photopolymerizations in commercial applications such as films, inks, and coatings for a variety of substrates (i.e. paper, metal, plastic, and wood). Although photopolymerizations have not been used to replace the for encapsulating microelectronic devices. transfer molding process used

photopolymerizations have still found extensive use in the electronics manufacturing industry; specifically, as UV curable adhesives (for applications in strain-relief, wire and parts tacking, coil terminating, tamper-proofing, structural bonding, and surface mount component attachment), as well as, UV curable coatings for potting, glob-topping, and conformal coatings.¹⁵

2.8. PHOTOPOLYMERIZATION OF THICK POLYMERS AND COMPOSITES

Photopolymerization of thick polymers and filled composites (such as encapsulants for microelectronic devices) is more challenging than photopolymerization of thin-film systems due to the exponential reduction in light intensity through the sample resulting from absorption and scattering. Therefore, for thick polymers and filled composites, proper selection of the illumination wavelength, initiating system (type of initiator, photosensitizer, concentration, etc.), resin, fiber or filler, and composite thickness is imperative to ensure that the samples cure throughout (including the portions of the sample furthest from the light). Specifically, the initiating wavelength must be carefully selected to ensure that the resin and filler are transparent to this wavelength, so that only the photoinitiator significantly absorbs light. This is accomplished by choosing a photoinitiator that has good absorbance in a spectral region different from where the other components of the system (resin, filler, etc.) absorb. In addition, the photoinitiator must "photobleach" at the initiating wavelength; that is, the initiating fragments should not absorb light at the initiating wavelength. Thus, the photoinitiator becomes transparent upon production of active centers, ensuring efficient penetration of light into the sample.

2.9. ADVANTAGES OF USING PHOTOPOLYMERIZATIONS TO ENCAPSULATE MICRODEVICES

As was mentioned earlier, photopolymerizations and a photopolymerizable liquid encapsulant offer a number of advantages that could alleviate many of the problems encountered in the conventional transfer molding process used to encapsulate microelectronic devices. In particular, the temporal control of photopolymerizations would allow the mold to be completely filled with a low viscosity resin before any reaction takes place, and a fast thermoset reaction could be initiated after the mold is completely filled. This decoupling of mold filling and reaction would permit complete control of the time allowed for flow of the resin formulation and would reduce waste and expensive clean-up by preventing premature reaction (gelation in the transfer lines). In addition, since there would be no need for high pressures or external heating of the mold, the photomolding process would be very energy efficient. Most importantly, the decoupling of mold filling and reaction would reduce the wire sweep problem.

Aside from the benefits of using photopolymerizations, there are a number of advantages to using a liquid formulation, as well. Specifically, liquid encapsulation dispensing equipment is less expensive than molding presses, especially when in-line automated factories are targeted. In fact, a cost analysis by Robinson *et al.*¹⁶ comparing the cost of molding and liquid encapsulation shows that, "liquid encapsulation is significantly lower in cost than molding and has the potential to displace mold compounds in several applications". Furthermore, the authors write that using liquid encapsulants, "will allow package design changes without costly retooling. Minor package and dispense changes are quickly implemented and immediately verifiable.

Shorter cure times, reduced cycle time, and low initial capital expense requirements will also enable higher manufacturing productivity".¹⁶

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Chapter 3

RESEARCH OBJECTIVES

As Chapter 2 demonstrated, photopolymerizations offer tremendous potential for the development of improved, high-speed, low-cost encapsulation methods for microelectronic devices. This research project will address several issues that need to be resolved in order to establish photopolymerizable liquid encapsulants (PLEs) as a feasible alternative to traditional transfer molding compounds. Therefore, a general goal of this project is to make an impact in the microelectronics encapsulation arena by circumventing many of the problems and limitations associated with the current transfer molding technology. Meeting the following general goals will allow us to demonstrate the feasibility of PLEs for microelectronic encapsulants: i) Develop a highly filled photopolymerizable liquid encapsulant that has the material properties required by the microelectronics industry for traditional transfer molding compounds (i.e. flexural modulus and strength, coefficient of thermal expansion, glass transition temperature, thermal conductivity, adhesion, etc.); ii) Develop a photopolymerizable formulation with a much lower viscosity than other transfer molding compounds in order to minimize problems such as wire sweep; iii) Demonstrate that a highly filled photopolymerizable liquid encapsulant can exhibit similar, if not faster, in-mold cure times than conventional thermally cured transfer molding compounds.

To meet these general goals, the specific objectives of this research project are as follows:

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- Identify appropriate materials (resins, fillers, initiators, *etc.*) for a photopolymerizable liquid encapsulant;
- 2. Characterize the viscosity of highly filled suspensions and determine the effect of blending two different filler particle size distributions on the viscosity;
- 3. Determine the effect of silane coupling agents on the viscosity of a highly filled suspension;
- 4. Determine the effect of UV illumination time, postcure time, filler loading, and initiation scheme on the following material properties: flexural modulus and strength, coefficient of thermal expansion, glass transition temperature, and thermal stress parameter.
- 5. Determine the thermal conductivity of photopolymerizable liquid encapsulants.
- 6. Characterize the degree of adhesion between the photopolymerizable liquid encapsulant and leadframe materials.

By meeting these research objectives, this research project will establish photopolymerizable liquid encapsulants as a feasible and viable alternative for microelectronic encapsulation.

Chapter 4

SELECTION OF MATERIALS FOR THE PHOTOPOLYMERIZABLE LIQUID ENCAPSULANT

4.1 RESIN MATRIX

Preliminary studies focused on determining the appropriate resin matrix for the photopolymerizable liquid encapsulant. The resins used for this evaluation included epoxy vinyl ester resins from the DERAKANE product line available from Dow Chemical (DERAKANE 411-C-50, 441-400, 470-45, 510A, and 8084). Figure 4.1 shows the general structure of the DERAKANE resins. The primary properties that were used to assess the resins were cure time, coefficient of thermal expansion, and viscosity.

Cure time studies were performed on the full complement of DERAKANE resins filled with powdered E-glass fibers and the photoinitiator, benzoin ethyl ether (BEE). These samples were photopolymerized in polyethylene vials using near-UV light with an intensity of 200 mW/cm² and a BEE concentration of 0.2 wt.% (based on resin weight). For each resin, the time required for complete cure for 6.5 mm thick samples was determined as a function of fiber loading, as shown in Figure 4.2. Clearly, shorter cure times are desirable in order to meet the high-speed requirements of mass production. Current molding compounds cure in 2 to 3 minutes at a temperature of 175°C, and require a postcure of 4 to 8 hours at this elevated temperature. In addition, the typical thickness of an encapsulant is one to three millimeters thick. In our photopolymerization systems, the cure is performed with no external heating, and the cure time decreases markedly as the sample thickness is reduced. Therefore, a cure time of a few minutes for a 6.5 mm thick sample would easily meet the cure rate requirements for microelectronic encapsulants. Figure 4.2 clearly illustrates that DERAKANE resins, 411, 441, and 470-45, cure in the shortest amount of time at high fiber loadings and, therefore, the 510A and 8084 resins were eliminated from further study.

After the elimination of the 510A and 8084 resins, the coefficients of thermal expansion of the remaining resins were measured. The coefficient of thermal expansion (CTE) is a very important parameter in microelectronic encapsulation because a significant CTE mismatch between the encapsulant, leadframe, and the silicon chip can lead to cracking of the chip or encapsulant. Since the CTE for the silicon chip is between 3 and 4 μ m/m°C, and for the leadframe between 12-16 μ m/m°C, encapsulants with low CTE values between 16 and 25 µm/m°C are desired. Figure 4.3 contains experimental results for the coefficient of thermal expansion of photopolymerized samples with 0 and 50 wt.% powdered E-glass fibers for the three different resins. These samples were cured for 3.5 minutes using 0.2 wt.% BEE and an intensity of 200 mW/cm². As Figure 4.3 illustrates, only samples prepared with DERAKANE 470-45 and 50 wt.% fiber are within the recommended 16 to 25 μ m/m°C range. This result, combined with the fact that DERAKANE 470-45 had the lowest viscosity of the three remaining resins (viscosity at 25°C is 45.6 cP, as opposed to 100 cP for DERAKANE 411 and 400 cP for DERAKANE 441-400) led to the selection of DERAKANE 470-45 as the base resin for the photopolymerizable liquid encapsulant.

In addition, acrylates were also evaluated to see their potential as a base resin (since acrylates are predominantly used in photopolymerization systems). In particular, 1,3 butylene glycol diacrylate was selected because of its low viscosity (9 cP at 25°C) and relatively high glass transition temperature (101°C). However, this resin performed quite poorly when photocured; all samples created from this resin displayed numerous cracks and were unusually brittle. Therefore, this resin was discontinued from further study.

4.2. FILLER

The primary roles of the filler are to reduce the coefficient of thermal expansion, improve the mechanical properties, and increase the thermal conductivity of the cured encapsulant. Also, the addition of fillers reduces encapsulant shrinkage by replacing much of the resin with an inert compound that does not participate in the crosslinking process. Fused silica is the most commonly used filler in transfer molding compounds since it possesses the optimum combination of properties. In particular, it has a low coefficient of thermal expansion $(0.5-0.6 \times 10^{-6} \text{ °C}^{-1})$ and it has a low enough abrasiveness to provide a reasonable molding tool lifetime, as opposed to aluminum nitride.¹ In addition, fused silica is transparent to UV light, and is therefore appropriate for UV curing.² Based upon these considerations, the filler selected for the PLE was crushed (angular), untreated fused silica from the commercial MIN-SIL product line offered by MINCO, Inc. Three different fused silica products, each with its own continuous particle size distribution, were used for the PLE. These fillers were chosen specifically for their particle sizes and associated distributions. The broadest distribution of particles (which also contained the largest particles), MIN-SIL 40 (henceforth referred to as particle size distribution A, or PSD-A) had a volume average particle size = 32.42 μ m, and a median particle size = 22.11 μ m. The second distribution of particles. MIN-

SIL 20, (henceforth referred to as PSD-B) had a volume average particle size = 19.37 μ m and a median particle size = $13.17 \,\mu\text{m}$. The narrowest distribution of particles (which contained the largest fraction of small particles), MIN-SIL 550 (henceforth referred to as PSD-C) had a volume average particle size = $10.37 \,\mu m$ and a median particle size = 6.03 μ m. For microelectronic encapsulants, fused silica particles larger than ~100 μ m should be avoided to prevent particles from becoming trapped in the gates (a gate admits the molding compound into the cavity of the device to be molded and can be as narrow as 150 microns but are typically 200-250 microns) or caught between the leads of high pincount packages (the interlead spacing can be as little as 100 microns).¹ None of the fused silica products that we have chosen to use has fused silica particles greater than 150 microns. Ideally, we would also want to use spherical fused silica particles, because spherical fused silica is much more effective in decreasing the viscosity than crushed fused silica.³ In addition, spherical silica leads to increased filler loadings. However, a spherical fused silica supplier in the United States was not found before these studies were performed.

4.3. PHOTOINITIATOR

Since most monomers, oligomers, or prepolymers do not produce initiating species with a sufficient quantum yield upon light exposure, it is necessary to use low molecular weight organic molecules called photoinitiators to start the polymerization.⁴ A photoinitiator is the chemical species which produces active centers (free radicals or cations) upon absorption of photons of the appropriate wavelength. Generally, free radical photoinitiators fall into two categories: cleavable and non-cleavable

photoinitiators. Cleavable photoinitiators directly produce free radicals upon absorption of photons and are further classified according to the mechanism by which they undergo photolysis as α -cleavable, β -cleavable, and γ -cleavable. Non-cleavable photoinitiators require a co-initiator such as an amine (electron transfer agent) or an alcohol (a hydrogen donor) in order to produce free radicals.

Most of the commonly used free radical photoinitiators are α -cleavable initiators and these include a number of compounds, such as benzoyl phosphine oxides, benzoin ethers, dialkoxyacetophenones, hydroxy alkyl ketones, amino ketones, morpholino ketones, and benzoyl oxime esters.⁵ These α -cleavable free radical photoinitiators undergo a fairly simple sequence of photochemical transitions. Specifically, they are excited to the singlet state, undergo efficient intersystem crossing to the triplet state, and then undergo photolysis to form free radicals. The free radicals then initiate polymerization in the presence of monomer, oligomer, or prepolymer.

The proper selection of a photoinitiator for UV-curing thick and filled systems depends upon a number of factors, such as the emission spectrum of the light source, absorption spectrum of the photoinitiator, absorbance by the monomer and other additives, absorbance and scattering properties of the filler, and the photobleaching exhibited by the photoinitiator. Specifically, there are a number of criteria that must be satisfied. First, the photoinitiator must clearly have significant absorbance in the region where the light source emits. Second, the photoinitiator must exhibit good absorbance in a spectral region different from where the other constituents of the formulation (resin, filler, additives, etc.) absorb. Finally, the photoinitiator must undergo significant photobleaching upon illumination. Photobleaching occurs when the products of photolysis do not absorb in the same region as the original initiator molecule. The net result of photobleaching is an increase in transmittance of the system as a function of illumination time, which, in turn, allows for deeper penetration of the incident light.

Based on these considerations, the photoinitiator selected for the photopolymerizable liquid encapsulant was bis(2,4,6-trimethylbenzoyl)phenyl phosphine oxide (IRGACURE 819, Ciba), whose structure is shown in Figure 4.4. This photoinitiator is in the family of bisacylphosphine oxide photoinitiators and is denoted as BAPO. These photoinitiators are very versatile and have found widespread use in pigmented and filled systems for the following reasons. First, bisacylphosphine oxides have absorption spectra with maxima between 350 and 380 nm and extending well into the visible, as shown by the absorption spectrum of bis(2,4,6-trimethylbenzoyl)phenyl phosphine oxide in Figure 4.5. As a result, these photoinitiators are especially suited for use with light in the near-UV-vis part of the spectrum, where many pigments and fillers are sufficiently transparent.⁶ Second, bisacylphosphine oxide photoinitiators exhibit significant photobleaching since photolysis results in cleavage of the carbon phosphorus bond, thereby destroying the chromophore which absorbs in the near UV-vis region (350 to 410 nm).⁶ Thus, the optical density of the system containing this photoinitiator decreases in the near UV-vis range during the curing process, and light can effectively penetrate deep into the sample (which is imperative to cure thick samples).

4.4. THERMAL INITIATOR

Curing techniques using both light and heat to initiate polymerization have been well documented.⁶ When a radical polymerization is activated by both a photoinitiator

and a thermal initiator, the process is referred to as "dual cure" or "dual initiating". In this initiating method, the photoinitiator is used to give a fast cure of the surface, which is easily accessible for the incident light. The heat evolved from the exothermic photopolymerization then elevates the temperature, resulting in the production of additional active centers by the thermal initiator. The primary advantage of this dual initiating method is that the degree of cure is greatly enhanced, since the thermal initiator is used to create active sites in areas where light may not be able to sufficiently penetrate the system. As a result, this method is especially appropriate for increasing the degree of cure in systems where the sample is opaque, such as in a composite with high filler loading.

In order to effectively utilize a thermal initiator in a photopolymerizable formulation, the thermal initiator should not absorb the initiating light and should be susceptible to rapid dissociation at moderate temperatures (80 to 100°C). Based on these considerations, benzoyl peroxide (Aldrich) was selected as the thermal initiator for the photopolymerizable liquid encapsulant (peroxides are well known as thermal initiators for radical polymerization). The chemical structure of benzoyl peroxide is shown in Figure 4.6.

4.5. SILANE COUPLING AGENT

Silane coupling agents are organofunctional compounds that act as molecular bridges at the interface between the polymer matrix and the filler particles of the composite. They are linear molecules which have a reactive group at one end capable of being incorporated into the matrix of a curing polymer and a silicon-based group at the other end which bonds to inorganic fillers. Silane coupling agents are included in the formulation because they offer several benefits, including improved processability, reduced particle settling, better adhesion to substrates such as the leadframe, and improved mechanical and electrical properties.

The silane coupling agent chosen for the photopolymerizable liquid encapsulant was 3-methacryloxypropyltrimethoxysilane (Z-6030, Dow Corning), whose structure is shown in Figure 4.7. This particular silane was chosen because of its chemical compatibility with the epoxy vinyl ester resin. It is particularly effective in improving the properties of free radical-cured plastics, such as vinyl ester resins, and it has a very low viscosity (2.5 cP at 25°C).



Figure 4.1. General chemical structure of DERAKANE epoxy vinyl ester resins.



Figure 4.2. Cure time as a function of fiber loading for various DERAKANE epoxy vinyl ester resins.



Figure 4.3. Effect of filler loading on the coefficient of thermal expansion for three different DERAKANE resins.



Figure 4.4. Chemical structure of bis(2,4,6-trimethylbenzoyl)phenyl phosphine oxide.



Figure 4.5. Absorbance spectrum of bis(2,4,6-trimethylbenzoyl)phenyl phosphine oxide. The concentration is 5.1×10^{-4} g/ml in acetone.



Figure 4.6. Chemical structure of benzoyl peroxide.

 $\begin{array}{c} O & CH_3 \\ \parallel & \parallel \\ (CH_3O)_3SiCH_2CH_2CH_2OC - C = CH_2 \end{array}$

Figure 4.7. Chemical structure of 3-methacryloxypropyltrimethoxysilane.

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4.6. REFERENCES

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Chapter 5

VISCOSITY CHARACTERIZATION OF HIGHLY FILLED PHOTOPOLYMERIZABLE LIQUID ENCAPSULANTS

5.1. INTRODUCTION

A microelectronic device consists of a silicon chip that is mounted on a metal leadframe, and gold or aluminum wires that electrically connect the chip circuits to the leadframe. Microelectronic devices are typically encapsulated in a thermoset molding compound, which serves to protect the silicon chip from both physical and chemical damage. The three most commonly used techniques for encapsulation are transfer molding, potting, and conformal coating, with transfer molding being the predominant method to encapsulate integrated circuits.¹ In this process, the thermoset molding compound (typically a solid epoxy preform) is dielectrically preheated and then placed into the pot of the molding tool. Transfer molding is accomplished by lowering a plunger that forces the molding compound into the runners and gates of the mold. The molding compound then flows over the chips, wirebonds, and leadframes, encapsulating the microelectronic device. Although transfer molding is the predominant means to encapsulate integrated circuits, it does suffer from a few problems. Three problems commonly encountered during transfer molding are: i) incomplete mold filling; ii) leadframe movement during cavity filling; and iii) wire sweep, which is displacement or deformation of the wires that provide electrical interconnection between the integrated circuit and the leadframe. Each of these molding problems is directly related to the processing conditions and the rheological characteristics of the molding compound used for encapsulation.^{2,3}

Photopolymerizable liquid encapsulants (PLEs) for microelectronic devices may offer important advantages over traditional transfer molding compounds (which are solid at room temperature), including alleviation of the three problems mentioned above. These liquid encapsulants are formulated using low-viscosity epoxy novolac-based vinyl ester resins that cure rapidly upon exposure to UV light. The use of light, rather than heat, to initiate the polymerization allows the reaction to be triggered only after mold filling is complete, and the resin remains in the low-viscosity, uncured state throughout the mold filling process. Typically, liquid encapsulants are used when the part configuration cannot be easily transfer molded, or when the capital costs of transfer molding are too high. In the past, liquid systems have been limited to low-end consumer electronic products where cost and size were the primary issues and environmental reliability was of secondary importance. However, recent research on liquid encapsulants has demonstrated that liquid encapsulants can meet or exceed the performance of traditional transfer molding compounds.⁴ In addition, liquid encapsulants offer added benefits such as allowing package design changes without costly retooling, reduced cycle time, and low initial capital expense requirements.

