

Development of New Low Stress Epoxies for MEMS Device Encapsulation

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Abstract—In this study, a series of new low stress epoxies was introduced as conformal encapsulants, which show a high promise to meet all the requirements for the protection of the pressure sensor system. Mechanical properties such as initial Young's modulus, toughness and ultimate tensile stress were evaluated. The more critical issue of material's contamination resistance to the jet fuel was improved. And the mechanism behind materials low stress and toughness behaviors was investigated from the viewpoint of microstructure.

Index Terms—Contamination resistance, low stress epoxies, microelectromechanical systems (MEMS), toughness.

I. INTRODUCTION

MICROELECTROMECHANICAL systems, or MEMS, is an emerging technology that may fundamentally affect every aspect of our lives. The hallmark of next thirty years of the silicon revolution will be the incorporation of new types of functionality onto the chip; structures that will enable the chip to not only think, but to sense, act and communicate as well. This revolution will be enabled by MEMS [1]. Currently, automobile accelerometers, medical equipment, and sensing systems utilizing MEMS technology have already been commercialized, and its exploding market is predicted to be approximately 30 billion dollars by the year of 2001. However, one of the major issues of today's MEMS technology is the packaging that provides mechanical and environmental protection to MEMS devices. Unlike ICs, the packaging for MEMS is much more difficult, because most MEMS devices have complex topography and delicate moving parts which need to be protected but not affected/hindered by the package, and thus both materials and application techniques need to be developed.

Currently, the Boeing Company is anticipating to use MEMS technology in a critical aerospace application for monitoring the static pressure on the wings, tail, nacelle, engine, and body of an airplane during flight test, where several thousand of pressure sensors need to be used. There are two critical needs in this application. One is a standard communication interface, the other is a low-cost packaging approach [2]. Each sensor is actually a multichip module containing a piezo pressure sensor fabricated with MEMS technology and analog/digital driving ICs. The most challenging task, besides those conventional pack-

aging issues, is to protect the MEMS sensor against extremely adverse environment without affecting the moving parts and sensitivity. All the sensors will experience extreme temperature variation (-55 to 140 °C), mechanical shock and vibration, high humidity, jet fuel contamination, and UV radiation, etc. Therefore, a multifunctional conformal coating and appropriate applying method is urgently needed. The success of this packaging approach will not only benefit the design and improvement of military and commercial airplanes, but also be a breakthrough in the MEMS packaging field.

Reliable nonhermetic conformal encapsulants have been widely applied since the 1970s [3]. Recent applications have been aimed at the automotive, communication and aerospace markets. Hermetic sealing has shown a significant limitation to some specific devices. In this study, a primary focus to ensure the operating reliability of MEMS devices exposed to hostile environments is to use conformal coatings that exhibit improved resistance to moisture ingress, mobile ions such as Na^+ , K^+ , Li^+ , Cl^- permeation, low residual stress, good interfacial adhesion, planarization and uniform low profile. Low stress is a critical factor for the design of the conformal coating. Because the signal of static pressure will be accepted through the movement of piezo pressure sensor, any stress from conformal coating will affect the accuracy of sensing. In addition, chemical resistance is also a big concern for the material design. Since some of the sensors will be attached to the site exposed to the fume of combusted jet fuel during flight test, resistance to the contamination of jet fuel became an additional critical request.

Historically, reliable nonhermetic encapsulation materials include high purity epoxies, silicones, acrylics, polyurethane and Parylene family (para-xylyene, type N, C, D, F) [4]–[6]. These conformal coatings can meet a broad variety of environmental protection criteria. However, none of them can simultaneously meet all the requirements aforementioned.

In this study, a new low stress epoxy was investigated, which shows a high promising to satisfy the key requirements for this application. And series thermal and mechanical evaluation and jet fuel contamination resistance characterization were conducted afterwards.