The microelectronic encapsulation process requires a low viscosity of the molding compound so it can flow into the mold with minimum deformation of the leadframe and wirebonds.⁵ Monodisperse suspensions are not favored for this application (or any other highly filled suspension for that matter) because of the resulting high viscosity of the system.⁶ It is generally known that blending particles of various sizes in the proper proportions can significantly reduce the viscosity of highly filled systems at a fixed loading level.⁷ This is clearly demonstrated by the work of authors such as Farris⁸,

Hoffman⁹, Rodriguez *et al.*¹⁰, and Zaman and Moudgil⁶. In these polydisperse systems, the spaces between larger particles may be occupied by smaller particles, and the combination of the small particles and the suspending medium can behave essentially as a fluid to the larger particles.⁸ In addition, bimodal and trimodal particle size distributions are used in highly filled systems to achieve maximum filler loadings (thereby improving composite material properties, i.e., decreasing the coefficient of thermal expansion and increasing the thermal conductivity for the case of thermoset encapsulants). For example, the maximum packing fraction of a spherical monomodal particle distribution is 64 vol.% due to the inherent spaces between particles. In contrast, a bimodal distribution allows a packing fraction of 83 vol.% to be theoretically achieved, ¹¹

Silane coupling agents are organofunctional compounds that act as molecular bridges at the interface between the polymer matrix and the filler particles of the composite. They are linear molecules which have a reactive group at one end capable of being incorporated into the matrix of a curing polymer and a silicon-based group at the other end which bonds to inorganic fillers. Silane coupling agents are included in the formulation because they offer several benefits, including improved processability, reduced particle settling, better adhesion to substrates such as the leadframe, and improved mechanical and electrical properties. In addition, the coupling agents can either increase or decrease the viscosity of the formulation.³ For this reason, it is important to characterize the effect of silane coupling agents on the viscosity. In our research, we are investigating novel, highly-filled PLEs formulated using epoxy novolac-based vinyl esters that cure in a relatively short amount of time to yield a composite exhibiting appropriate values for the flexural modulus and strength, coefficient of thermal expansion, glass transition temperature, and chemical resistance.^{12,13} We have found that these PLEs exhibit appropriate cure characteristics and material properties, and are therefore quite promising for microelectronic encapsulation. Because the viscosity of the encapsulation material is such an important parameter, the viscosity of the photopolymerizable liquid encapsulants has been characterized in this chapter. We have identified a blend of two particle size distributions of fused silica that provides a reduced viscosity at high filler loadings, and we have characterized the effect of silane coupling agents on the photopolymerizable liquid encapsulants.

5.2. BACKGROUND ON THE VISCOSITY OF CONCENTRATED SUSPENSIONS

The viscosity of concentrated suspensions has been the subject of extensive research due to the widespread use of concentrated suspensions in a host of applications, including paints, foods, cements, filled polymers, cosmetics, *etc.* For efficient processing and handling of these highly filled solid-liquid suspensions, it is important to understand how their rheology depends upon a variety of factors. For this reason, several authors have developed models to predict the effect of the solids loading, particle shape, particle size distribution, and the viscosity of the suspending medium on the viscosity of the suspension (for reviews, see Zaman and Moudgil⁶, Barnes¹⁴, Han¹⁵, and Probstein *et al.*¹⁶). Most descriptions of concentrated suspensions are extensions of Einstein's early work on dilute suspensions of rigid, uniform-sized spheres.^{17,18} Einstein's equation

relates the viscosity of the suspension, η , to the viscosity of the suspending medium, η_o , and the volume fraction of the spheres, ϕ , as shown in Equation 5.1.

$$\eta = \eta_a (1 + 2.5\phi) \tag{5.1}$$

However, this equation is not applicable to concentrated suspensions because it neglects particle-particle interactions, and does not account for particle size.¹⁴

A number of authors extended Einstein's equation to suspensions of higher concentrations¹⁹⁻²² using the maximum packing fraction, ϕ_m , to account for the particle-particle interactions.¹⁴ For example, the Krieger-Dougherty equation²² is often used to describe highly filled suspensions and is given in Equation 5.2:

$$\eta = \eta_o (1 - \frac{\phi}{\phi_m})^{-(\eta)\phi_m} \tag{5.2}$$

where $[\eta]$ is defined as the intrinsic viscosity. The maximum packing fraction is the volume fraction of particles that makes flow impossible, i.e. the viscosity goes to infinity. Because of the sensitivity of the maximum packing fraction to the particle size distribution and particle shape, the Krieger-Dougherty equation effectively takes these variables into account when predicting the viscosity of a concentrated suspension. The Krieger-Dougherty equation can be extended to a binary mixture of particles, as shown in Equation 5.3.¹⁴

$$\eta = \eta_o (1 - \frac{\phi_1}{\phi_{m1}})^{-(\eta_1)\phi_{m1}} (1 - \frac{\phi_2}{\phi_{m2}})^{-(\eta_2)\phi_{m2}}$$
(5.3)

In Equation 5.3, the subscript 1 denotes particles of one size, while the subscript 2 corresponds to a second particle size. Each of these subscripts can refer to a particle size distribution if the maximum packing fraction is calculated accordingly.

For the purposes of modeling the experimental viscosity data, Equation 5.3 was used. The maximum packing fractions ϕ_{m1} and ϕ_{m2} were calculated directly from our particle size distributions using the equations developed by Ouchiyama and Tanaka²³ and reported in the paper by Poslinski *et al.*²⁴ (Equations 5.4 through 5.7 shown below):

$$\phi_{m} = \frac{\sum D_{i}^{3} f_{i}}{\sum (D_{i} \sim D_{a})^{3} f_{i} + \frac{1}{\beta} [(D_{i} + D_{a})^{3} - (D_{i} \sim D_{a})^{3}] f_{i}}$$
(5.4)

where

$$\beta = 1 + \frac{4}{13} (8\phi_M^o - 1)D_a \frac{\sum (D_i + D_a)^2 [1 - \frac{\frac{3}{8}D_a}{(D_i + D_a)}]f_i}{\sum [D_i^3 - (D_i \sim D_a)^3]f_i}$$
(5.5)

and

$$D_a = \sum D_i f_i$$
 (5.6)

where

$$f_{i} = \frac{\frac{v_{i}}{D_{i}^{3}}}{\sum \frac{v_{i}}{D_{i}^{3}}}$$
(5.7)

In these equations, ϕ_m^o is the maximum packing fraction of spheres of uniform size and a value of 0.619 was used, as suggested by the authors. In addition, D_i is the diameter of the *i*-th component, f_i is the number fraction of the *i*-th component, v_i is the volume fraction of the *i*-th component, D_a is the average diameter of the different sizes of the particulates, and $(D_i \sim D_a)$ is defined as:

$$(D_i \sim D_a) = 0 \qquad \text{for } D_i \leq D_a,$$

and
$$(D_i \sim D_a) = D_i - D_a \qquad \text{for } D_i > D_a,$$

Once the maximum packing fractions were determined using these equations, the viscosity data was fit to Equation 5.3 by nonlinear regression using the two intrinsic viscosities as the fitting parameters.

5.3. EXPERIMENTAL

5.3.1. Materials

The photopolymerizable liquid encapsulant consisted of a base resin, photoinitiator, silane coupling agent, and filler. The base resin was an epoxy novolacbased vinyl ester resin commercially available from Dow Chemical (DERAKANE 470-45). This resin was chosen primarily because of its low viscosity ($\eta_o = 0.0456$ Pa·s or 45.6 cP at 30°C). In addition, it exhibits an appropriate polymerization rate, and good material properties upon cure. The photoinitiator was bis(2,4,6-trimethylbenzoyl)phenyl phosphine oxide (IRGACURE 819, Ciba). This photoinitiator, which we will denote as BAPO, has been shown to be especially appropriate for curing relatively thick polymers and composites due to its efficient photobleaching.^{25, 26} The silane coupling agent was 3methacryloxypropyltrimethoxysilane, (Z-6030, Dow Corning) and the filler was fused silica (MINCO, Inc.).

The primary roles of the filler are to reduce the coefficient of thermal expansion and enhance the thermal conductivity of the cured encapsulant. Fused silica is the most commonly used filler in transfer molding compounds since it possesses the optimum combination of properties. In particular, it has a low coefficient of thermal expansion $(0.5-0.6 \times 10^{-6} \text{ °C}^{-1})$ and it has low enough abrasiveness to provide a reasonable molding tool lifetime, as opposed to aluminum nitride.³ Based upon these considerations, the fillers selected for this study were crushed (angular), untreated fused silica from the commercial MIN-SIL product line offered by MINCO, Inc. Three different fused silica products, each with its own continuous particle size distribution, were used in this study. The broadest distribution of particles (which also contained the largest particles), MIN-SIL 40 (henceforth referred to as particle size distribution A, or PSD-A) had a volume average particle size = 32.42μ m, and a median particle size = 22.11μ m. The second distribution of particles, MIN-SIL 20, (henceforth referred to as PSD-B) had a volume average particle size = 19.37μ m and a median particle size = 13.17μ m. The narrowest distribution of particles (which contained the largest fraction of small particles), MIN-SIL 550 (henceforth referred to as PSD-C) had a volume average particle size = 6.03μ m. For microelectronic encapsulants, fused silica particles larger than ~100 μ m should be avoided to prevent particles from becoming trapped in the gates (which can be as narrow as 150 microns and are typically 200-250 microns) or caught between the leads of high pincount packages (the interlead spacing can be as little as 100 microns).³</sup>

5.3.2. Sample Preparation

To determine the effect of blending two different fused silica particle size distributions on the viscosity of the PLE, the DERAKANE 470-45 resin was mixed with 70.0 wt.% fused silica, 0.20 wt.% BAPO photoinitiator (based on resin weight), and 1.43 wt.% of the silane coupling agent (based on filler weight). The epoxy novolac-based vinyl ester was blended with 0.20 wt.% BAPO photoinitiator (based on resin weight) until the photoinitiator completely dissolved in the resin. Next, the silane coupling agent was added dropwise to the desired 1.43 wt.% (based on the filler weight) and the resin mixture was again stirred on a magnetic stir plate. Fused silica (with the appropriate

particle size distribution) in the amount of 70.0 wt.% was added to the system, which was thoroughly mixed by using a vortex mixer until the silica was completely dispersed and a homogeneous mixture was achieved. Lastly, the PLE was degassed in a vacuum oven.

In this initial study, all samples contained 70.0 wt.% (0.526 volume fraction) of fused silica. The fused silica particle size distribution was varied by preparing binary mixtures of the individual distributions, PSD-A, PSD-B, and PSD-C, as shown in Table 5.1.

A second set of studies was performed to investigate the effect of the silane coupling agent on PLE viscosity. To prepare these samples, the epoxy novolac-based vinyl ester resin was mixed with 70.0 wt.% fused silica (using the optimal particle size distribution determined from the first set of experiments), 0.2 wt.% BAPO photoinitiator (based on resin weight), and 0 to 1.43 wt.% of the silane coupling agent (based on filler weight). In the final set of studies, the effect of higher filler loadings on the PLE viscosity was investigated. Specifically, the optimal blend determined from the first set of studies was investigated in systems containing fused silica loadings of 72.0 and 74.0 wt.%. It is important to investigate this apparently small increase in the filler loading because the encapsulant containing 74.0 wt.% filler exhibits a lower coefficient of thermal expansion and an enhanced thermal conductivity compared to an encapsulant containing 70.0 wt.% filler.

Viscosities were measured using a Brookfield DV I+ Viscometer equipped with the Small Sample Adapter (SC4-34 spindle and 13R chamber). For this particular spindle and chamber setup, the required sample volume was 10 ml. The temperature of the sample was kept at 30°C using a thermostated circulating water bath connected to the water jacket on the sample chamber. Viscosities were recorded 30 minutes after the spindle started turning to ensure that the system had equilibrated at the desired temperature. The spindle speed was set to 2 RPM (for this particular spindle and chamber geometry, the shear rate is 0.56 sec⁻¹ at 2 RPM). Each reported viscosity is the average of three independent measurements.

5.4. **RESULTS AND DISCUSSION**

5.4.1. Effect of Fused Silica Particle Size Distribution

Figure 5.1 illustrates the effect of the fused silica particle size distribution on the viscosity of the resulting PLE. All samples contained a total volume fraction of fused silica of 0.526 (70.0 wt.%), 1.43 wt.% silane coupling agent (based upon filler weight), 0.2 wt.% BAPO (based upon resin weight), and the balance epoxy vinyl ester resin. Each bar in the bar chart represents the average of three measurements while the error bars indicate one standard deviation above and below the mean. Figure 5.1 contains data for samples containing between 0.263 and 0.526 volume fraction of PSD-A, and the remainder (up to a total filler loading of 0.526 volume fraction or 70.0 wt.%) either PSD-B or PSD-C. Figure 5.1 clearly illustrates that, for a given filler loading (0.526 volume fraction total), the system viscosity can vary significantly for different particle size distributions. For example, the system containing a 50:50 mixture of PSD-A and PSD-B (0.263 volume fraction of each) has a viscosity that is more than four times greater than the system containing a 50:50 mixture of PSD-A and PSD-C. Moreover, Figure 5.1 shows that the viscosity of the encapsulant formulation actually increases as the amount of PSD-B is increased, but decreases considerably as the amount of PSD-C is increased. Therefore, it is readily apparent that the PSD-A/PSD-C combination provides much better viscosity reduction than the PSD-A/PSD-B combination. The system containing 0.526 volume fraction (70.0 wt.%) of a 50:50 mixture of PSD-A and PSD-C exhibits a relative viscosity of ~100 (a viscosity less than 5.0 Pa•s). This viscosity is more than three times lower than that exhibited by a system containing 0.526 volume fraction of PSD-A (with no second filler component) and, therefore, the blending of these two particle size distributions in order to reduce the viscosity at a given filler loading was successful. For microelectronic encapsulants, it is undesirable to reduce the viscosity further than that exhibited by the 50:50 mixture of PSD-A and PSD-C since molding problems such as resin bleed and flash may occur.

Figure 5.2 contains data for samples containing between 0 and 0.263 volume fraction of PSD-C, and the remainder (up to a total filler loading of 0.526 volume fraction or 70.0 wt.%) either PSD-A or PSD-B. All samples contained a total volume fraction of fused silica of 0.526 (70.0 wt.%), 1.43 wt.% silane coupling agent (based upon filler weight), 0.2 wt.% BAPO (based upon resin weight), and the balance epoxy vinyl ester resin. Each value represents the average of three measurements while the error bars indicate one standard deviation above and below the mean. The viscosities of the samples containing 0.526 or 0.474 volume fraction PSD-B were out of the range of the instrument (implying that the viscosity was above 30.0 Pa·s) for the spindle and shear rate under investigation. Figure 5.2 demonstrates that the PSD-C/PSD-A system has a much lower viscosity than the formulation containing PSD-C and PSD-B. In addition the data in Figure 5.2 clearly illustrates what is known as the "Farris Effect" – a large reduction in the viscosity seen near a fraction of 0.6 of large particles.¹⁴ Our data is also in agreement with that of Zaman and Moudgil⁶ who found that the lowest level of

viscosities is obtained if the volume ratio of small and large particles lies in the range of 50/50 or 45/55.

The data in Figures 5.1 and 5.2 clearly illustrate that PLEs containing 0.526 volume fraction (70.0 wt.%) of a 50:50 mixture of PSD-A and PSD-C exhibit the lowest viscosity; therefore, this mixture was selected for further experiments on (i) the effect of the silane coupling agent and (ii) higher fused silica loadings. Our data is in general agreement with the results of previous investigators who have observed a decrease in the viscosity of concentrated suspensions as the ratio of the large particles to the small particles was increased.⁸, ⁹, ²⁷, ²⁸ Based upon the volume average particle sizes, the particle size ratio of PSD-A to PSD-C is 3.13, the particle size ratio of PSD-B to PSD-C is 1.87, and the particle size ratio of PSD-A to PSD-C have the lowest viscosity, blends of PSD-B and PSD-C have a higher viscosity, and blends of PSD-A and PSD-B have the highest viscosity.

The curves drawn in Figure 5.2 correspond to values obtained by fitting the experimental data to the Krieger-Dougherty equation (Equation 5.3). The nonlinear regression analysis was performed using the commercial software package Origin 5.0 (Microcal Software, Inc.) after the maximum packing fractions of PSD-A, PSD-B, and PSD-C were determined using Equations 5.4-5.7. For each calculation, the two intrinsic viscosities were used as the fitting parameters. The calculated maximum packing fractions were 0.836 for PSD-A, 0.802 for PSD-B, and 0.754 for PSD-C. As expected, the maximum packing fraction increases as the breadth of the particle size distribution is increased. For the PSD-A/PSD-C system, the best fit intrinsic viscosities were 7.2 for

PSD-A, and 8.4 for PSD-C. For the PSD-B/PSD-C system, the best fit intrinsic viscosities were 8.9 for PSD-B, and 7.0 for PSD-C. These values for the intrinsic viscosity are quite reasonable. Figure 5.2 illustrates that the experimental data is well correlated by the Krieger-Dougherty equation.

5.4.2. Effect of Silane Coupling Agent

A series of experiments were performed to investigate the effect of the silane coupling agent on the viscosity of the highly filled liquid encapsulants. The experimental results are shown in Figure 5.3. All samples contained 0.526 volume fraction (70.0 wt.%) fused silica filler (50% PSD-A, 50 % PSD-C) and 0.2 wt.% BAPO (based on resin weight) and the balance epoxy vinyl ester resin. Each bar in this bar chart represents the average value of three viscosity measurements and the error bars indicate one standard deviation above and below the mean. The data show that as the amount of the silane coupling agent was increased, the viscosity of the system decreased, with the sample containing 1.43 wt.% silane exhibiting the lowest viscosity. As was mentioned earlier in the introduction, it has been reported that coupling agents can either increase or decrease the viscosity of the formulation.³ The data in Figure 5.3 illustrate that for our system, the coupling agent does not increase the viscosity of the PLE formulations, but decreases it slightly. Silane concentrations above 1.43 wt.% may decrease the viscosity further, but they were not evaluated because they lead to an undesirable increase in the coefficient of thermal expansion of the cured encapsulant.²⁹

5.4.3. Effect of Higher Filler Loadings

Further experiments were performed to investigate the effect of higher filler loadings on the viscosities of the photopolymerizable liquid encapsulants. Specifically,
fused silica loadings of 72.0 and 74.0 wt.% were studied. It is important to investigate this apparently small increase in the filler loading because the encapsulant containing 74.0 wt.% filler exhibits a lower coefficient of thermal expansion and an enhanced thermal conductivity compared to an encapsulant containing 70.0 wt.% filler. Unfortunately, as the filler loading is increased from 70.0 wt.% to 74.0 wt.%, the increase in viscosity can be quite dramatic. For these studies, a 50:50 mixture of PSD-A and PSD-C was used, and the PLEs contained 1.0 wt.% of the silane coupling agent (based upon filler weight). The experimental results are shown in Table 5.2. As expected, the viscosity was found to increase as the filler loading was increased from 70.0 to 72.0 wt.%, silica was still quite easy to handle and process, and could still be appropriate for encapsulating microelectronic devices. The viscosity of the PLE containing 74.0 wt.% silica was too high to be measured with the specified spindle and shear rate (implying that the viscosity was higher than 30.0 Pa-s).