II. EXPERIMENTAL

A. Formulation

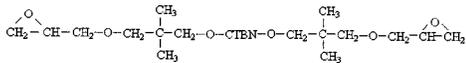
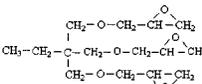
The developed low stress epoxies consist of three major components, elastomer modified epoxy (Epon™ 85005, Shell Chemical Co.), tri-functional phthalic epoxy (Epon Modifier 48, Shell Chemical Co.) and cycloaliphatic anhydride (HMPA,

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TABLE I
WEIGHT PERCENTAGES OF CTBN AND M48 IN SERIES LOW STRESS EPOXIES

Composition	EPON 58034	Epon Modifier 48
Chemical Structure		
ID	CTBN (wt%)	M48 (wt%)
LS30	34.39	0
LS31	33.95	0.99
LS32	33.50	1.95
LS33	33.07	2.92
LS34	32.63	3.88
LS35	32.20	4.84
LS36	30.07	9.54
LS37	28.00	14.10
LS38	25.85	18.54
LS39	24.03	22.86
LS40	22.12	27.06

Aldrich Chemical). Imidazol type amine 2M4E-Z (Shikuku, Japan) was used as catalyst. All these materials were applied without any treatment. Formulated materials were stored in a freezer at $-40\text{ }^{\circ}\text{C}$ when not in use.

B. Differential Scanning Calorimeter (DSC) Analysis

Thermal behavior of polymerization of the formulation was conducted by DSC analysis (Modulated DSC, model 2920, TA Instruments). Approximately 10 mg of each formulated samples was put into DSC pan and run the DSC test thereafter for identifying the peak curing temperature of the studied formulation. The DSC test is from room temperature to $200\text{ }^{\circ}\text{C}$ with a heating rate of $5\text{ }^{\circ}\text{C}/\text{min}$. Nitrogen was used as purging gas for the environmental protection of the DSC chamber.

C. Dynamic Mechanical Analyzer (DMA)

Modulus measurement of materials was generated on the Dynamic Mechanical Analyzer, model 2980 (TA Instruments). Materials were cured at $150\text{ }^{\circ}\text{C}$ for 60 min, and then stripped into specifications of $20 \times 8 \times 1.0\text{ mm}$. During measurement, a film tension mode was selected for the low modulus material test. Measurement temperature was set from $-100\text{ }^{\circ}\text{C}$ to $100\text{ }^{\circ}\text{C}$ according to the temperature point of glass transition temperature (T_g). Heating rate is controlled at $3\text{ }^{\circ}\text{C}/\text{min}$.

D. Tensile Test

Tensile test is a typical measure to evaluate mechanical property of the interested materials, such as initial Young's modulus, tensile strength, percentage of elongation at break, and noncrack fracture energy. In this study, the tensile test was done using Instron tensile tester (Model MTI1000, Materials Test Company) under a displacement control mode with a displacement rate of $2.54\text{ mm}/\text{min}$. Rectangular samples of $1.5 \times 0.5\text{ in}$ were prepared according to the formulation in Table I with a thickness of $1.0 \sim 1.2\text{ mm}$ and used for no-crack tensile test.

E. Microstructure Analysis

Scanning electron microscope (SEM) (by Hitachi Model S-800) technique was used for infrastructure analysis on these series samples through the observation of sample fractures, which was prepared by quickly breaking the strip samples after being frozen in liquid nitrogen for 1 min. A thin layer of gold was deposited on each sample for better conductivity during SEM experiment. Microstructures of sample fractures were shown.

F. Jet Fuel Contamination Analysis

Resistance to the jet fuel contamination of low stress epoxy was investigated through measuring the adhesion change before and after sample immersion in gasoline for 10 or 20 min. The adhesion value was conducted based on die shear mode by using die shear tester (Royce Instruments System 552).

III. RESULTS AND DISCUSSION

In this study, the design strategy of low stress epoxies is to introduce flexible polymer segment into the epoxy system. Epon™ 85 034 rubber modified epoxy formed from the reaction of diglycidyl ether of 1, 3-isopantediol and a carboxyl terminated butadiene–acrylonitrile elastomer with 50 wt% for each. The use of this epoxy will result in an improved flexibility, adhesion properties, and fatigue resistance. The concentration of Epon Modifier 48 (M48) was gradually increased for the decrease of viscosity and the increase of structural crosslinking density. Cycloaliphatic dianhydride HMPA was used as a hardener. Imidazole 2E4MZ-CN with 2 wt% of base resin was used as a catalyst. Major components in low stress epoxies of the studied samples were listed in Table I.

A. Curing Temperature and Time

DSC is a common method to measure the endotherm or exotherm of polymerization with respect to temperature during sample cure. Fig. 1 shows the change in heat flow as a function of temperature as well as the variation of CTBN concentration in the formulations. It can be observed that the peak curing

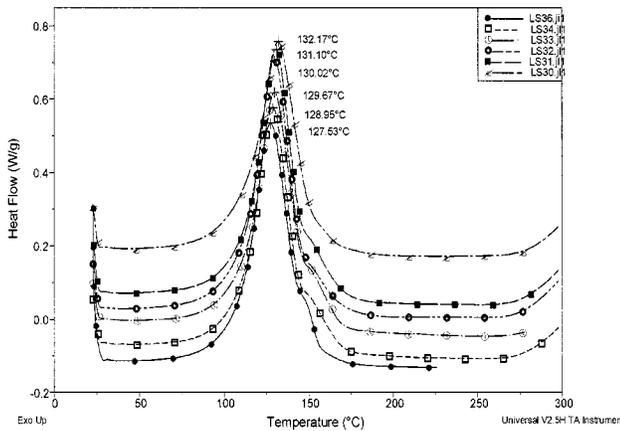


Fig. 1. DSC results of the series epoxies with respect to the change of CTBN concentration.

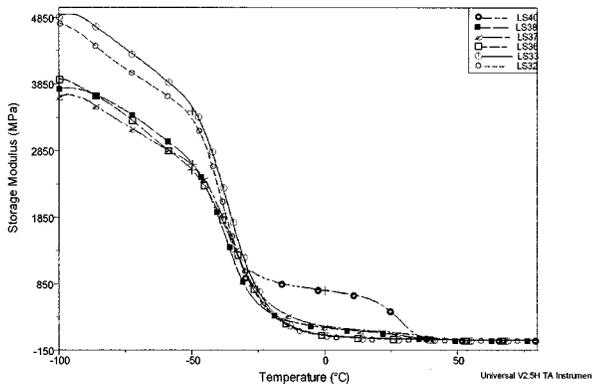


Fig. 2. DMA results on the series low stress epoxies.

temperature for all the samples is around 130 °C and tends to decrease a little bit with the decrease of CTBN concentration. And a tiny side peak on the right shoulder of the main peak might associate with the reaction between CTBN modified epoxy and HMPA. To make sure the complete cure of epoxy specimens, 150 °C/60 min with a heating rate of 10 °C/min was selected as the curing procedure. And all the samples used for the later analysis were prepared according to this curing procedure.

B. Storage Modulus Characterization

Storage moduli of series low stress epoxies were tested by DMA from -100 to 100 °C with a heating rate of 3 °C/min. Fig. 2 illustrates the dynamic mechanical analysis results. With the CTBN concentration decreases, the storage moduli of the samples increase before T_g and decrease after T_g . And the glass transition temperature range becomes wider, which attributes to the high reactivity of the aliphatic epoxy and the polymerization occurred at low temperature. The lowest T_g of the specimen is around -42 °C.