5.5. CONCLUSIONS

In this chapter, we have characterized the viscosity of highly filled photopolymerizable liquid encapsulants to investigate the blending of two different particle size distributions to tailor the viscosity for a given filler loading. For encapsulating microelectronic devices, it is desired to achieve a low enough viscosity to allow the molding compound to easily flow over the chip, wirebond, and leadframe assembly, thereby minimizing problems associated with incomplete mold filling, leadframe displacement, and wire sweep. We have characterized the viscosity of PLEs containing 70.0, 72.0, and 74.0 wt.% silica, and found that a blend of particle size

distributions with a particle size ratio of 3.13 (PSD-A and PSD-C) resulted in the best viscosity reduction. For example, in experiments performed for a constant filler loading of 0.526 volume fraction (70.0 wt.%), the particle size distribution had a marked effect on the viscosity of the PLE. A 50:50 mixture of PSD-A and PSD-C resulted in a PLE viscosity three times lower than that obtained using only the PSD-A filler, and four times lower than a PLE prepared using a 50:50 mixture of PSD-A and PSD-B. In addition, the 50:50 mixture of PSD-A and PSD-C resulted in a PLE viscosity 40% lower that obtained using a 50:50 mixture of PSD-A and PSD-B. In addition, the 50:50 mixture of PSD-A and PSD-C. The experimental results for the effect of the particle size distribution on the PLE viscosity were well correlated by the Krieger-Dougherty equation to account for the blending of two particle size distributions. Experiments performed to investigate the effect of the silane coupling agent on the viscosity of the PLE revealed that the viscosity decreased slightly with increasing concentration of the coupling agent.

As the fused silica loading was increased from 70.0 to 74.0 wt.%, the PLE viscosity increased markedly. This apparently small increase in the fused silica loading can be important for microelectronic encapsulants because it can lead to a lower coefficient of thermal expansion and an enhanced thermal conductivity. As the amount of fused silica was increased from 70.0 to 72.0 wt.%, the viscosity increased by a factor of 2.3, and as the fused silica loading was increased from 70.0 to 74.0 wt.%, the viscosity increased more than five-fold. The current epoxy molding compounds are solid at room temperature, therefore even the PLE containing 74.0 wt.% fused silica has a much lower viscosity at ambient temperature than the traditional molding compounds. Thus, the

resulting PLEs exhibit low viscosities at ambient temperature while maintaining desirable material properties for microelectronic applications.

5.6. NOMENCLATURE

 D_a = average diameter of the different sizes of the particulates

 D_i = diameter of *i*-th component

 f_i = number fraction of *i*-th component

PLE = photopolymerizable liquid encapsulant

PSD = particle size distribution

 v_i = volume fraction of *i*-th component

 β = parameter in Equations 4 and 5

 η = viscosity of suspension

 η_o = viscosity of suspending medium

 η/η_o = relative viscosity

 $[\eta]$ = intrinsic viscosity

 ϕ = volume fraction

 ϕ_{ml} = maximum packing fraction of first particle size distribution

 ϕ_{m2} = maximum packing fraction of second particle size distribution

 ϕ_m^o = maximum packing fraction of spheres of uniform size = 0.619

	Ф PSD-А	Ф PSD-В	Ø PSD-C
100% PSD-A	0.526	0	-
90% PSD-A, 10% PSD-B	0.474	0.052	-
80% PSD-A, 20% PSD-B	0.421	0.105	-
70% PSD-A, 30% PSD-B	0.368	0.158	-
60% PSD-A, 40% PSD-B	0.316	0.210	-
50% PSD-A, 50% PSD-B	0.263	0.263	-
100% PSD-A	0.526	-	0
90% PSD-A, 10% PSD-C	0.474	-	0.052
80% PSD-A, 20% PSD-C	0.421	-	0.105
70% PSD-A, 30% PSD-C	0.368	-	0.158
60% PSD-A, 40% PSD-C	0.316	-	0.210
50% PSD-A, 50% PSD-C	0.263	-	0.263
100% PSD-B	-	0.526	0
90% PSD-B, 10% PSD-C	-	0.474	0.052
80% PSD-B, 20% PSD-C	-	0.421	0.105
70% PSD-B, 30% PSD-C	-	0.368	0.158
60% PSD-B, 40% PSD-C	-	0.316	0.210
50% PSD-B, 50% PSD-C	-	0.263	0.263

Table 5.1. Volume fractions of individual fused silica distributions in the binary mixtures.

Table 5.2. Viscosity of PLEs with 70.0, 72.0, and 74.0 wt.% fused silica filler.

Wt.% Fused Silica	Viscosity (Pa•s)	Standard Deviation (Pa•s)
70.0	5.92	0.114
72.0	13.9	0.995
74.0	Out of range (>30.0)	-

.



Figure 5.1. Relative viscosity as a function of volume fraction of PSD-A. The balance of the filler is either PSD-B or PSD-C. The viscosity of the suspending medium, η_o , is 0.0456 Pa-s (45.6 cP).



Figure 5.2. Relative viscosity as a function of volume fraction of PSD-C in the filler. The balance of the filler is either PSD-A or PSD-B. The curves correspond to values obtained from the Krieger-Dougherty equation. The viscosity of the suspending medium, η_o , is 0.0456 Pa·s (45.6 cP).



Figure 5.3. Relative viscosity as a function of weight percent of silane coupling agent. The viscosity of the suspending medium, η_o , is 0.0456 Pa•s (45.6 cP).

5.7. **REFERENCES**

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Chapter 6

MECHANICAL AND THERMOMECHANICAL PROPERTIES OF PHOTOPOLYMERIZABLE LIQUID ENCAPSULANTS

6.1. INTRODUCTION

Microelectronic devices are complex and delicate devices that require effective encapsulation and packaging to ensure their long-term reliability. The encapsulant must exhibit excellent physical, electrical, and mechanical properties for the hostile and extreme temperature cycling requirements. Indeed, the mechanical and thermomechanical behavior of the encapsulant plays a key role in the reliability of the microelectronic device.

The encapsulant is typically characterized by a set of mechanical and thermal properties that determine the suitability of the molding compound for a given application and process. Specific tests are performed on encapsulants to ascertain design parameters, guarantee reproducible moldability, assure lot uniformity, and analyze package construction.

In this chapter, an extensive series of studies on the mechanical and thermal properties, as well as the degree of cure of photopolymerizable liquid encapsulants, is described. We have characterized the flexural modulus, flexural strength, coefficient of thermal expansion, glass transition temperature, and thermal stress parameter of PLEs containing 70.0-74.0 wt.% fused silica. In addition, the effects of the illumination time, postcure time, fused silica loading, and the inclusion of a thermal initiator on the thermal and mechanical properties of the final cured encapsulants have been investigated.

6.2. EXPERIMENTAL

6.2.1. Preparation of Photopolymerizable Liquid Encapsulant

The photopolymerizable liquid encapsulant is comprised of a base resin, fused silica filler, photoinitiator, silane coupling agent, and in some cases a thermal initiator. The base resin used in these studies was an epoxy novolac-based vinyl ester resin (DERAKANE 470-45, Dow Chemical) that was chosen for its low initial viscosity 0.0456 Pa•s (45.6 cP) at 25 °C, as well as, its appropriate thermal and mechanical properties upon cure. The photoinitiator used was bis(2,4,6-trimethylbenzoyl) phenylphosphine oxide (IRGACURE 819, Ciba). This photoinitiator, which we will henceforth denote as BAPO, has been shown to be especially appropriate for curing relatively thick polymers and composites due to its efficient photobleaching.^{1,2} In some systems, the thermal initiator, benzoyl peroxide (Aldrich), was used in order to investigate the effects of a dual photo/thermal initiation scheme on the resulting material properties of the encapsulant. The fillers used were crushed (angular), untreated fused silica obtained from MINCO, Inc. silane coupling Α agent, 3methacryloxypropyltrimethoxysilane (Z-6030, Dow Corning), was used to provide a stable bond between the base resin and the fused silica filler, and to improve the processability of the liquid encapsulant formulation.

Fused silica, which is the most common filler for commercial microelectronic encapsulants, was selected for these experiments because it possesses the optimum combination of properties. Specifically, it exhibits a low coefficient of thermal expansion (~ $0.6 \times 10^{-6} \circ C^{-1}$) and a low enough abrasiveness to provide a relatively long molding tool lifetime, especially when compared to aluminum nitride.³ In addition, fused silica is

transparent to UV light, and is therefore appropriate for UV curing.⁴ To minimize the viscosity of the PLE, fused silica products with two different particle size distributions were used: (i) MIN-SIL 40 (volume average particle size = $32.42 \mu m$, median particle size = $22.11 \mu m$) and (ii) MIN-SIL 550 (volume average particle size = $10.37 \mu m$, median particle size = $6.026 \mu m$). In Chapter 5, it was shown that PLEs comprised of a 50:50 wt.% blend of MIN-SIL 40 and MIN-SIL 550 provided the best rheological properties and processability. Therefore, this blend has been used for all of the PLEs in this investigation.

The PLEs were prepared by adding 0.2 wt.% BAPO photoinitiator (based on resin weight) to the epoxy novolac-based vinyl ester resin and stirring at room temperature on a magnetic stir plate until the photoinitiator completely dissolved (~3 minutes). In some cases the thermal initiator, benzoyl peroxide, was also added in the amount of 1.2 wt.% (based on resin weight) and, again the system was stirred until dissolution was complete (~8 minutes). The silane coupling agent was added dropwise to the desired 1 wt.% (based on filler weight) and the resin mixture was stirred on the magnetic stir plate. Fused silica was added in the amount of 70.0, 72.0, or 74.0 wt.% and the system mixed by using a vortex mixer until the filler was completely dispersed and a homogeneous mixture was achieved. The PLE was then degassed in a vacuum oven. Once these steps were completed, the PLE was ready to use for preparing samples required for the material property characterization studies.

6.2.2. Flexural Modulus and Strength

Specimens for flexural testing were prepared by photopolymerizing the liquid encapsulant in rectangular silicone molds with unfiltered UV light (200 mW/cm² UVA

intensity) from a 3000 W arcless mercury vapor lamp (Fusion UV Systems, model F450T). Light intensities were measured (over the 320-390 nm range) using a UVICURE Plus high energy UV integrating radiometer. The specimens were 76.2 mm long, 12.7 mm wide, and 3.2 mm deep. To investigate the effect of the illumination time, the samples were illuminated for 60.0, 90.0, 120.0, 150.0, and 180.0 seconds. To determine the effect of thermal postcure (after UV illumination) on the resulting thermal and mechanical properties, some specimens were postcured at 170°C in a laboratory oven for 2, 4, 6, and 8 hours.

The flexural modulus and strength of the photocured samples were determined using a United SFM-20 instrument in accordance with the ASTM D 790 method. The flexural properties were measured using the three point flexural test with a span length of 50.8 mm (2 inches), a span-to-depth ratio of 16:1, a 454 kg (1000 lb.) load cell, and a downdrive rate of 1.7 mm/min (0.07 in/min). Flexural modulus and strength values were calculated using DATUM 97 software (United Testing Systems).

6.2.3. Degree of Cure

The degree of cure was determined using differential scanning calorimetry (DSC). In these experiments, cure was monitored by measuring the heat released by the sample as the exothermic reaction proceeded. The ultimate conversion achieved during a given set of cure conditions was determined by measuring the additional cure attained at an elevated temperature (180°C) after the completion of the specified cure cycle. Cure conditions that were investigated include: (A) photopolymerization for two minutes without the addition of a thermal initiator, (B) photopolymerization for two minutes without the addition of a thermal initiator followed by postcure for 6 hours at 170°C, (C)

photopolymerization for two minutes with the addition of a thermal initiator, and (D) photopolymerization for two minutes with the addition of a thermal initiator followed by postcure for 6 hours at 170°C. In each of these experiments the photopolymerization was initiated at room temperature using the 3000 Watt Fusion Systems lamp without external heating or cooling. The temperature of 180°C was selected because it is higher than any temperature that the samples experienced during the cure cycles (and higher than the glass transition temperature of the samples) but lower than the degradation temperature of the cured PLEs.

Samples for the DSC experiments were prepared in the following manner. First, rectangular bars of the same dimensions as described above for the flexural tests were prepared according to the four different cure conditions. Four rectangular bars were prepared for each cure condition (all samples contained 74.0 wt.% fused silica). After the cure cycle was complete, a piece was cut from each rectangular bar and ground into smaller pieces with a mortar and pestle to prepare a sample for the DSC studies. The mass of each DSC sample was in the range of 18.0 to 25.0 mg. The samples were weighed both before and after the DSC cure experiment and no change in mass was observed for these solid samples.

The DSC experiments were performed using a Perkin Elmer DSC 7 Differential Scanning Calorimeter interfaced with a computer via the TAC 7/DX Thermal Analysis Instrument Controller. The Perkin Elmer Pyris Software package for Windows was used for the temperature control programs. The experimental procedure was as follows. A solid DSC sample weighing between 18.0 and 25.0 mg was placed in an aluminum DSC pan, which, in turn, was placed in the sample holder of the DSC instrument. An empty aluminum DSC pan was used in the reference holder. After the samples were placed in the DSC pans, the sample cells were rapidly heated from 25°C to 180°C by the DSC instrument. Once a temperature of 180°C was attained (in approximately 30 seconds) the instrument began to collect data for heat flow from the sample as a function of time. The heat flow was measured while the sample was maintained isothermally at 180°C for 150 minutes. It was generally observed that the heat flux from the sample ceased (indicating that the reaction was finished) in less than 20 minutes, therefore the duration of 150 minutes for the experiment was ample time to ensure that the reaction went to completion. For the analysis of the data, the values of the heat flux from the sample were normalized by the mass of the sample.

DSC experiments were also performed on the uncured liquid formulation containing 74 wt.% fused silica. These studies allowed the entire reaction exotherm corresponding to complete cure to be established. Four independent DSC runs were performed on the liquid formulation containing only the photoinitiator and four additional runs were performed on the liquid formulation containing both the photoinitiator and thermal initiator. In each of these experiments, a drop of the liquid formulation with a mass between 18.0 and 25.0 mg was placed in an aluminum DSC pan and an empty aluminum DSC pan was used in the reference holder. The heat flow was measured while the samples were maintained isothermally at 110°C for 250 minutes. A lower temperature was used for these studies to minimize evaporation of the styrene in the resins. The samples were weighed both before and after the experiment to determine how much evaporation took place. The PLE samples with both photoinitiator and thermal initiator lost an average of 1.13% of their total weight, while the PLE samples with only the photoinitiator lost an average of 8.62% of their total weight. As will be shown in Section 6.3.4, the liquid system without the thermal initiator did not polymerize at 110°C since the photoinitiator is stable at this temperature. This explains why more evaporation of the monomer was observed for this case. For the system containing both the photoinitiator and the thermal initiator, the final weight of the sample was used to normalize the heat flow data in the reaction exotherm profile.

6.2.4. Coefficient of Thermal Expansion and Glass Transition Temperature

Specimens for coefficient of thermal expansion (CTE) testing were cut from the samples that had been used for flexural testing so that the thermal stress parameter of the photocured encapsulants could be estimated. The dimensions of the samples were 11.0 mm length x 8.0 mm width x 3.2 mm thickness. All samples were cut using a diamond wafering saw. The CTE below glass transition (α_1) and CTE above glass transition (α_2) were both measured using a DuPont 943 thermomechanical analyzer (TMA) interfaced with a DuPont model 9900 thermal analyzer controller. The samples were heated from room temperature (23°C) to 234°C at a constant rate of 3°C/min. The change in the sample thickness during heating was recorded in the personal computer and α_1 was obtained from the inclined line connecting two points on the TMA curve, 50°C and 70°C. To determine α_2 , the inclined line connecting 200°C and 230°C was used. The glass transition temperature was taken to be the temperature at the intersection of these two lines.

6.3. RESULTS AND DISCUSSION

6.3.1. Effect of UV Illumination Time on Flexural Modulus and Strength

An important mechanical property for microelectronic encapsulants is the flexural modulus, which characterizes the stiffness of a material under an applied load.⁵ The optimal value of the flexural modulus provides a balance between two conflicting requirements. A high value of the flexural modulus is desired to maximize the protection of the chip from an applied load; however, lower values of the flexural modulus lead to lower thermal stresses. Thermal stresses associated with high modulus encapsulants can lead to failure of the microelectronic device. In particular, this stress has been reported to cause interfacial cracking and breakage of the wirebond leads, as well as passivation layer cracking and aluminum pattern deformation.^{6,7} To reduce the thermal shrinkage stresses, while maintaining appropriate protection against mechanical shock, vibration, *etc.*, a flexural modulus near 1000 kg/mm² (9800 MPa) is desired.³

Experimental results for the effect of filler loading and UV illumination time on the flexural modulus and strength of the photocured encapsulants filled with 70.0 to 74.0 wt.% fused silica are shown in Figures 6.1 and 6.2, respectively. All samples contained 1.0 wt.% silane coupling agent (based on filler weight), 0.2 wt.% BAPO (based on resin weight), and the balance epoxy novolac-based vinyl ester resin. Samples were photocured with UV light of 200 mW/cm² UVA intensity. Each bar in these bar charts represents the average of 5 samples and the error bars indicate one standard deviation above and below the mean. As expected, the flexural modulus and flexural strength increase with fused silica content. In addition, the flexural properties do not change significantly as the illumination time is increased beyond 120 seconds. Therefore, 120 seconds was chosen for the in-mold illumination time for subsequent experiments. Note that the values of the flexural modulus are near the desired value of $1000 \text{ kg}/\text{mm}^2$. The results shown in Figure 6.1 suggest that the PLEs could allow the in-mold cure time to be reduced significantly below 120 seconds (which is the typical in-mold cure time for transfer molding compounds). For example, the mechanical properties observed after 90 seconds are essentially equivalent to those after 120 seconds, and an ejectable hardness is certainly achieved even earlier. This result is significant because the in-mold cure time consumes approximately 70% of the overall cycle time and an in-mold cure time reduction of even 15 seconds can translate to a productivity increase of about 10%.³

The data in Figure 6.2 illustrate that the flexural strength of the samples as they are taken from the mold, immediately after illumination, range from 3 to 4.5 kg_f/mm² (~ 30 to 45 MPa). Current microelectronic encapsulants exhibit a flexural strength of at least 9 kg_f/mm², therefore the strength of the PLEs immediately after illumination is below the range of desired values. To address this point, we investigated the effect of a postcure step (after photocuring the samples for 120 seconds) on the flexural modulus and the flexural strength.