C. Non-Crack Tensile Test

The use of elastomer modified epoxy in the basic epoxy formulation provides a way to introduce elastomer particles into the epoxy matrix. Principally, the effect of CTBN on toughness improvement is its allowing the advanced energy to be dissi-

ated into a relative large volume of phase at the crack tips. The fracture behavior of CTBN-modified epoxy resin may be considered on the basis of an elastic-plastic model based on J. R. Rice theory [7]. In our study, the elastomer particles were formed essentially by a precipitation process during the polymerization. Therefore the boundary between particle and matrix is diffuse. As thus, under high stress, this region becomes a highly plasticized region that dominates shear deformation and inhibits micro-crack initiation and propagation. The large plastic zone is always developed at the crack tip before local microcracks can coalesce and advance the main crack front. This mechanism of toughening by dispensed elastomer particles has been discussed by Bucknall [8] and by Sultan and McGarry [9].

Non-crack tensile test is a common technique to evaluate the toughness of elastomer materials. Young's modulus, tensile strength, elongation, and fracture energy of the sample can be generated from the same measurement. Table II lists the sample identification and their corresponding tensile test results got from their load-displacement profiles. These results indicate that the initial Young's modulus shows constant with the concentration of CTBN decrease from 33.50 wt% to 30.07 wt% then swiftly increases with CTBN concentration further decreases to 22.12 wt%. The partial reason is that the cross-linking density of the polymer system increases with the concentration of M48 increase. Percentages of elongation at break, ultimate tensile stress and fracture energy show the same trend as that to the initial Young's modulus. And the possible mechanism will be given afterwards.

Fig. 3 illustrates the fracture energy changed with respect to the concentration of CTBN in the formula. Fracture energy is a physical property to evaluate the toughness of certain materials. It is identified as the energy used for generating a unit new fracture surface at the instant of crack propagation. In our study, we use noncrack tensile test to approximately get fracture energies of elastomer materials, which could indicate the trend of toughness change with the decrease of CTBN concentration. It can be obviously observed from Fig. 3 that when CTBN weight percentage changed within 33.5 to 30.07%, the toughness of the low stress epoxy does not show big change. However, once the CTBN concentration continuously decreases, then the toughness of the epoxy increase rapidly. This result is completely consistent to the conclusion of Riew's [10] work.

D. Microstructure Analysis

A microstructure examination of fracture specimens was carried out using scanning electronic microscope (SEM). Fracture morphology of specimen LS30, LA36 and LS40 are illustrated in Fig. 4. LS30 is a CTBN-modified-epoxy resin system. The SEM of LS30 [Fig. 4(a)] shows somewhat diffused rubber domains, indicative of approaching a "blend" rather than distinctive "particulate" phase. This suggested that at 34 wt% CTBN rubber content is too high for the toughening and result in a flexiblized sample. The addition of M48 can improve the toughness of CTBN-modified-epoxy system by generating a two-particle-size resin system. LS36 contains 30 wt% of CTBN and its fracture morphology illustrates large particles of $\sim 20 \mu\text{m}$ diameter and small particles of less than $1 \mu\text{m}$ [Fig. 4(b)]. Continuing the decrease of CTBN content, a multiparticle-size resin

TABLE II
EFFECT OF CTBN CONCENTRATION ON MECHANICAL PROPERTIES OF SERIES LOW STRESS EPOXIES

Sample ID	CTBN (wt%)	Young's modulus (MPa)	Elongation (%)	Ultimate tensile stress (MPa)	Fracture energy (kJ/m ²)
LS32	33.50	2.61	119.00	2.77	23.53
LS33	33.07	2.52	125.78	2.37	23.27
LS34	32.63	2.29	100.04	2.47	27.08
LS35	32.20	4.70	98.45	2.48	19.62
LS36	30.07	3.21	100.71	2.65	21.36
LS39	24.03	120.25	163.14	3.13	28.04
LS40	22.12	137.65	267.51	6.94	237.56