6.3.2. Effect of Postcure Time on Flexural Modulus and Strength

After the several minute cycle in the molding tool, almost all molding compounds are postcured for 4 to 8 hours at 170 to 175°C, in order to fully develop the material properties of the encapsulant. Postcuring is a key step in microelectronic encapsulation because encapsulation materials do not reach 100% chemical conversion during the transfer molding process. Typically, the reaction is continued in the mold until the encapsulant reaches a suitable ejectable hardness and then the encapsulant is postcured.

The effects of postcure time and filler loading on the flexural modulus and strength of the photocured encapsulants are shown in Figures 6.3 and 6.4, respectively. Each bar in these bar charts represents the average of 5 samples and the error bars indicate one standard deviation above and below the mean. The results shown in Figures 6.3 and 6.4 illustrate that postcure has little effect on the flexural modulus, but has a significant impact on the flexural strength of the specimens. For example, a comparison of the flexural modulus data for no postcure to the data corresponding to 8 hours of postcure, demonstrates that the values are not significantly different (for all three fused silica loadings, the mean flexural modulus and the associated standard deviations are nearly the same). In contrast, the flexural strength increases consistently as the postcure time is increased from zero to six hours. For example, the samples filled with 74.0 wt.% fused silica exhibit an increase in the flexural strength from a value of 4 kg/mm^2 with no postcure to more than 8 kg/mm² after a postcure time of 6 hours. We attribute the increase in flexural strength associated with the postcure step to additional thermal cure that occurs at the elevated temperatures, and possibly annealing of the polymer. Other authors have reported this result, as well. For example, Cook and Johannson reported significant increases in tensile strength, flexural strength, and fracture toughness for composites postcured at 100°C for 24 hours.⁸ A sample that has vitrified at room temperature can experience additional cure at elevated temperatures due to the enhanced molecular mobility that allows unreacted double bonds to encounter active centers. The enhancement in cure associated with the postcure step was characterized using differential scanning calorimetry, as will be explained in Section 6.3.4.

6.3.3. Effect of Thermal Initiator on Flexural Modulus and Strength

To investigate the effects of a dual photo/thermal initiation scheme, we included the thermal initiator, benzoyl peroxide, in addition to the photoinitiator BAPO in some PLEs. Tables 6.1 and 6.2 both illustrate the effect of the inclusion of the thermal initiator on the flexural strength of the resulting composites. The data in Table 6.1 corresponds to samples that were UV cured for 120 seconds under a light intensity of 200 mW/cm², while the data in Table 6.2 corresponds to samples that were UV cured for 120 seconds under a light intensity of 200 mW/cm² and then postcured for 6 hours at 170°C after UV illumination. In addition to the fused silica at the indicated loading (70.0, 72.0, or 74.0 wt.%), all samples contained 1.0 wt.% silane coupling agent (based on filler weight), 0.2 wt.% BAPO (based on resin weight), and the balance epoxy novolac-based vinyl ester resin. Samples with thermal initiator also contained 1.2 wt.% benzoyl peroxide (based on resin weight). The reported flexural strength values are the average of five samples, and the indicated range corresponds to one standard deviation.

The data in Tables 6.1 and 6.2 illustrate that the inclusion of the thermal initiator has a significant effect on the flexural strength of the cured encapsulants (for each filler loading, the flexural strength increased by approximately $2 \text{ kg}/\text{mm}^2$ upon the addition of the thermal initiator). As illustrated by the calorimetric studies described in the next section, the increase in the flexural strength can be attributed to an enhancement in the degree of cure associated with the addition of the thermal initiator. Moreover, a 6 hour postcure step at 170°C also enhances the flexural strength of the encapsulants containing both the photoinitiator and thermal initiator. The flexural strength of the samples containing the thermal initiator and 72.0 or 74.0 wt.% fused silica (and postcured for 6 hours) now fall in the range of typical flexural strength values for encapsulants.

The effect of the thermal initiator on the flexural modulus of the cured encapsulants is illustrated by the data in Tables 6.3 and 6.4. The data in Table 6.3 corresponds to samples that were UV cured for 120 seconds under a light intensity of 200 mW/cm^2 , while the data in Table 6.4 corresponds to samples that were UV cured for 120 seconds under a light intensity of 200 mW/cm² and then postcured for 6 hours at 170°C after UV illumination. In addition to the fused silica at the indicated loadings (70.0, 72.0, or 74.0 wt.%), all samples contained 1.0 wt.% silane coupling agent (based on filler weight), 0.2 wt.% BAPO (based on resin weight), and the balance epoxy novolac-based Samples with thermal initiator also contained 1.2 wt.% benzoyl vinyl ester resin. peroxide (based on resin weight). The reported flexural modulus values are the average of five samples, and the indicated range corresponds to one standard deviation. The data in Tables 6.3 and 6.4 illustrate that the values of the flexural modulus for the samples containing both the photoinitiator and thermal initiator are essentially equivalent to those for the samples containing only a photoinitiator. In addition, the values of the flexural modulus are close to the 1000 kg_f/mm² value recommended by Manzione for microelectronic encapsulants.³

6.3.4. Degree of Cure

The degree of cure was determined using differential scanning calorimetry by measuring the heat released from the sample as the exothermic reaction proceeded. The ultimate conversion achieved during a given set of cure conditions was determined by measuring the additional cure attained at an elevated temperature after the completion of

the specified cure cycle. These experiments were performed to investigate the effect of postcure and the inclusion of the thermal initiator on the additional cure. To find the conversion attained during this additional cure, the total heat released from the solid samples (that had gone through a given cure cycle) was divided by the total heat released from the liquid formulation.

A representative reaction DSC profile for the uncured liquid formulation containing both the photoinitiator and thermal initiator is shown in Figure 6.5. This figure contains a plot of the heat flow from the sample as a function of time and the reaction profile exhibits a shape that is characteristic of free radical polymerizations.⁹ Since the polymerization reaction is exothermic, the area under this curve is proportional to the degree of cure. Although the data was collected for 150 minutes, the cure was generally complete (the profile becomes horizontal) in ~15 minutes, as illustrated in Figure 6.5. The baseline for integrating the area under the curve was established by horizontal extrapolation of the final steady-state value. The integration was performed using the commercial data analysis software package Origin 5.0 (Microcal Software, Inc.).

Cure conditions that were investigated in this study include: (A) photopolymerization for two minutes without the addition of a thermal initiator, (B) photopolymerization for two minutes without the addition of a thermal initiator followed by postcure for 6 hours at 170°C, (C) photopolymerization for two minutes with the addition of a thermal initiator, and (D) photopolymerization for two minutes with the addition of a thermal initiator followed by postcure for 6 hours at 170°C, and (D) photopolymerization for two minutes with the addition of a thermal initiator followed by postcure for 6 hours at 170°C. These samples will henceforth be referred to as A, B, C, and D, respectively. After the given cure cycle,

each photopolymerized (solid) encapsulant was subject to a DSC postbake at 180°C for 150 minutes. Based upon the heat released during this DSC postbake experiment, the degree of cure was determined indirectly by measuring the additional cure that could be attained at this elevated temperature. For a given solid sample, the additional degree of cure was determined by dividing the area under the corresponding DSC reaction profile by the area corresponding to complete cure. The latter value was obtained from the reaction exotherm exhibited by the previously unreacted liquid formulation (Sample E). The experimental data for samples containing 74 wt.% silica is shown in Table 6.5. The values in this table represent the average of four samples, and the indicated range corresponds to one standard deviation.

The data in Table 6.5 help to explain the effect of the cure cycle on the flexural strength that was identified in the previous section. Recall that flexural strength was enhanced by postcure and by the presence of the thermal initiator. The data in Table 6.5 illustrate that either of these factors leads to a significant enhancement in the conversion attained during the cure cycle (an enhancement of ~8%). For example, the effect of postcure is illustrated by comparing the data for Sample A to that for Sample B, while the effect of the inclusion of the thermal initiator is illustrated by comparing the data for Sample A to that for Sample B, while the samples may arise from an increased degree of cure. The data for Sample D further illustrate that the highest degree of cure is obtained if a thermal initiator is included and the sample is subject to postcure. This is the sample that also exhibited the highest flexural strength; however, if Sample D is compared to Sample B or Sample C, it is

unclear why the relatively small increase in conversion would lead to the relatively large increase in the flexural strength.

6.3.5. Effect of Postcure Time on CTE below Glass Transition

The linear coefficient of thermal expansion (CTE) is defined as the ratio of the change in the length of the sample to the change in temperature per unit initial length.¹⁰ This parameter is very important in semiconductor encapsulation because a significant CTE mismatch between the encapsulant, leadframe, and the silicon chip can lead to the build up of internal stresses in the semiconductor device, and could lead to cracking of the chip or encapsulant. Current encapsulants exhibit α_1 values (CTE below glass transition) in the range of 16-25 µm/m°C, while copper leadframes possess a value of 16-17 µm/m°C and silicon exhibits a value of 3-4 µm/m°C.¹¹ The service temperature for microelectronic encapsulants is typically between 75 and 85°C, which is well below the glass transition temperature of the encapsulant.³ For this reason, the value of the CTE above the glass transition temperature, α_2 , is not as important as the CTE below the glass transition temperature, α_1 .

For the PLEs, the experimental results for the coefficient of thermal expansion below glass transition are shown in Figure 6.6. Figure 6.6 illustrates the effect of the postcure time on the observed CTE for samples filled with 70.0 to 74.0 wt.% fused silica. All samples contained 1.0 wt.% silane coupling agent (based on filler weight), 0.2 wt.% BAPO (based on resin weight), and the balance epoxy novolac-based vinyl ester resin. Each bar in the following bar charts represents the average of 5 samples and the error bars indicate one standard deviation above and below the mean. The data illustrate that for all three filler loadings, a significant reduction in α_1 is observed after just 2 hours of postcure. This reduced value of the CTE may be attributed to the enhanced cure (~8% additional cure as determined using calorimetry) associated with the postcure step. Most of this additional cure occurs within the first two hours of postcure. After a two hour postcure, all of the photocured samples exhibit α_1 values well within the range required for current encapsulants. As expected, α_1 decreased as the fused silica loading was increased from 70.0 to 74.0 wt.%. The 74.0 wt.% silica system looks especially promising for microelectronic encapsulants because of its low α_1 value (~20 µm/m°C).

6.3.6. Effect of Thermal Initiator on CTE below Glass Transition

The effect of the inclusion of the thermal initiator on the value of α_1 is illustrated in Table 6.6. All samples contained 70.0, 72.0, or 74.0 wt.% fused silica, 1.0 wt.% silane coupling agent (based on filler weight), 0.2 wt.% BAPO (based on resin weight), and the balance epoxy novolac-based vinyl ester resin. Samples with thermal initiator also contained 1.2 wt.% benzoyl peroxide (based on resin weight). All samples were photocured for 2 minutes with UV light of 200 mW/cm² UVA intensity and then postcured for 6 hours at 170°C in a laboratory oven. CTE values are the average of five samples, and the indicated range corresponds to one standard deviation. The data illustrate that the thermal initiator does not have any appreciable effect on the value of α_1 . For all three fused silica loadings, the mean α_1 values and the associated standard deviations are nearly the same.

6.3.7. Effect of Postcure Time and Thermal Initiator on CTE above Glass Transition

The CTE above the glass transition temperature, α_2 , was also measured as a function of filler loading and postcure time for systems containing only the photoinitiator, as well as, for systems containing both the photoinitiator and thermal initiators. Figure

6.7 illustrates the effect of the postcure time on the CTE above glass transition for samples filled with 70.0 to 74.0 wt.% fused silica and containing only the photoinitiator. All samples contained 1.0 wt.% silane coupling agent (based on filler weight), 0.2 wt.% BAPO (based on resin weight), and the balance epoxy novolac-based vinyl ester resin. Figure 6.7 illustrates that the CTE above glass transition decreases with an increase in fused silica content and is essentially independent of the postcure time. In addition, all of the values ranged between 55 and 65 μ m/m°C.

The values for the samples postcured for six hours and containing 70.0, 72.0, and 74.0 wt.% fused silica (and no thermal initiator) were 66.74 ± 3.45 , 61.78 ± 1.70 , and $56.68 \pm 2.91 \,\mu\text{m/m}^\circ\text{C}$, respectively. The values for the samples postcured for six hours and containing 70.0, 72.0, and 74.0 wt.% fused silica (and both photoinitiator and thermal initiator) were 69.44 ± 1.30 , 63.46 ± 2.37 , and $59.24 \pm 2.39 \,\mu\text{m/m}^\circ\text{C}$, respectively. These values were essentially independent of the presence of the thermal initiator.

6.3.8. Effect of Postcure Time on Glass Transition Temperature

To provide effective protection of the microelectronic device, an encapsulant must exist in the glassy state at the use temperature ($\sim 80^{\circ}$ C). Commercial encapsulants typically exhibit glass transition temperatures in the range of 140 to 180°C. Figure 6.8 shows experimental data for the glass transition temperature of the photopolymerized encapsulants as a function of the postcure time for samples containing 70.0, 72.0, and 74.0 wt.% fused silica. As expected, the glass transition temperature generally increases with increasing postcure time, and reaches a plateau in \sim 6 hours, consistent with the previous results for the flexural strength and the CTE. After 2 hours of postcure, all of

the samples exhibited glass transition values between 145 and 155°C, within the range required for microelectronic encapsulants.

6.3.9. Effect of Thermal Initiator on Glass Transition Temperature

The effect of the thermal initiator on the glass transition temperature is illustrated in Table 6.7. All samples contained 70.0, 72.0, or 74.0 wt.% fused silica, 1.0 wt.% silane coupling agent (based on filler weight), 0.2 wt.% BAPO (based on resin weight), and the balance epoxy novolac-based vinyl ester resin. Samples with thermal initiator also contained 1.2 wt.% benzoyl peroxide (based on resin weight). All samples were photocured for 2 minutes with UV light of 200 mW/cm² UVA intensity and then postcured for 6 hours at 170°C in a laboratory oven. Glass transition temperatures are the average of five samples, and the indicated range corresponds to one standard deviation. The data illustrate that the samples exhibit glass transition temperatures appropriate for microelectronic encapsulants, and that the presence of the thermal initiator has little effect on the glass transition temperature.

6.3.10. Thermal Stress Parameter

As was mentioned previously, lowering the stress parameter leads to improved device reliability. The thermal stress parameter, σ^* , is typically calculated using Equation 6.1.³

$$\sigma' = (\alpha_{pg} - \alpha_i) E_{pg} (T_g - T_l)$$
(6.1)

Here α_{pg} represents the coefficient of thermal expansion below glass transition of the encapsulation material, α_i is the coefficient of thermal expansion of the silicon device or metal leadframe, E_{pg} is the modulus of elasticity (tensile or flexural) of the encapsulant, and T_g is the glass transition temperature of the encapsulant (°C). In order to evaluate the

thermal stress parameter for the photopolymerized encapsulants of this study, the experimental values for α_{pg} , E_{pg} (flexural) and T_g were substituted into this equation along with literature values for α_i and T_I . Specifically, we used the CTE of a copper metal leadframe (16.3 µm/m°C) for α_i and -65°C for T_I , since this is the usual starting temperature for temperature cycling tests as specified by Mil. Std. 38510 Group D.³

Data for the thermal stress parameter of photopolymerized encapsulants with and without the thermal initiator are shown in Table 6.8. All samples contained 70.0, 72.0, or 74.0 wt.% fused silica, 1.0 wt.% silane coupling agent (based on filler weight), 0.2 wt.% BAPO (based on resin weight), and the balance epoxy novolac-based vinyl ester resin. Samples with thermal initiator also contained 1.2 wt.% benzovl peroxide (based on resin weight). All samples were photocured for 2 minutes with UV light of 200 mW/cm² UVA intensity and then postcured for 6 hours at 170°C in a laboratory oven. Thermal stress parameter values are the average of five samples, and the indicated range corresponds to one standard deviation. First of all, the data illustrate that the presence of the thermal initiator has little, if any, effect on the thermal stress parameter. More importantly, Table 6.8 illustrates that the photopolymerized encapsulants containing 74.0 wt.% fused silica exhibit a thermal stress parameter between 1.0 and 1.2 kg/mm². These values compare quite favorably to those reported for current encapsulants. For example, using the literature values for α_{pg} , E_{pg} (flexural) and T_g , reported by Nakamura et al.¹² and Lin et al.¹³ along with the previously mentioned values for α_i and T_i , (16.3 µm/m°C and -65°C, respectively) current epoxy encapsulants exhibit a thermal stress parameter of ~1.3 kg_f/mm^2 .

6.4. CONCLUSIONS

In this chapter, we have characterized the degree of cure, flexural modulus, flexural strength, coefficient of thermal expansion, glass transition temperature, and thermal stress parameter of novel photopolymerizable liquid encapsulants comprised of an epoxy novolac-based vinyl ester resin (~25 wt.%), fused silica (70-74 wt.%), and small amounts of a photoinitiator, silane coupling agent, and in some cases, a thermal initiator. The effects of the fused silica loading, UV illumination time, and postcure time on these thermal and mechanical properties were also investigated. The results indicate that a photocurable encapsulant loaded with 74.0 wt.% fused silica is very promising for this application since the material properties (flexural strength, flexural modulus, coefficient of thermal expansion, glass transition temperature, and thermal stress parameter) meet or exceed those of current commercial encapsulants, while the viscosity and in-mold cure time are reduced. These formulations are liquid at room temperature (current formulations are solid) and cure to an ejectable hardness in less than two minutes for an initiating light intensity of 200 mW/cm^2 . The photocured samples exhibit appropriate values for the above mentioned material properties. Specific observations are as follows:

 The flexural modulus and flexural strength increased with UV light illumination time until reaching a plateau value in ~90 to 120 seconds. This result indicates that the inmold cure time of the PLEs could be as low 75 or 90 seconds at a moderate light intensity of 200 mW/cm².

- The flexural strength and glass transition temperature increased with increasing postcure time at 170°C before reaching a plateau in ~4 to 6 hours. Current encapsulants are typically postcured 4 to 8 hours at 170 or 175°C.
- The coefficient of thermal expansion below the glass transition decreased with increasing postcure time at 170°C before reaching a plateau in ~4 to 6 hours.
- 4. Inclusion of a thermal initiator, benzoyl peroxide, in the photopolymerizable liquid encapsulant significantly increased the flexural strength of the samples, but had little effect on the other material properties;
- 5. The ultimate degree of cure attained in a given cure cycle was significantly enhanced by the inclusion of a thermal initiator (in addition to the photoinitiator) and by postcure at an elevated temperature.



Figure 6.1. Flexural modulus as a function of UV illumination time for samples containing 70.0, 72.0, and 74.0 wt.% fused silica.



Figure 6.2. Flexural strength as a function of UV illumination time for samples containing 70.0, 72.0, and 74.0 wt.% fused silica.



Figure 6.3. Flexural modulus as a function of postcure time for samples containing 70.0, 72.0, and 74.0 wt.% fused silica. Samples were photocured for 2 minutes with UV light of 200 mWcm² UVA intensity and then postcured at 170°C in a laboratory oven.



Figure 6.4. Flexural strength as a function of postcure time for samples containing 70.0, 72.0, and 74.0 wt.% fused silica. Samples were photocured for 2 minutes with UV light of 200 mW/cm² UVA intensity and then postcured at 170°C in a laboratory oven.



Figure 6.5. Representative DSC reaction profile at 110°C for the liquid formulation containing 74.0 wt.% fused silica, 1.0 wt.% silane coupling agent (based on filler weight), 0.2 wt.% BAPO (based on resin weight), 1.2 wt.% benzoyl peroxide (based on resin weight), and the balance epoxy novolac-based vinyl ester resin.


Figure 6.6. CTE below glass transition as a function of postcure time for samples containing 70.0, 72.0, and 74.0 wt.% fused silica. Samples were photocured for 2 minutes with UV light of 200 mW/cm² UVA intensity and then postcured at 170°C in a laboratory oven.



Figure 6.7. CTE above glass transition as a function of postcure time for samples containing 70.0, 72.0, and 74.0 wt.% fused silica. Samples were photocured for 2 minutes with UV light of 200 mW/cm² UVA intensity and then postcured at 170°C in a laboratory oven.



Figure 6.8. Glass transition temperature as a function of postcure time for samples containing 70.0, 72.0, and 74.0 wt.% fused silica. Samples were photocured for 2 minutes with UV light of 200 mW/cm² UVA intensity and then postcured at 170°C in a laboratory oven.

Wt.% Fused Silica	Flexural Strength (kg _f /mm ²) Without Thermal Initiator	Flexural Strength (kg _f /mm ²) With Thermal Initiator
70.0	3.70 ± 0.52	5.25 ± 0.38
72.0	3.92 ± 0.23	5.50 ± 0.65
74.0	4.24 ± 0.38	5.71 ± 0.36

Table 6.1. Effect of the inclusion of thermal initiator on flexural strength for samples that were not postcured.

Table 6.2. Effect of the inclusion of thermal initiator on flexural strength for samples that were postcured for 6 hours.

Wt.% Fused Silica	Flexural Strength (kg _f /mm ²) Without Thermal Initiator	Flexural Strength (kg _f /mm ²) With Thermal Initiator
70.0	6.71 ± 0.69	8.83 ± 1.68
72.0	7.59 ± 0.24	9.28 ± 0.95
74.0	8.12 ± 0.69	9.92 ± 1.44

Table 6.3. Effect of the inclusion of thermal initiator on flexural modulus for samples that were not postcured.

Wt.% Fused Silica	Flexural Modulus (kg _f /mm ²) Without Thermal Initiator	Flexural Modulus (kg _f /mm ²) With Thermal Initiator
70.0	995.28 ± 130.20	939.12 ± 111.47
72.0	1076.50 ± 59.27	1051.48 ± 89.64
74.0	1166.24 ± 55.73	1121.40 ± 88.30

Wt.% Fused Silica	Flexural Modulus (kg _f /mm ²) Without Thermal Initiator	Flexural Modulus (kg _f /mm ²) With Thermal Initiator
70.0	1059.24 ± 111.18	973.40 ± 89.13
72.0	1160.11 ± 62.23	1139.05 ± 123.83
74.0	1240.38 ± 96.62	1206.61 ± 116.55

Table 6.4. Effect of the inclusion of thermal initiator on flexural modulus for samples that were postcured for 6 hours.

Table 6.5. Heat released during DSC postbake and additional cure for photopolymerized encapsulants subject to various cure cycles.

	Sample A	Sample B	Sample C	Sample D	Sample E
Heat Released (J/g resin)	26.36 ± 0.97	2.80 ± 1.22	2.41 ± 0.58	1.02 ± 0.24	323.87 ± 11.91
Additional Cure (%)	8.14	0.86	0.74	0.31	-

Table 6.6. Effect of thermal initiator on the CTE below glass transition of the photopolymerized encapsulants.

Wt.% Fused Silica	α ₁ (µm/m°C) Without Thermal Initiator	α ₁ (µm/m°C) With Thermal Initiator
70.0	22.26 ± 0.63	22.70 ± 1.10
72.0	22.62 ± 0.64	20.92 ± 0.54
74.0	20.50 ± 0.57	20.12 ± 1.41

Wt.% Fused Silica	Glass Transition Temperature (°C) Without	Glass Transition Temperature (°C) With
	Thermal Initiator	Thermal Initiator
70.0	148 ± 2	150 ± 2
72.0	150 ± 4	151 ± 1
74.0	152 ± 3	150 ± 1

Table 6.7. Effect of thermal initiator on the glass transition temperature of the photopolymerized encapsulants.

Table 6.8. Effect of thermal initiator on thermal stress parameter of the photopolymerized encapsulants.

Wt.% Fused Silica	σ* (kg _f /mm ²) Without Thermal Initiator	σ* (kg _f /mm ²) With Thermal Initiator
70.0	1.34 ± 0.20	1.35 ± 0.32
72.0	1.58 ± 0.20	1.14 ± 0.23
74.0	1.13 ± 0.19	1.02 ± 0.47

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Chapter 7

EVALUATION OF REDUCED IN-MOLD CURE TIMES FOR PHOTOPOLYMERIZABLE LIQUID ENCAPSULANTS

7.1. INTRODUCTION

In conventional transfer molding processes used to encapsulate microelectronic devices, the in-mold cure consumes the majority of the cycle time. For this reason, reducing the in-mold cure times of molding compounds is the most efficient way to reduce cycle times and increase productivity. For example, the in-mold cure time consumes approximately 70% of the overall cycle time and an in-mold cure time reduction of even 15 seconds can translate to a productivity increase of about 10%.¹ With conventional systems, the cure time required before the parts can be ejected from the mold varies from 2 to 3 minutes. However, future developments will require in-mold cure times to be in the range of 60-90 seconds to achieve an overall cycle time of 2 minutes.¹

Photopolymerizable liquid encapsulants (PLEs) are promising for reducing the inmold cure time compared to conventional thermal systems. As was shown in Chapter 6, PLE samples containing a thermal initiator that were photocured for 120 seconds and then postcured for 6 hours have the necessary material properties required by the microelectronics industry. These results demonstrate that an in-mold cure time of 2 minutes is achievable using PLEs. However, since future productivity requirements necessitate even shorter in-mold cure times, the objective of this chapter is to determine if the UV illumination time (which corresponds to the in-mold cure time) for the PLEs can be reduced even further (while still retaining the 6 hour postcure step at 170°C). Specifically, in this chapter we will examine the material properties (flexural strength and modulus, coefficients below and above glass transition, glass transition temperature, and thermal stress parameter) of PLEs cured with UV illumination times of 60 and 90 seconds. In addition, the effects of both UV initiation (using only a photoinitiator) and dual initiation (using both a photo- and thermal initiator) will be examined.

7.2. EXPERIMENTAL

7.2.1. Preparation of Photopolymerizable Liquid Encapsulant

The photopolymerizable liquid encapsulant is composed of a base resin, photoinitiator, thermal initiator, fused silica filler, and silane coupling agent. The base resin used in these studies was DERAKANE 470-45 (Dow Chemical), an epoxy novolac-based vinyl ester resin that was chosen primarily for its low initial viscosity (0.0456 Pa·s or 45.6 cP at 30°C). The photoinitiator used was bis(2,4,6-trimethylbenzoyl) phenylphosphine oxide (IRGACURE 819, Ciba) and was selected because of its effective photobleaching in the wavelength range of 360-450 nm. The thermal initiator, benzoyl peroxide (Aldrich), was also used in order to determine the effects of a dual initiation scheme on the resulting material properties. The fillers used were all crushed (angular), untreated fused silica obtained from MINCO, Inc. Fused silica was selected because it is the most commonly used filler in transfer molding compounds and it possesses the optimum combination of properties. Fused silica products with two different particle size distributions were used: (i) MIN-SIL 40 (median particle size = $22.11 \mu m$) and (ii) MIN-SIL 550 (median particle size = $6.03 \mu m$). All compositions used a 50:50 wt.% blend of

MIN-SIL 40 to MIN-SIL 550 for a particular filler loading, as this was found to result in a formulation with a low initial viscosity and improved processability. In addition, a silane coupling agent, 3-methacryloxypropyl-trimethoxysilane (Z-6030, Dow Corning), was used to provide a stable bond between the base resin and the fused silica filler, as well as, to improve the processability of the liquid encapsulant formulation.

Photocurable formulations were prepared by adding 0.2 wt.% (based on resin weight) of IRGACURE 819 photoinitiator to DERAKANE 470-45 resin and stirring at room temperature on a magnetic stir plate until the photoinitiator completely dissolved. The silane coupling agent was then added dropwise to the desired 1 wt.% (based on filler weight) and the formulation was again mixed. Fused silica in the amount of 70.0, 72.0, or 74.0 wt.% was added to the formulation and mixed by using a vortex mixer until the filler was completely dispersed and a homogeneous mixture was achieved. The formulation was then degassed in a vacuum oven. Once these steps were completed, the photocurable formulation was ready to use for preparing samples required for the material property characterization studies.

To determine the effects of a dual initiation scheme, the thermal initiator, benzoyl peroxide, was also added to the liquid formulation. In this case, benzoyl peroxide in the amount of 1.2 wt.% (based on resin weight) was added (after the photoinitiator had completely dissolved) and stirred until complete dissolution.

7.2.2. Flexural Modulus and Strength

Specimens for flexural testing were prepared by photopolymerizing the liquid encapsulant formulation in rectangular-shaped, silicone molds with unfiltered UV light of 200 mW/cm² UVA intensity from a 3000 W arcless mercury vapor lamp (Fusion UV

Systems, model F450T). Light intensities were measured using a UVICURE Plus high energy UV integrating radiometer (over the 320-390 nm range). Specimens were 76.2 mm length x 12.7 mm width x 3.2 mm depth and were photocured for various times (60, 90, and 120 seconds). To fully develop the material properties, specimens were postcured at 170°C in a laboratory oven for 6 hours after UV curing.

The flexural strength and modulus of the photocured samples were determined using a United SFM-20 instrument in accordance with the ASTM D 790 method. The flexural properties were measured using the three point flexural test with a span length of 50.8 mm (2 inches), a 454 kg (1000 lb.) load cell, and a downdrive rate of 1.9 mm/min (0.07 in/min). Flexural strength and modulus values were calculated using DATUM 97 software (United Testing Systems).

7.2.3. Coefficient of Thermal Expansion and Glass Transition Temperature

Specimens for coefficient of thermal expansion (CTE) testing were cut from the samples used for flexural testing so that the thermal stress parameter of the photocured encapsulants could be estimated. Dimensions of the cut-away samples were approximately 11 mm length x 8 mm width x 3.2 mm thickness. All samples were cut using a diamond wafering saw. The CTE below the glass transition (α_1) and CTE above glass transition (α_2) were both measured using a DuPont 943 thermomechanical analyzer (TMA) interfaced with a DuPont model 9900 thermal analyzer controller. The photopolymerized samples were heated from room temperature (23°C) to 234°C at a constant rate of 3°C/min. The change in the sample thickness during heating was recorded in the personal computer and α_1 was obtained from the inclined line connecting two points on the TMA curve, 50°C and 70°C. To determine α_2 , the inclined line

connecting 200°C and 230°C was used. The glass transition temperature was taken to be the temperature at the intersection of these two lines.

7.3. RESULTS AND DISCUSSION

7.3.1. Flexural Modulus and Strength

Encapsulants must have excellent mechanical properties in order to withstand mechanical shock, vibration, and handling during assembly. One of the more important mechanical properties is the flexural modulus, which characterizes the stiffness of a material under an applied load (it is the slope of a plot of stress versus strain in the elastic portion of the curve).² By reducing the flexural modulus, the thermal stress (also known as the stress parameter) is also reduced, and recent research indicates that this leads to improved device reliability. In particular, this stress causes interfacial cracking and breakage of wirebond leading, as well as, passivation layer cracking and aluminum pattern deformation.^{3,4} To reduce the thermal shrinkage stresses, a flexural modulus near or below 1000 kg/mm² is recommended.¹

7.3.2. Effect of Reduced UV Illumination Times on Flexural Modulus and Strength

Table 7.1 shows the effect of reduced UV illumination times on flexural modulus for both UV-initiated and dual initiated samples containing 70.0, 72.0, and 74.0 wt.% fused silica. Each entry in Table 7.1 represents the average of 5 samples and the range corresponds to one standard deviation above and below the mean. All samples contained 1.0 wt.% silane coupling agent (based on filler weight), 0.2 wt.% BAPO (based on resin weight), 1.2 wt.% benzoyl peroxide (based on resin weight), and the balance epoxy novolac-based vinyl ester resin. Samples were photocured with UV light of 200 mW/cm² UVA intensity and then postcured for 6 hours at 170°C in a laboratory oven. From Table 7.1, it can be seen that a reduction in UV illumination time followed by postcure has no deleterious effect on the flexural modulus of the PLEs. All of the PLEs (including those cured for only 60 seconds) had sufficient green strength to maintain their shape and integrity when ejected from the mold. In addition, after postcure, all samples exhibited flexural modulus values near the desired value of 1000 kgr/mm². For example, flexural modulus values for samples filled with 70.0 wt.% fused silica ranged from 940 to 1060 kgr/mm², those with 72.0 wt.% fused silica had modulus values between 1020 and 1160 kgr/mm². In addition, in agreement with the results from Chapter 6, the inclusion of the thermal initiator has no effect on the flexural modulus.

Table 7.2 illustrates the effect of reduced UV illumination times on flexural strength for both UV-initiated and dual initiated samples containing 70.0, 72.0, and 74.0 wt.% fused silica. From Table 7.2, two findings are evident. First, in agreement with our results from Chapter 6, the inclusion of the thermal initiator increases the flexural strength of the PLEs, typically by 1 to 2 kg_f/mm². The flexural strength values for samples with the thermal initiator, again, meet the requirements for molding compounds (flexural strength values of at least 9 kg_f/mm²). Second, the flexural strengths for UV illumination times of 60 seconds and 90 seconds are essentially equivalent to the values of 120 seconds. This is further evidence that the in-mold cure time of the PLEs can be successfully reduced to 60 seconds.

7.3.3. Effect of Reduced UV Illumination Times on Coefficient of Thermal Expansion below Glass Transition

The linear coefficient of thermal expansion (CTE) is defined as the ratio of the change in the length of the sample to the change in temperature per unit initial length.⁵

This parameter is very important in semiconductor encapsulation because a significant CTE mismatch between the encapsulant, leadframe, and the silicon chip can lead to the build up of internal stresses in the semiconductor device, and could lead to cracking of the chip or encapsulant. Current encapsulants exhibit α_1 values (CTE below glass transition) in the range of 15-30 µm/m°C, while copper leadframes possess a value of 16-17 µm/m°C and silicon exhibits a value of 3-4 µm/m°C.⁶ The service temperature for microelectronic encapsulants is typically between 75 and 85°C, which is well below the glass transition temperature of the encapsulant.¹ For this reason, the value of the CTE above the glass transition temperature, α_2 , is not as important as the CTE below the glass transition temperature, α_1 .

Table 7.3 shows the effect of reduced UV illumination times on the coefficient of thermal expansion below glass transition for samples that were photocured with UV light of 200 mW/cm² UVA intensity and then postcured for 6 hours at 170°C. Again, each entry in Table 7.3 represents the average of 5 samples and the range corresponds to one standard deviation above and below the mean. All samples contained 1.0 wt.% silane coupling agent (based on filler weight), 0.2 wt.% BAPO (based on resin weight), 1.2 wt.% benzoyl peroxide (based on resin weight), and the balance epoxy novolac-based vinyl ester resin. Samples were photocured with UV light of 200 mW/cm² UVA intensity and then postcured for 6 hours at 170°C in a laboratory oven. From Table 7.3, again, there is no significant difference in α_1 between specimens photopolymerized for 60 seconds (and then postcured for 6 hours) and specimens photopolymerized for 90 and 120 seconds (and then postcured for 6 hours). This is to be expected, since the reduction

in the coefficient of thermal expansion occurs primarily in the postcure step. In addition, the addition of the thermal initiator has little effect on α_1 .

7.3.4. Effect of Reduced UV Illumination Times on Coefficient of Thermal Expansion above Glass Transition

Table 7.4 shows the effect of reduced UV illumination times on the coefficient of thermal expansion above glass transition for samples that were photocured with UV light of 200 mW/cm² UVA intensity and then postcured for 6 hours at 170°C. The results are similar to the results for the coefficient of thermal expansion below glass transition. Table 7.4 illustrates that the CTE above glass transition decreases with an increase in fused silica content and is essentially independent of both the illumination time and the inclusion of a thermal initiator.

7.3.5. Effect of Reduced UV Illumination Times on Glass Transition Temperature

Table 7.5 shows the effect of reduced UV illumination times on the glass transition temperature (T_g) for samples that were photocured with UV light of 200 mW/cm² UVA intensity and then postcured for 6 hours at 170°C. The T_g values range between 152 and 155°C for samples that were photocured for 60 seconds and postcured for 6 hours, while the observed T_g values fell between 148 and 152°C for samples that were photocured for 6 hours). Therefore, as in the previous chapter, the glass transition temperature for all of the PLE samples is observed to be around 150°C.

7.3.6. Effect of Reduced UV Illumination Times on Thermal Stress Parameter

Table 7.6 shows the effect of reduced UV illumination times on the thermal stress parameter (σ^{\bullet}) for samples that were photocured with UV light of 200 mW/cm² UVA

intensity and then postcured for 6 hours at 170°C. The thermal stress parameter, which is calculated using Equation 6.1, depends upon the flexural modulus, the coefficient of thermal expansion below glass transition, and the glass transition temperature. The relatively high degree of uncertainty in the values of σ^* shown in Table 7.6 arises from the combined uncertainty of the three material properties used in the calculation. As the value of σ^* increases, the likelihood of thermally induced stresses also increases. Therefore low values of σ^* are desired. Conventional microelectronic encapsulants typically exhibit thermal stress parameters between 0.5 and 1.5 kg/mm². The data in Table 7.6 illustrate that the PLEs in this study generally exhibit σ^* values ranging from 0.6 to 1.3 kg/mm², and are therefore within the range of values exhibited by current encapsulants.

7.4. CONCLUSIONS

Current trends in microelectronic encapsulation will require in-mold cure times for molding materials to be reduced from 120 seconds to 60-90 seconds. With current thermally cured systems this reduced cure time is difficult to achieve. In this chapter, we have shown that photopolymerizable liquid encapsulants (PLEs) based upon epoxy novolac-based vinyl ester resins filled with fused silica can meet this requirement. Photopolymerizable liquid encapsulants that were photocured for 60 and 90 seconds had appropriate ejectable hardness, and upon postcure, exhibited material properties (flexural strength and modulus, coefficient of thermal expansion, glass transition temperature, and thermal stress parameter) that were equivalent or better than those of conventional encapsulants. It was also shown that the addition of a thermal initiator does not negatively affect any of the material properties, and leads to improved flexural strength.

Table 7.1. Effect of reduced UV illumination times on flexural modulus for both UV-initiated and dual initiated samples containing 70.0, 72.0, and 74.0 wt.% fused silica. Samples were photocured with UV light of 200 mW/cm² UVA intensity and then postcured for 6 hours at 170°C.