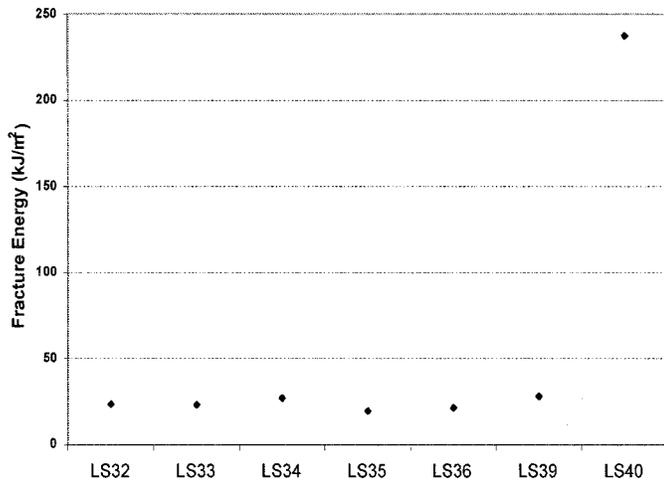


Fig. 3. Fracture energy changed with the weight percentage of CTBN.

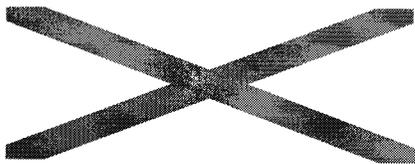


Fig. 4. SEM analysis on the fracture surfaces of low stress epoxies.

system of LS40 was formed and illustrated in Fig. 4(c). The maximum particle size is $\sim 40 \mu\text{m}$. The toughness of LS40 is almost 10 times that of LS32. Through the observation of the fracture morphology in Fig. 4(b) and (c), it can be seen that the fracture mostly happened along the surface of large particles, which served as a sort of nucleation site for local shear deformation and be easily pulled out of the matrix. This phenomenon implies that during fracture the large particles changed the local deformation to an intensive shear mode and then prevented the small particles from dilatational rupture. This situation is again accord to the result of Riew's, that the small particle is associated with shear deformation, whereas the large particles involve crazing around particles. Therefore, the synergetic effect of multiparticle system is apparent, and the relation of fracture mechanism and phase structure needs to be further investigated.

E. Contamination Test

Resistance of the low stress epoxy to the jet fuel contamination was a critical issue met during the initial flight test. In this study, contamination resistance of the developed epoxies

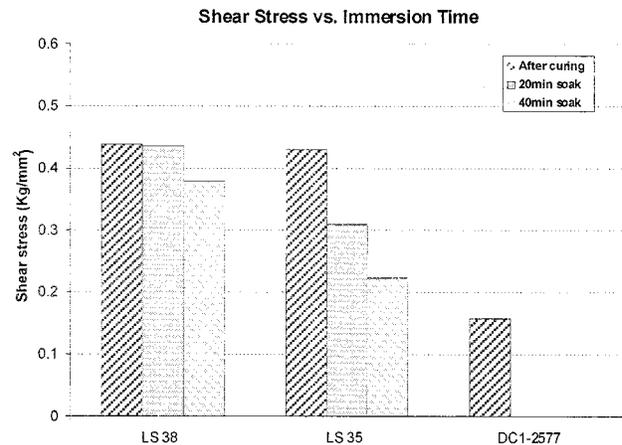


Fig. 5. Adhesion stress changed with contamination time.

was evaluated by comparing the adhesion before and after the adhesion test samples were immersed into gasoline (substitution of jet fuel) for certain period of time. Adhesion measure was done follow a die shear test mode. Results were shown in Fig. 5. Adhesion of the best performed low stress epoxy decayed up to 0.51% after 20 min immersion and up to 13.63% after 40 min immersion. While the control sample of DC1-2577 (an initial selection), a silicone from Dow Corning, almost completely swelled after 20 min immersion in the gasoline. Therefore no data can be obtained.

IV. CONCLUSION

A series low stress epoxies has been developed by introduce a flexible elastomer segment into the epoxy system to form a copolymer. The multiparticle-size resin system can be formed through the precipitation of rubbery particles from the polycondensation. This unique intrinsic microstructure can greatly improve the toughness, elongation and fracture energy of the typical epoxy base resin system. At the same time, it remains enough contamination resistance to the jet fuel. The low stress epoxies developed in this study show a high potential for the protection of pressure sensors in aeronautics application.

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