UV Illumination Time (seconds)	Wt.% Fused Silica	Flexural Modulus (kg _f /mm ²) Without Thermal Initiator	Flexural Modulus (kg _f /mm ²) With Thermal Initiator
60	70.0	987.97 ± 49.80	1059.77 ± 131.59
60	72.0	1163.80 ± 72.36	1118.11 ± 81.59
60	74.0	1209.34 ± 98.95	1247.32 ± 66.39
90	70.0	945.18 ± 44.39	966.90 ± 59.53
90	72.0	1023.84 ± 111.34	1119.90 ± 157.61
90	74.0	1254.49 ± 137.12	1234.05 ± 108.82
120	70.0	1059.25 ± 111.18	973.40 ± 89.13
120	72.0	1160.11 ± 62.23	1139.05 ± 123.83
120	74.0	1240.38 ± 96.62	1206.61 ± 116.55

Table 7.2. Effect of reduced UV illumination times on flexural strength for both UVinitiated and dual initiated samples containing 70.0, 72.0, and 74.0 wt.% fused silica. Samples were photocured with UV light of 200 mW/cm² UVA intensity and then postcured for 6 hours at 170°C.

UV Illumination Time (seconds)	Wt.% Fused Silica	Flexural Strength (kg _f /mm ²) Without	Flexural Strength (kg _f /mm ²) With
		I nermal initiator	I nermal initiator
60	70.0	7.18 ± 1.61	8.72 ± 0.97
60	72.0	8.37 ± 1.38	9.41 ± 0.95
60	74.0	8.87 ± 1.30	9.80 ± 1.55
90	70.0	7.88 ± 0.71	9.07 ± 0.73
90	72.0	8.41 ± 0.83	8.75 ± 1.00
90	74.0	8.29 ± 1.13	11.11 ± 1.09
120	70.0	6.71 ± 0.69	8.83 ± 1.68
120	72.0	7.59 ± 0.24	9.28 ± 0.95
120	74.0	8.12 ± 0.69	9.92 ± 1.44

Table 7.3. Effect of reduced UV illumination times on coefficient of thermal expansion below glass transition for both UV-initiated and dual initiated samples containing 70.0, 72.0, and 74.0 wt.% fused silica. Samples were photocured with UV light of 200 mW/cm^2 UVA intensity and then postcured for 6 hours at 170°C.

UV Illumination Time (seconds)	Wt.% Fused Silica	α ₁ (μm/m°C) Without Thermal Initiator	α ₁ (µm/m°C) With Thermal Initiator
60	70.0	22.10 ± 1.57	20.84 ± 1.35
60	72.0	19.80 ± 0.87	20.20 ± 1.43
60	74.0	20.02 ± 1.27	19.36 ± 1.23
90	70.0	22.04 ± 0.71	22.30 ± 1.26
90	72.0	19.40 ± 1.21	20.20 ± 0.51
90	74.0	18.58 ± 0.45	19.44 ± 1.20
120	70.0	22.26 ± 0.63	22.70 ± 1.10
120	72.0	22.62 ± 0.64	20.92 ± 0.54
120	74.0	20.50 ± 0.57	20.12 ± 1.41

Table 7.4. Effect of reduced UV illumination times on coefficient of thermal expansion above glass transition for both UV-initiated and dual initiated samples containing 70.0, 72.0, and 74.0 wt.% fused silica. Samples were photocured with UV light of 200 mW/cm^2 UVA intensity and then postcured for 6 hours at 170°C.

UV Illumination Time (seconds)	Wt.% Fused Silica	α ₂ (µm/m°C) Without Thermal Initiator	α ₂ (µm/m°C) With Thermal Initiator
60	70.0	70.70 ± 2.18	65.26 ± 1.75
60	72.0	66.46 ± 3.22	64.18 ± 1.35
60	74.0	62.74 ± 1.68	63.14 ± 1.56
90	70.0	71.56 ± 4.85	70.56 ± 3.52
90	72.0	66.46 ± 1.29	63.98 ± 1.83
90	74.0	60.30 ± 1.83	58.96 ± 2.70
120	70.0	66.74 ± 3.45	69.44 ± 1.30
120	72.0	61.78 ± 1.70	63.46 ± 2.37
120	74.0	56.68 ± 2.91	59.24 ± 2.39

Table 7.5. Effect of reduced UV illumination times on glass transition temperature for both UV-initiated and dual initiated samples containing 70.0, 72.0, and 74.0 wt.% fused silica. Samples were photocured with UV light of 200 mW/cm² UVA intensity and then postcured for 6 hours at 170°C.

UV Illumination Time (seconds)	Wt.% Fused Silica	T _g (°C) Without Thermal Initiator	T _g (°C) With Thermal Initiator
60	70.0	156 ± 2	155 ± 2
60	72.0	153 ± 1	154 ± 2
60	74.0	153 ± 2	153 ± 1
90	70.0	152 ± 1	149 ± 2
90	72.0	152 ± 2	150 ± 2
90	74.0	150 ± 1	150 ± 2
120	70.0	148 ± 2	150 ± 2
120	72.0	150 ± 4	151 ± 1
120	74.0	152 ± 3	150 ± 1

Table 7.6. Effect of reduced UV illumination times on thermal stress parameter (σ^{\bullet}) for both UV-initiated and dual initiated samples containing 70.0, 72.0, and 74.0 wt.% fused silica. Samples were photocured with UV light of 200 mW/cm² UVA intensity and then postcured for 6 hours at 170°C.

UV Illumination Time (seconds)	Wt.% Fused Silica	σ [•] (kg _f /mm ²) Without Thermal Initiator	σ [•] (kg _f /mm ²) With Thermal Initiator
60	70.0	1.27 ± 0.37	1.06 ± 0.38
60	72.0	0.88 ± 0.21	0.95 ± 0.36
60	74.0	0.99 ± 0.39	0.84 ± 0.36
90	70.0	1.18 ± 0.18	1.24 ± 0.24
90	72.0	0.68 ± 0.23	0.95 ± 0.23
90	74.0	0.62 ± 0.17	0.84 ± 0.34
120	70.0	1.34 ± 0.20	1.35 ± 0.32
120	72.0	1.58 ± 0.20	1.14 ± 0.23
120	74.0	1.13 ± 0.19	1.05 ± 0.38

7.5. REFERENCES

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Chapter 8

THERMAL PROPERTIES OF PHOTOPOLYMERIZABLE LIQUID ENCAPSULANTS

8.1. INTRODUCTION

Thermal management plays a vital role in the packaging of high performance electronic devices. Specifically, it is important that the silicon chip does not overheat during operation. Since the device generates a significant amount of heat during use, the thermal conductivity of an encapsulating compound plays an important role in the thermal management of the device. Indeed, the thermal conductivity determines the amount of heat that can be removed from the device and thus affects operating temperatures of electronic components. As semiconductor devices increase in transistor densities, the heat dissipation requirements also increase, resulting in the need for packaging materials with enhanced thermal conductivity.

In order to attain high thermal conductivities, a high weight fraction of filler must be used in the molding compound. Typically, large chip, small package devices are transfer molded using a polymer composite consisting of 20-30 wt.% (30-45 vol.%) epoxy resin and 70-80 wt.% (55-70 vol.%) fused silica filler. Although the polymer portion of the composite provides excellent electrical insulation and environmental protection, it does not offer adequate thermal conductivity or dimensional stability. As a result, ceramic fillers such as fused and crystalline silica, aluminum nitride, beryllium oxide, and silicon carbide are used to provide improvements in thermal conductivity and dimensional stability. Fused silica is the most widely used filler in epoxy molding compounds for microelectronic encapsulation because the resulting encapsulants exhibit excellent performance in most key areas, including dimensional stability (a low coefficient of thermal expansion), high moisture resistance, and superior stress and electrical characteristics.¹ Fillers such as crystalline silica, aluminum nitride, boron nitride, and silicon carbide do lead to encapsulants that exhibit higher thermal conductivities. However, due to its overall performance advantages, fused silica remains the predominant filler in epoxy molding compounds and was, therefore, the filler used in this study.

The goal of these experiments is simply to determine the thermal conductivity of the photopolymerizable liquid encapsulants as a function of fused silica loading in order to confirm that the thermal conductivity values are in the range necessary for microelectronic encapsulants. Furthermore, the experimental results were compared with the model of Agari and Uno^2 for predicting the thermal conductivity of a composite.

8.2. EXPERIMENTAL

8.2.1. Preparation of Photopolymerizable Liquid Encapsulant

The photopolymerizable liquid encapsulant (PLE) used for the thermal conductivity experiments is comprised of a base resin, fused silica filler, photoinitiator, thermal initiator, and silane coupling agent. The base resin was an epoxy novolac-based vinyl ester resin (DERAKANE 470-45, Dow Chemical) that was chosen for its low initial viscosity (0.0456 Pa•s or 45.6 cP at 30°C), as well as, its appropriate thermal and mechanical properties upon cure. The photoinitiator used was bis(2,4,6-trimethylbenzoyl) phenylphosphine oxide (IRGACURE 819, Ciba). This photoinitiator, which will henceforth be denoted as BAPO, has been shown to be especially appropriate for curing relatively thick polymers and composites due to its efficient photobleaching.

The thermal initiator used was benzoyl peroxide (Aldrich). The fillers used were crushed (angular), untreated fused silica (MIN-SIL 40 and MIN-SIL 550) obtained from MINCO, Inc. A silane coupling agent, 3-methacryloxypropyltrimethoxysilane (Z-6030, Dow Corning), was used to provide a stable bond between the base resin and the fused silica filler, and to improve the processability of the liquid encapsulant formulation.

The PLEs were prepared by adding 0.2 wt.% BAPO photoinitiator (based on resin weight) to the epoxy novolac-based vinyl ester resin and stirring at room temperature on a magnetic stir plate until the photoinitiator completely dissolved. The thermal initiator, benzoyl peroxide, was also added in the amount of 1.2 wt.% (based on resin weight) and, again the system was stirred until dissolution was complete. The silane coupling agent was then added dropwise to the desired 1 wt.% (based on filler weight) and the resin mixture was stirred on the magnetic stir plate. The fused silica (a 50:50 wt.% blend of MIN-SIL 40 and MIN-SIL 550) was added in the amount of 70.0, 72.0, or 74.0 wt.% and the system was mixed by using a vortex mixer until the filler was completely dispersed and a homogeneous mixture was achieved. The PLE was then degassed in a vacuum oven to remove air bubbles. Once these steps were completed, the PLE was ready to use for preparing specimens required for the thermal conductivity studies.

8.2.2. Specimen Preparation for Thermal Conductivity Testing

Specimens were prepared by photopolymerizing the liquid encapsulant in rectangular silicone molds with unfiltered UV light (200 mW/cm² UVA intensity) for 90 seconds from a 3000 W arcless mercury vapor lamp (Fusion UV Systems, model F450T). Light intensities were measured (over the 320-390 nm range) using a UVICURE Plus high energy UV integrating radiometer. Following UV illumination, the specimens were

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postcured in a laboratory oven for 6 hours at 170°C. The final dimensions of the cured specimens were 76.2 mm length, 25.4 mm width, and 3.2 mm depth. The cured specimens were then machined into disks with a diameter of 12.7 mm and a thickness of 1.0 mm for thermal conductivity testing.

8.2.3. Laser Flash Method

Thermal conductivity measurements are difficult and time-consuming, and require relatively large specimens. However, thermal conductivity may be calculated from measurements of thermal diffusivity, specific heat, and bulk density using Equation 8.1.

$$k = \alpha \rho C_p \tag{8.1}$$

Here, k is the thermal conductivity, α is the thermal diffusivity, ρ is the bulk density, and C_p is the specific heat.

The laser flash method (ASTM E1461-92) for determining thermal conductivity has been applied to a wide range of materials, including composites, plastics, ceramics, metals, glasses, crystals, and foams. One advantage of this technique is that it requires only a small amount of material. In this technique, the measurement of the thermal diffusivity of a material is carried out by rapidly heating one side of a flat disk sample and measuring the temperature as a function of time (the temperature rise curve) on the opposite side. Based upon this temperature profile, the through-plane diffusivity is measured, and the thermal conductivity is calculated using the known values of the specific heat and bulk density.

All measurements to determine the thermal conductivity by the laser flash method were performed by Holometrix, Inc. (Bedford, MA) using the Holometrix Thermaflash

2200 Laser Flash system and in accordance with ASTM E1461-92. In this system, the sample disk made from the PLE was aligned between a neodymium glass laser (1.06 µm wavelength) and an indium antimonide (InSb) IR detector in a tantalum tube furnace. In order to prevent penetration of the laser beam into the sample, the PLE samples were coated with a 0.1 µm gold film. In addition, because the PLE samples do not have a high value of emissivity or absorptivity, the samples were also coated with a 5 µm graphite film before testing. The graphite film increases the energy absorbed on the laser side and increases the temperature signal on the rear face of the sample. A Type C thermocouple in contact with the PLE sample was used to control the temperature of the sample and its surroundings between 20 and 2000°C. Once the sample was stabilized at 25°C, the laser was fired several times over a span of a few minutes and the necessary data was recorded for each laser shot. The laser beam energy strikes and is absorbed by the front surface of the sample, causing a heat pulse to travel through the thickness of the sample. The resulting sample temperature rise is fairly small (ranging from about 0.5 to 2°C) and is kept in the optimal range by adjustable filters between the laser and the furnace. A lens focuses the back surface image of the sample onto the IR detector and the temperature rise signal vs. time is amplified and recorded with a high speed A/D converter. The thermal diffusivity is determined from a numerical analysis of the IR detector output. In addition, the specific heat can be measured with the laser flash method by comparing the temperature rise of a reference sample of known specific heat tested under the same conditions. The instrument is fully automated to control all systems and record, analyze, and report the thermal diffusivity, specific heat, and the calculated thermal conductivity.

8.3. RESULTS AND DISCUSSION

8.3.1. Thermal Conductivity

Experimental data showing the thermal conductivity of the PLEs as a function of fused silica loading are shown in Figure 8.1. All samples contained 70.0 to 74.0 wt.% fused silica, 1.0 wt.% silane coupling agent (based on filler weight), 0.2 wt.% BAPO (based on resin weight), 1.2 wt.% benzoyl peroxide (based on resin weight), and the balance epoxy novolac-based vinyl ester resin. Samples were photocured for 90 seconds with UV light of 200 mW/cm² UVA intensity and then postcured for 6 hours at 170°C. Each bar in the bar chart represents the average of 3 samples and the error bars indicate one standard deviation above and below the mean. As expected, the thermal conductivity of the PLEs increases as the fused silica content is increased, and the values range between 0.56 and 0.62 W/m·K. Clearly, the thermal conductivity of a molding compound is largely dependent on the filler used and, therefore, the thermal conductivity values of the PLEs filled with fused silica ($k = 1.5 \text{ W/m}\cdot\text{K}$) will not be as high as molding compounds loaded with higher thermal conductivity fillers, such as silicon carbide (k =85 W/m•K), aluminum nitride (k = 150-220 W/m•K), and boron nitride (k = 250-300W/m•K). However, the thermal conductivity values of the PLEs are all within the 0.5 to 0.7 W/m•K range of epoxy molding compounds filled with fused silica. As a result, the PLEs are more suitable for applications with low stress requirements, rather than devices with high heat outputs.

In order to predict the thermal conductivity of encapsulants at higher filler loadings, theoretical and empirical models are often used. Although other additives are typically present in encapsulants, such as initiators and coupling agents, the concentration added is rather small when compared to that of the fillers. Thus, from a thermal transport point of view, the encapsulant behaves like a two-phase composite.³ Although there are several second order models used to predict the thermal conductivity of a two-phase composite (Agari and Uno², Hatta and Taya⁴, Hashin and Shtrikman⁵, and Nielsen⁶), the model developed by Agari and Uno describes the thermal conductivity of encapsulants quite well.^{7,8} Indeed, the model is especially suited for composites with high filler loadings (30 to 60 vol.%) and irregularly shaped filler particles, such as fused silica. The model is described by Equation 8.2,

$$\log k_{c} = \phi C_{2} \log(k_{f}) + (1 - \phi) \log(C_{1}k_{m})$$
(8.2)

and can be rearranged to give Equation 8.3,

$$k_{c} = k_{f}^{\phi C_{2}} \left[(C_{1} k_{m})^{(1-\phi)} \right]$$
(8.3)

where k_c , k_f , and k_m are the thermal conductivities of the composite, filler, and resin matrix, respectively, and ϕ is the volume fraction of the filler. In addition, C_1 is a constant used to measure the effect of filler particles on the secondary structure of the resin matrix and C_2 is a constant used to measure the ease with which the filler particles begin to form conductive chains.² For the purpose of modeling the experimental thermal conductivity data, reported literature values for fused silica ($k_f = 1.5$ W/m·K) and for epoxy novolac-based vinyl ester resin ($k_m = 0.182$ W/m·K) were used. The fused silica volume fractions, ϕ , were calculated using Equation 8.4,

$$\phi = \frac{W}{W + (1 - W)\frac{\rho_f}{\rho_m}}$$
(8.4)

where W is the weight fraction of fused silica, ρ_f is the density of the filler ($\rho_f = 2.20$ g/cm³ for fused silica), and ρ_m is the density of the resin matrix ($\rho_m = 1.048$ g/cm³ for epoxy novolac-based vinyl ester resin). Table 8.1 shows the calculated volume fractions corresponding to the 70.0, 72.0, and 74.0 wt.% fused silica loadings.

Table 8.1. Calculated volume fractions corresponding to 70.0, 72.0, and 74.0 wt.% fused silica loadings.

Weight Fraction Fused Silica W	Volume Fraction Fused Silica ϕ	
0.70	0.526	
0.72	0.551	
0.74	0.576	

Once the volume fractions were determined, the experimental thermal conductivity data was fit to Equation 8.3 by nonlinear regression using C_1 and C_2 as the fitting parameters. The nonlinear regression analysis was performed using the commercial software package Origin 5.0 (Microcal Software, Inc.).

Figure 8.2 compares the experimental thermal conductivity results to the predicted values obtained using the model of Agari and Uno. The curve drawn in Figure 8.2 corresponds to values obtained by fitting the experimental data to Equation 8.3, from 0 to 80.0 wt.% fused silica (0 to 65.6 vol.%). The best fit values for C_1 and C_2 were 0.997 and 1.064, respectively. These values are quite reasonable since C_1 values reported by Agari and Uno for various composite systems are approximately 1 and C_2 values range from 1 to 1.5.⁹ Since C_1 is nearly 1, the secondary structure of the epoxy novolacbased vinyl ester resin is largely unaffected by the fused silica particles. Figure 8.2

model of Agari and Uno. The model can be used to effectively predict the thermal conductivity of the PLEs at both lower and higher filler loadings.

Figure 8.3 provides a "close-up" comparison of the experimental data to the model of Agari and Uno between 60.0 and 80.0 wt.% fused silica (41.7 and 65.6 vol.%). This range of fused silica loadings was chosen because most encapsulants are filled with 60.0 to 80.0 wt.% fused silica. Looking at Figure 8.3, the model predicts that the thermal conductivity of the PLEs will be 0.44 W/m•K at 60.0 wt.% fused silica and 0.74 W/m•K at 80.0 wt.% fused silica. Therefore, PLEs filled with 60.0 wt.% fused silica would not have an appropriate value (since the values do not fall within the 0.5 to 0.7 W/m•K range of epoxy molding compounds filled with fused silica). Figure 8.3 shows that the PLEs must be filled with at least 66.0 wt.% fused silica in order have thermal conductivity values within this range.

8.3.2. Specific Heat

Specific heat is a measure of the quantity of heat a material must absorb to raise its temperature a specified increment.¹⁰ Figure 8.4 shows the effect of fused silica loading on the specific heat of the PLE samples. Each bar in the bar chart represents the average of 3 samples and the error bars indicate one standard deviation above and below the mean. The specific heat of the unfilled epoxy novolac-based vinyl ester resins is approximately 1.2 J/g•K as reported by the manufacturer. As shown in Figure 8.4, the specific heat for the PLEs ranges between 0.83 and 0.87 J/g•K. In agreement with the results of Bujard *et al.*¹¹, the specific heat decreases when the weight content of the fused silica increases. In addition, the values of the specific heat for the PLEs filled with 70.0 wt.% fused silica are very close to the values reported by Bujard *et al.* for epoxy molding compounds filled with 70.0 wt.% fused silica.

8.3.3. Thermal Diffusivity

The thermal diffusivity indicates how rapidly heat can diffuse through the molding compound.¹¹ The higher the thermal diffusivity of a substance, the higher the rate of temperature propagation. That is, materials with high thermal diffusivities will respond quickly to changes in their thermal environment, while materials with low thermal diffusivities will respond more slowly, taking longer to reach a new equilibrium condition.¹² Figure 8.5 shows the effect of fused silica loading on the thermal diffusivity of the PLEs. Each bar in the bar chart represents the average of 3 samples and the error bars indicate one standard deviation above and below the mean. The results show that the thermal diffusivity increases as the fused silica content increases, and that all of the values range between 3.7×10^{-3} and 4.2×10^{-3} cm²/s.

8.4. CONCLUSIONS

In this chapter, the thermal conductivity, specific heat, and thermal diffusivity of photopolymerizable liquid encapsulants (PLEs) were measured as a function of fused silica loading by the laser flash method. Photopolymerizable liquid encapsulants loaded with 70.0, 72.0, and 74.0 wt.% fused silica exhibited thermal conductivities between 0.56 and 0.62 W/m•K, which is within the 0.5 to 0.7 W/m•K range exhibited by most fused silica loaded molding compounds. The thermal conductivity values of the PLEs were approximately three times that of the unfilled epoxy novolac-based vinyl ester resin (k = 0.182 W/m•K).

The experimental thermal conductivity data was fit to the second order model of Agari and Uno in order to predict the thermal conductivity of the PLEs at filler loadings lower than 70.0 wt.% and filler loadings higher than 74.0 wt.%. Indeed, the experimental thermal conductivity data was well correlated by the model of Agari and Uno. This model can be used to accurately predict the thermal conductivity of the PLEs over a wide range of filler loadings.

The specific heat for the PLEs ranged between 0.83 and 0.87 J/g•K and was shown to decrease with increasing fused silica content, in agreement with the results of other authors.¹¹ In addition, values for the thermal diffusivity ranged between 3.7×10^{-3} and 4.2×10^{-3} cm²/s and were shown to increase with increasing fused silica content.

8.5. NOMENCLATURE

- C_{p} = specific heat
- C_1 = constant used to measure the effect of the filler on the secondary structure of resin
- C_2 = constant used to measure the ease with which filler particles begin to form

conductive chains

k = thermal conductivity

 $k_{\rm c}$ = thermal conductivity of composite

 $k_{\rm f}$ = thermal conductivity of filler

 $k_{\rm m}$ = thermal conductivity of resin matrix

W = weight fraction of filler

 α = thermal diffusivity

 ϕ = volume fraction filler

 ρ = density

 $\rho_{\rm f}$ = density of filler

 $\rho_{\rm m}$ = density of resin matrix



Figure 8.1. Thermal conductivity of PLEs at 25°C as a function of fused silica loading.



Figure 8.2. Comparison of experimental thermal conductivity results to the predicted values obtained using the model of Agari and Uno from 0 to 80.0 wt.% fused silica (0 to 65.6 vol.%).



Figure 8.3. Comparison of experimental thermal conductivity results to the predicted values obtained using the model of Agari and Uno from 60.0 to 80.0 wt.% fused silica (41.7 to 65.6 vol.%).


Figure 8.4. Specific heat of PLEs at 25°C as a function of fused silica loading.



Figure 8.5. Thermal diffusivity of PLEs at 25°C as a function of fused silica loading.

8.6. REFERENCES

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Chapter 9

ADHESION BETWEEN PHOTOPOLYMERIZABLE LIQUID ENCAPSULANTS AND ALLOY 194

9.1. INTRODUCTION

The adhesion of an epoxy molding compound to the leadframe is a critical parameter for encapsulated microelectronic devices. The on-going trends of increasing silicon chip size and thinner packages, as well as the push towards surface mount operations, have increased the importance of proper adhesion between the molding compound and leadframe.^{1,2} Specifically, improved adhesion between the molding compound and the leadframe leads to enhanced reliability and resistance to package and chip cracking. In addition, inadequate adhesion leads to popcorn problems in surface mount devices, as well as delamination and subsequent thermomechanical failure.^{2,3} Furthermore, a high degree of adhesion limits moisture-induced corrosion by preventing penetration of water along the leadframe.⁴

A number of non-destructive and destructive experimental techniques have been used to characterize adhesion between molding compounds and the leadframe. While non-destructive tests, such as Scanning Acoustic Microscopy (SAM), are applied primarily for *qualitative* inspections (to determine whether adhesion exists or not), destructive tests can provide valuable *quantitative* information about the adhesion strength.⁴ The most widely used destructive tests to measure adhesive strength between molding compounds and the leadframe are the shear (lap and button), tab pull, and peel test methods.⁵ Of the many destructive tests available, Kim reported that the 180 degree peel test is the most sensitive, and provides an accurate measure of adhesion between the encapsulants and the leadframe.² Therefore, in this chapter, the degree of adhesion between the photopolymerizable liquid encapsulants (PLEs) and the leadframe metal was measured by the 180 degree peel test.

The most widely used leadframe metals for integrated circuit assembly are copper-based alloys (e.g. Alloys 151, 190, and 194) and an iron-nickel alloy (Alloy 42). The advantages of copper-based alloys are that they have higher thermal and electrical conductivity and lower cost compared to Alloy 42. However, molding compounds generally do not adhere to copper alloys as well as they adhere to other alloys. Copper and copper-based alloys are difficult metals to bond to for three primary reasons: (i) the catalytic activity of its surface oxide which alters adhesive curing conversion, (ii) the activity of copper in the presence of oxidizing and reducing agents in the environment, and (iii) the poor intrinsic adhesion that is linked to the oxide layer at the oxide/metal interface.⁶ Because they represent the most challenging leadframe metals for encapsulant adhesion, a copper alloy was chosen for the studies in this chapter. Specifically, the adhesion of the PLEs to Alloy 194 was evaluated using the 180 degree peel test and the fracture surfaces were characterized using environmental scanning electron microscopy (ESEM).

Significant research has been devoted to improving the degree of adhesion between copper leadframes and epoxy molding compounds by using adhesion promoters, metal plating, vacuum deposition, and chemical oxidation.⁷ Previous research by Song *et al.* has demonstrated that both silane coupling agents and azole compounds can improve peel strength.^{8,9} Therefore, two commercial silane coupling agents and two azole compounds were evaluated to determine the effect of various surface pretreatments on the

peel strength. Silane coupling agents improve adhesion by forming covalent linkages between the metal surface and the polymeric encapsulant. Azole compounds are used as corrosion inhibitors to improve the bond durability between epoxy resins and copper.⁸ These compounds have active protons to form a complex with the cuprous hydroxide on the copper surface and functional groups such as amine and carboxylic acid to interact with epoxy resins.¹⁰

9.2. EXPERIMENTAL

9.2.1. Preparation of Photopolymerizable Liquid Encapsulant

The photopolymerizable liquid encapsulant (PLE) used for the adhesion experiments is comprised of a base resin, fused silica filler, photoinitiator, thermal initiator, and silane coupling agent. The base resin was an epoxy novolac-based vinyl ester resin (DERAKANE 470-45, Dow Chemical) that was chosen for its low initial viscosity (40-80 cP at 25 °C) as well as its appropriate thermal and mechanical properties upon cure. The photoinitiator used was bis(2,4,6-trimethylbenzoyl) phenylphosphine oxide (IRGACURE 819, Ciba). This photoinitiator, which will henceforth be denoted as BAPO, has been shown to be especially appropriate for curing relatively thick polymers and composites due to its efficient photobleaching. The thermal initiator used was benzoyl peroxide (Aldrich). The fillers used were crushed (angular), untreated fused silica (MIN-SIL 40 and MIN-SIL 550) obtained from MINCO, Inc. A silane coupling agent, 3-methacryloxypropyltrimethoxysilane (Z-6030, Dow Corning), was used to provide a stable bond between the base resin and the fused silica filler, and to improve the processability of the liquid encapsulant formulation. The PLEs were prepared by adding 0.2 wt.% BAPO photoinitiator (based on resin weight) to the epoxy novolac-based vinyl ester resin and stirring at room temperature on a magnetic stir plate until the photoinitiator completely dissolved. The thermal initiator, benzoyl peroxide, was also added in the amount of 1.2 wt.% (based on resin weight) and, again the system was stirred until dissolution was complete. The silane coupling agent was then added dropwise to the desired 1 wt.% (based on filler weight) and the resin mixture was stirred on the magnetic stir plate. The fused silica (a 50:50 wt.% blend of MIN-SIL 40 and MIN-SIL 550) was added in the amount of 70.0, 72.0, or 74.0 wt.% and the system was mixed by using a vortex mixer until the filler was completely dispersed and a homogeneous mixture was achieved. The PLE was then degassed in a vacuum oven to remove any air bubbles. Once these steps were completed, the PLE was ready to use for preparing peel test specimens.

9.2.2. Solvent Degreasing Pretreatment of Alloy 194

Alloy 194 was selected as the leadframe metal for the 180 degree peel test because of its widespread use in microelectronic packages. It is a copper-based leadframe metal, comprised of 97.5% copper, 2.35% iron, 0.12% zinc, and 0.03% phosphorus.¹¹ Thin foil sheets of Alloy 194 (C194, Olin Brass) with thickness 0.0127 mm (0.0005 in.) were cut into rectangular strips of dimensions 215.9 mm (8.5 in.) length and 12.7 mm (0.5 in.) width. The thin foil was necessary for the peel test in order to permit a turn back at an approximate 180° angle in the expected loading range of the test without failure. Prior to applying the PLE to the leadframe metal, the copper alloy was pretreated in order to provide a surface to which the resin can adhere. Typically, metals available for industrial applications are covered with a contaminant layer that has

properties that differ from the bulk metal and, consequently, this alters the degree of adhesion between the metal and polymer. The contaminant layer may consist of processing lubricants and oils, water, or other contaminants from the atmosphere which can adsorb on the high energy metal surfaces.¹² A solvent degreasing pretreatment is typically the minimum pretreatment used to remove this contaminant layer.

The Alloy 194 strips were cleaned and degreased by first dipping them in 0.1 M HCl for 30 seconds in order to remove the weak copper oxide, then rinsing with a series of solvents in the following order: distilled water; methanol; distilled water; acetone. The strips were then dried gently with compressed air. Environmental scanning electron microscopy (ESEM) was conducted to determine the surface characteristics of the foils. The microscope was a Philips Electroscan 2020 environmental scanning electron microscope (ESEM) equipped with a Lab6 filament. The accelerating voltage was 20 kV and the operating pressure ranged between 2-3 Torr. Scanning electron micrographs of leadframe strips before and after pretreatment are shown in Figures 9.1 and 9.2, respectively. Figure 9.1 shows the dirt and oil (dark-colored circles) on the "as-received" Alloy 194 strips, confirming that a pretreatment step is necessary in order to clean the surface and adequately prepare it for adhesion. Figure 9.2 shows a much cleaner surface after the Alloy 194 strips were pretreated, demonstrating that the pretreatment was successful in removing the surface contaminants. Following pretreatment, the Alloy 194 strips were primed with silane coupling agents or azole compounds, as described below.

9.2.3. Treatment of Alloy 194 Strips with Silane Coupling Agents

Two different silane coupling agents were used for priming the copper surfaces, 3-methacryloxypropyltrimethoxysilane (Z-6030, Dow Corning) and a silane composed of

an amino-alkyltrimethoxysilane and a polyol diluted with methanol (Z-6026, Dow Corning). These coupling agents, Z-6030 and Z-6026, will henceforth be denoted as MPMS and AAMS, respectively. Coupling agent solutions using MPMS were made to a concentration of 5.0 wt.% in methanol. Alloy 194 strips were dipped in the solution for 1 minute, removed, blown gently with air, and cured at 115°C for 30 minutes.

Coupling agent solutions using AAMS were made to a concentration of 0.5 wt.% in water. The pH was then adjusted to 4.5 with acetic acid. Alloy 194 strips were dipped in the solution for 1 minute, removed, gently blown with air, and cured at 115°C for 30 minutes.

9.2.4. Treatment of Alloy 194 Strips with Azole Compounds

The two azole compounds used were benzotriazole-5-carboxylic acid (Aldrich Chemical) and polybenzimidazole (Aldrich Chemical), and will henceforth be referred to as BTCA and PBI. The primer solutions using the azole compounds were prepared according to the procedure specified by Song *et al.*⁸ Solutions using BTCA were made to a concentration of 3×10^{-3} M in distilled water. Alloy 194 strips were dipped in the solution for 1 minute, removed, gently blown with air, and cured at 150°C for 30 minutes. Solutions using PBI were made to a concentration of 0.1 wt.% in dimethyl formamide (EM Science). Alloy 194 strips were dipped in the solution for 1 minute, removed at 150°C for 30 minutes.

9.2.5. Specimen Preparation for Peel Test

Following pretreatment, the Alloy 194 strips were inserted into rectangular cavities of a Teflon mold, with cavity dimensions of 101.6 mm (4 in.) length, 12.7 mm

(0.5 in.) width, and 3.5 mm (0.1378 in.) depth. The PLE was then injected, using a syringe, into the mold cavities and allowed to completely wet the metal strips. The specimens were photopolymerized for 90 seconds with unfiltered UV light of 200 mW/cm² UVA intensity from a 3000 W arcless mercury vapor lamp (Fusion UV Systems, model F450T) to create a bond length of 101.6 mm (4 in.) between the metal and photocured encapsulant. Light intensities were measured using a UVICURE Plus high energy UV integrating radiometer (over the 320-390 nm range). After photocuring, the samples were allowed to cool to room temperature for 24 hours prior to the peel test. The peel test was performed by peeling off the thin leadframe foil at a 180° angle from the photocured encapsulant with a United SFM-20 instrument at a rate of 127 mm/min (5 in./min) and a 9.07 kg (20 lb.) load cell. Peel strength was calculated using DATUM 97 software (United Testing Systems).

9.3. RESULTS AND DISCUSSION

9.3.1. Peel Strength of Surfaces Treated with Silane Coupling Agents

Experimental results showing the 180 degree peel strength between the photopolymerizable liquid encapsulants and the Alloy 194 strips treated with the silane coupling agents are shown in Figure 9.3. Each bar in the bar chart represents the average of 5 samples and the error bars indicate one standard deviation above and below the mean. As shown in Figure 9.3, the peel strength of strips that were not treated with silane coupling agents ranged from 18 to 40 g/cm. In addition, the peel strength of strips that were treated with MPMS ranged from 28 to 40 g/cm, demonstrating that the use of MPMS has a minimal effect in improving the peel strength. The only noticeable

improvement shown by MPMS occurs when the liquid encapsulant is filled with 74 wt.% fused silica. However, Figure 9.3 clearly shows that the use of AAMS significantly improves the peel strength, since the peel strength values for strips treated with AAMS were between 35 and 95 g/cm. At each level of filler loading, the peel strength is more than doubled for Alloy 194 strips that were treated with AAMS, as compared to strips that were not treated with any silane coupling agent.

In addition, Figure 9.3 shows that irrespective of whether the Alloy 194 strips are treated with a silane coupling agent, the peel strength reaches a maximum when the photopolymerizable liquid encapsulant is filled with 72 wt.% fused silica. This is somewhat unexpected, as other authors, most notably Kim, have shown that peel strength shows an inverse relationship with viscosity, i.e., the lower the viscosity the higher the peel strength.² The viscosity of the liquid encapsulant filled with 70.0 wt.% fused silica is 5.92 Pa•s (5920 cP), while that of the 72.0 wt.% encapsulant is 13.9 Pa•s (13,900 cP), and 74.0 wt.% is over 30 Pa-s (over 30,000 cP). Therefore, we would expect that the encapsulant filled with 70.0 wt.% fused silica to have the highest peel strength, followed by 72.0 wt.%, and then 74.0 wt.%. The reason for the discrepancy between the data shown in Figure 9.3 and the data of Kim is that Kim has altered the viscosity level by varying the catalyst levels and processing times, whereas, we have varied the viscosity levels by solely varying the filler loading. As a result, we have two competing effects on the peel strength: viscosity and internal stress. It appears that the PLE filled with 72.0 wt.% fused silica strikes the appropriate balance: it has a low enough viscosity to provide adequate wetting of the Alloy 194 strips, and enough fused silica to sufficiently reduce the internal stresses (which lower peel strength).

Commercial epoxy molding compounds generally exhibit 180 degree peel strengths of 40 to 200 g/cm when adhered to copper leadframe materials.² Figure 9.3 illustrates that the PLEs filled with 70.0 and 72.0 wt.% fused silica and that are molded onto Alloy 194 strips treated with AAMS exhibit peel strength values in this range. Therefore, these studies indicate that these materials exhibit appropriate adhesion for use as microelectronic encapsulants. In addition, it is noteworthy that the 180 degree peel strengths reported by Kim on the commercial encapsulants were performed using relatively thin samples (1.25 mm thick), whereas, the PLE specimens in this study were 3.0 mm thick (microelectronic encapsulants are generally 1-3 mm thick and we chose the high end of the range since it places the most stringent requirements upon cure and adhesion). Other investigators have shown that an increase in the encapsulant thickness can lead to increased internal stresses and decreased peel strengths.¹² Therefore, if the peel strengths of the PLEs and the commercial molding compounds were compared based upon identical specimen thicknesses, the PLEs should compare even more favorably than the values shown in Figure 9.3.

9.3.2. Mechanism of Bond Failure between PLE and Surfaces Treated with Silanes

Adhesive joints may fail in two ways: 1) adhesive failure, which is interfacial bond failure between the adhesive and the adherend (in this case the separation occurs at the adhesive-adherend interface), and 2) cohesive failure, in which a layer of adhesive remains on both surfaces (in this case separation occurs in the adhesive).¹³ Cohesive failure is the desirable mode of failure since it indicates that the adhesive bond was strong enough to prevent failure at the interface.

In this study, the mode of the failure of the adhesive joint was investigated using environmental scanning electron microscopy. Specifically, the Alloy 194 surface of the failed peel test specimen was examined. Figures 9.4, 9.5, and 9.6 reveal that the surfaces treated with either silane coupling agent, as well as the control surfaces (strips that were cleaned and degreased, but were not treated with silanes or azoles) showed cohesive failure. For these systems, the corresponding electron micrographs indicate that a layer of the cured PLE remained on the Alloy 194 surface after the peel test.

9.3.3. Peel Strength of Surfaces Treated with Azole Compounds

In contrast to the surfaces treated with silane coupling agents discussed above, peel test specimens prepared with Alloy 194 surfaces treated with azole compounds performed quite poorly. In fact, these specimens were significantly delaminated and, therefore, the peel strength between the PLE and Alloy 194 strips treated with azole compounds were too low to be measured. Not surprisingly, these samples showed adhesive failure as shown in the scanning electron micrographs in Figures 9.7 and 9.8 (the Alloy 194 surface is essentially bare metal with little, if any, PLE remaining).

9.4. CONCLUSIONS

The adhesive strength of photopolymerizable liquid encapsulants (PLEs) to Alloy 194 (a copper-based alloy) was measured using the 180 degree peel test. Peel strengths were measured as a function of wt.% fused silica in the PLE and the type of coupling agent used on the Alloy 194 surface. Specific observations are as follows:

1. The peel strength of strips that were not treated with silane coupling agents ranged from 18 to 40 g/cm. In addition, the peel strength of strips that were treated with the

silane coupling agent, 3-methacryloxypropyltrimethoxysilane (MPMS), ranged from 28 to 40 g/cm, demonstrating that the use of MPMS has a minimal effect in improving the peel strength.

- 2. Alloy 194 surfaces treated with a silane coupling agent composed of an aminoalkyltrimethoxysilane and a polyol diluted with methanol (AAMS) exhibited the highest peel strengths, with values ranging from 35 and 95 g/cm. At each level of filler loading, the peel strength is more than doubled for Alloy 194 strips that were treated with AAMS, as compared to strips that were not treated with any silane coupling agent.
- Irrespective of the coupling agent used on the Alloy 194 surface, the peel strength reaches a maximum when the photopolymerizable liquid encapsulant is filled with 72.0 wt.% fused silica.
- 4. All of the surfaces treated with either of the silane coupling agents, as well as, the control surfaces (strips that were cleaned and degreased, but were not treated with silanes or azoles) showed cohesive failure.
- 5. The peel strength between PLEs and surfaces treated with azole compounds could not be measured because of extensive delamination. All of these surfaces showed adhesive failure.
- The peel strengths of liquid encapsulants filled with 70.0 and 72.0 wt.% fused silica and molded onto Alloy 194 strips treated with AAMS are appropriate values for microelectronic encapsulants.



Figure 9.1. Scanning electron micrograph of Alloy 194 strip before cleaning.



Figure 9.2. Scanning electron micrograph of Alloy 194 after cleaning.



Figure 9.3. Peel strength between photopolymerizable liquid encapsulants and Alloy 194 strips treated with silane coupling agents.



Figure 9.4. Scanning electron micrograph of peel test specimen showing cohesive failure between PLE filled with 72 wt.% fused silica and Alloy 194 strip without any silane. The particles are remnants of the PLE adhered to the Alloy 194 surface after the 180 degree peel test.



Figure 9.5. Scanning electron micrograph of peel test specimen showing cohesive failure between PLE filled with 72 wt.% fused silica and Alloy 194 strip treated with MPMS. The particles are remnants of the PLE adhered to the Alloy 194 surface after the 180 degree peel test.



Figure 9.6. Scanning electron micrograph of peel test specimen showing cohesive failure between PLE filled with 72 wt.% fused silica and Alloy 194 strip treated with AAMS. The particles are remnants of the PLE adhered to the Alloy 194 surface after the 180 degree peel test.



Figure 9.7. Scanning electron micrograph of peel test specimen showing adhesive failure between PLE filled with 74 wt.% fused silica and Alloy 194 strip treated with BTCA. Note the lack of any significant amounts of the PLE remaining on the copper surface.



Figure 9.8. Scanning electron micrograph of peel test specimen showing adhesive failure between PLE filled with 74 wt.% fused silica and Alloy 194 strip treated with PBI. Note the lack of any significant amounts of the PLE remaining on the copper surface.

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Chapter 10

RESEARCH SUMMARY AND RECOMMENDATIONS FOR FUTURE WORK

10.1 SUMMARY OF RESULTS

This research project has demonstrated the tremendous potential of highly filled photopolymerizable liquid encapsulants (PLEs) for microelectronic devices. The PLE is comprised of an epoxy novolac-based vinyl ester resin (~25 wt.%), fused silica (70-74 wt.%), and small amounts of a photoinitiator, thermal initiator, and silane coupling agent. This research has led to the development of a highly filled photopolymerizable liquid encapsulant that has the material properties required by the microelectronics industry for traditional transfer molding compounds (i.e. flexural modulus and strength, coefficient of thermal expansion, glass transition temperature, thermal conductivity, and adhesion). In addition, these PLEs have much lower viscosities than other transfer molding compounds (in order to minimize wire sweep) and exhibit similar, if not faster, in-mold cure times. Table 10.1 provides a head-to-head comparison of the material properties between the PLEs and conventional transfer molding compounds. Table 10.1 shows that the material properties of the PLEs compare quite favorably to molding compounds. Much more significant is the reduced viscosity of the PLEs and the PLE flexural modulus values that are near 1000 kg_f/mm^2 .

	PLE	Molding Compound
Viscosity (cP)	5,000 - 30,000	15,000 - 100,000
	@30°C	@170°C
Flexural Modulus (kg _f /mm ²)	1,000 - 1,200	1,000 - 1,500
Flexural Strength (kg _f /mm ²)	9 - 11	9 - 15
CTE (µm/m°C)	19 - 22	16 - 25
T_{g} (°C)	145 - 155	140 - 180
Thermal Stress Parameter	0.6 - 1.3	0.5 - 1.5
Thermal Conductivity (W/m K)	0.56 - 0.62	0.50 - 0.70
180° Peel Strength (g/cm)	20 - 95	40 - 200

 Table 10.1. Comparison of material properties between PLEs and molding compounds

Based on the results presented in the previous chapters, the PLEs with differing amounts of fused silica each have their own advantages and disadvantages. Clearly, for applications with low stress requirements and for devices with high heat outputs, the PLE filled with 74.0 wt.% would be best because of the low coefficient of thermal expansion and high thermal conductivity. If an extremely low viscosity formulation is needed to minimize wire sweep, then the PLE filled with 70.0 wt.% fused silica is most appropriate. However, if a formulation is needed with a balance set of properties, then the PLE filled with 72.0 wt.% is ideal. More importantly, this formulation exhibited the highest degree of adhesion to Alloy 194, which is imperative to minimize delamination and corrosion. Specific research results, as well as, recommendations for future work in this area are presented in the remainder of this chapter.

10.1.1. Viscosity

For encapsulating microelectronic devices, it is desired to achieve a low enough viscosity to allow the molding compound to easily flow over the chip, wirebond, and leadframe assembly, thereby minimizing problems associated with incomplete mold filling, leadframe displacement, and wire sweep. As a result, we have characterized the viscosity of the highly filled photopolymerizable liquid encapsulants to investigate the blending of two different particle size distributions to tailor the viscosity for a given filler loading. Specifically, we characterized the viscosity of PLEs containing 70.0, 72.0, and 74.0 wt.% silica, and found that a blend of particle size distributions with a particle size ratio of 3.13 resulted in the best viscosity reduction. The experimental results for the effect of the particle size distribution on the PLE viscosity were well correlated by the Krieger-Dougherty equation to account for the blending of two particle size distributions.¹ In addition, it was found that the viscosity of the PLEs decreased slightly with increasing concentration of the silane coupling agent 3methacryloxypropyltrimethoxysilane.

As the fused silica loading was increased from 70.0 to 74.0 wt.%, the PLE viscosity increased markedly. This apparently small increase in the fused silica loading can be important for microelectronic encapsulants because it can lead to a lower coefficient of thermal expansion and an enhanced thermal conductivity. As the amount of fused silica was increased from 70.0 to 72.0 wt.%, the viscosity increased by a factor of 2.3, and as the fused silica loading was increased from 70.0 to 74.0 wt.%, the viscosity increased more than five-fold. The current epoxy molding compounds are solid at room temperature, therefore even the PLE containing 74.0 wt.% fused silica has a much lower viscosity at ambient temperature than the traditional molding compounds.

10.1.2. Mechanical and Thermomechanical Properties

We have characterized the degree of cure, flexural strength, flexural modulus, coefficient of thermal expansion, glass transition temperature, and thermal stress parameter of novel photopolymerizable liquid encapsulants. The effects of fused silica

loading, UV illumination time, and postcure time on these thermal and mechanical properties were also investigated. The results indicate that a photocurable encapsulant loaded with 74.0 wt.% fused silica is very promising for this application since the material properties (flexural strength, flexural modulus, coefficient of thermal expansion, glass transition temperature, and thermal stress parameter) meet or exceed those of current commercial encapsulants, while the viscosity and in-mold cure time are reduced. These formulations are liquid at room temperature (current formulations are solid) and cure to an ejectable hardness in less than two minutes for an initiating light intensity of 200 mW/cm². The photocured samples exhibit appropriate values for the above mentioned material properties. Specific observations are as follows:

- 1. The flexural strength and flexural modulus increased with UV light illumination time until reaching a plateau value in ~90 to 120 seconds.
- The flexural strength and glass transition temperature increased with increasing postcure time at 170°C before reaching a plateau in ~4 to 6 hours. Current encapsulants are typically postcured 4 to 8 hours at 170 or 175°C.
- 3. The coefficient of thermal expansion below the glass transition decreased with increasing postcure time at 170°C before reaching a plateau in ~4 to 6 hours.
- 4. Inclusion of a thermal initiator, benzoyl peroxide, in the photopolymerizable liquid encapsulant significantly increased the flexural strength of the samples, but had little effect on the other material properties;
- 5. The ultimate degree of cure attained in a given cure cycle was significantly enhanced by the inclusion of a thermal initiator (in addition to the photoinitiator) and by postcure at an elevated temperature.

10.1.3. Reduction of In-Mold Cure Time

Current trends in microelectronic encapsulation will require in-mold cure times for molding materials to be reduced from 120 seconds to 60-90 seconds. With current thermally cured systems, this reduced cure time is difficult to achieve. We have demonstrated that photopolymerizable liquid encapsulants can meet this requirement. Photopolymerizable liquid encapsulants that were photocured for 60 and 90 seconds had appropriate ejectable hardness, and upon postcure, exhibited material properties (flexural strength and modulus, coefficient of thermal expansion, glass transition temperature, and thermal stress parameter) that were equivalent or better than those of conventional encapsulants. It was also shown that the addition of a thermal initiator does not negatively affect any of the material properties, and leads to improved flexural strength.

10.1.4. Thermal Conductivity, Specific Heat, and Thermal Diffusivity

It is critical that the silicon chip does not overheat during normal operation. The thermal properties of the encapsulant determine the amount of heat that can be removed from the device and thus affect operating temperatures of the electronic components. The thermal conductivity, specific heat, and thermal diffusivity of photopolymerizable liquid encapsulants (PLEs) were measured as a function of fused silica loading by the laser flash method. Photopolymerizable liquid encapsulants loaded with 70.0, 72.0, and 74.0 wt.% fused silica exhibited thermal conductivities between 0.56 and 0.62 W/m·K, which is within the 0.5 to 0.7 W/m·K range exhibited by most fused silica loaded molding compounds. The thermal conductivity values of the PLEs were approximately three times that of the unfilled epoxy novolac-based vinyl ester resin (k = 0.182 W/m·K).

The experimental thermal conductivity data was fit to the second order model of Agari and Uno in order to predict the thermal conductivity of the PLEs at filler loadings lower than 70.0 wt.% and filler loadings higher than 74.0 wt.%.² The experimental thermal conductivity data was well correlated by the model of Agari and Uno; this model can be used to accurately predict the thermal conductivity of the PLEs over a wide range of filler loadings.

The specific heat for the PLEs ranged between 0.83 and 0.87 J/g•K and was shown to decrease with increasing fused silica content, in agreement with the results of other authors.³ In addition, values for the thermal diffusivity ranged between 3.7×10^{-3} and 4.2×10^{-3} cm²/s and were shown to increase with increasing fused silica content.

10.1.5. Adhesion

Proper adhesion between the encapsulant and the leadframe is critical in order to prevent delamination and corrosion. The adhesive strength of photopolymerizable liquid encapsulants (PLEs) to Alloy 194 (a copper-based alloy) was measured using the 180 degree peel test. Peel strengths were measured as a function of wt.% fused silica in the PLE and the type of coupling agent used on the Alloy 194 surface. Specific observations are as follows:

 The peel strength of strips that were not treated with silane coupling agents ranged from 18 to 40 g/cm. In addition, the peel strength of strips that were treated with the silane coupling agent, 3-methacryloxypropyltrimethoxysilane (MPMS), ranged from 28 to 40 g/cm, demonstrating that the use of MPMS has a minimal effect in improving the peel strength.

- 2. Alloy 194 surfaces treated with a silane coupling agent composed of an aminoalkyltrimethoxysilane and a polyol diluted with methanol (AAMS) exhibited the highest peel strengths, with values ranging from 35 and 95 g/cm. At each level of filler loading, the peel strength is more than doubled for Alloy 194 strips that were treated with AAMS, as compared to strips that were not treated with any silane coupling agent.
- Irrespective of the coupling agent used on the Alloy 194 surface, the peel strength reaches a maximum when the photopolymerizable liquid encapsulant is filled with 72.0 wt.% fused silica.
- 4. All of the surfaces treated with either of the silane coupling agents, as well as, the control surfaces (strips that were cleaned and degreased, but were not treated with silanes or azoles) showed cohesive failure.
- 5. The peel strength between PLEs and surfaces treated with azole compounds could not be measured because of extensive delamination. All of these surfaces showed adhesive failure.
- 6. Photopolymerizable liquid encapsulants filled with 70.0 and 72.0 wt.% fused silica and molded onto Alloy 194 strips treated with AAMS exhibited high enough peel strengths for the purposes of encapsulating microelectronic devices.

10.2. RECOMMENDATIONS FOR FUTURE WORK

Although this research has demonstrated the tremendous potential of using photopolymerizations for encapsulating microelectronic devices, further research is recommended in order to improve the existing formulation and fully establish

photopolymerizable liquid encapsulants as a viable alternative to traditional transfer molding compounds. Specific research recommendations are described in the following sections.

10.2.1. Increased Light Intensities

In all of the experiments reported in this work, the light intensity was held constant at 200 mW/cm². Increasing the light intensity is an excellent possibility to further reduce the in-mold cure time. An added benefit of increased light intensities is that they may be able to significantly increase the degree of cure to a point where the postcure step is unnecessary. Although numerous authors have reported on the benefits of using higher light intensities to reduce the cure time of composites, higher light intensities may also negatively affect some of the material properties.⁴⁻⁶ Therefore, further experiments should be conducted to determine the effects of higher light intensities (up to 500 mW/cm²) on the material properties of the photopolymerizable liquid encapsulants, as well as, the ability of higher intensities to further reduce the in-mold cure time.

10.2.2. Development of Photomolding Process to Encapsulate Actual Microdevices

As was stated in Chapter 3, the primary goal of this research project was to develop a photopolymerizable formulation that has the material properties required by the microelectronics industry to effectively protect semiconductor devices. Now that a photopolymerizable liquid encapsulant has been created, future research must focus on developing a process to use this formulation and to demonstrate that the PLEs can minimize problems that are plaguing the conventionally used transfer molding process. Fortunately, a photomolding process has been developed by Hanemann *et al.* that could

easily lend itself to the photopolymerizable liquid encapsulant.⁷ These authors recently photomolded unfilled poly(methylmethacrylate) and found that they could produce high quality parts more than five millimeters thick. Basically, the process is adapted from liquid injection molding and combined with the necessities of photopolymerization. Liquid injection molding is a reactive polymer processing method where low viscosity monomers or oligomers are injected into the mold and polymerized to form the hardened part. Injection molding technology represents an established process for manufacturing polymer products with high accuracy in large-scale production (which is exactly what is needed for molding microelectronic devices). The experimental setup used by Hanemann et al. consists of two parts: the lower part with the light source and the upper part with the molding tools. Specifically, the upper part contains the mold insert, the ejector pins, the connectors for vacuum pump and external temperature control, and the reservoir with the reactive mixture. The most distinguishing features of the process developed by Hanemann et al. compared to conventional injection molding are the use of an evacuated molding tool made from high accuracy glass (to allow light to shine through the mold and cure the photopolymerizable formulation) and the integration of a powerful UV light source. Clearly, in order to effectively utilize the BAPO photoinitiator and to properly cure the photopolymerizable liquid encapsulant, the selection of the proper light source for this process is imperative. Medium-pressure mercury lamps have only a few predominant emission lines at 405 and 436 nm that can be absorbed by the photoinitiator. However, medium pressure gallium-doped lamps have an improved emission over 400 nm and, therefore, it is recommended that this light source be used in conjunction with a conventional medium-pressure mercury lamp in order to generate radiation that can penetrate into the deeper layers of the encapsulant and increase the degree of cure.⁸

There are a number of advantages in using a photomolding process. First, molding at ambient temperature results in only a small temperature rise due to the released polymerization enthalpy. Second, high filler loadings to increase the thermal conductivity and to lower the coefficient of thermal expansion can be accommodated while still achieving lower viscosities than epoxy molding compounds since the base resin is a low viscosity liquid at room temperature. Third, high thermal conductivity fillers (which are much more abrasive than fused silica) may be tolerated better in this process because lower pressures and lower velocities could be used to minimize erosion of the mold.⁹

10.2.3. Accelerated Testing

Once a photomolding process has been developed that can use the PLE and effectively encapsulate microelectronic devices, the molded devices must be tested for their reliability. In the microelectronics industry, extensive accelerated testing is performed specifically for this purpose. Accelerated testing is conducted to cause the life aging of products to occur at a rate faster than would be obtained under normal operating conditions. Commonly used accelerated tests for microelectronic devices are high temperature tests, temperature cycling tests, humidity tests, and pressure cooker tests.

10.2.4. Glob-top Encapsulation

Because the PLEs are able to meet the stringent requirements of molding compounds, it is likely that the PLEs can meet the needs of lower end encapsulation methods, such as glob-top encapsulants. A glob-top encapsulant is a moderately viscous

liquid or paste and is used to encapsulate a chip-on-board or a hybrid on a substrate.¹⁰ Glob-top encapsulants are typically thermoset epoxy or silicone resin formulations, filled to a medium level with inorganic fillers, and are traditionally meant for low-end disposable electronic products. The glob-top encapsulant is applied through a dispenser (usually a syringe fitted with a positive displacement valve to minimize the variation in the volume and rate of encapsulant delivered) to an assembled, cleaned, and tested chip on a board.¹¹ Epoxies formulated for glob-top applications typically take between 6 to 15 minutes at 120°C to cure.¹² For optimum properties, further postcuring is recommended for at least another 6 hours. It has already been demonstrated that the photopolymerizable liquid encapsulants can cure in a shorter amount of time and exhibit a viscosity suitable for this application. However, actual electronic components on circuit boards must be encapsulated using PLEs, as well as the glob-top process, to demonstrate the suitability of the PLEs as glob-top encapsulants.

10.3. REFERENCES

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