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Synthesis of Epoxy Functional Siloxane and its Effect on Thermal Stress

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Abstract: Epoxy resin based encapsulants are widely used in semiconductor packaging applications. Epoxy resin based encapsulants are often subject to crack or delamination during the reliability test due to the thermal stress caused by high modulus nature of epoxy resins. Epoxy functional siloxanes are often added into epoxy resin to reduce the modulus so that the thermal stress can be reduced.

Epoxy functional siloxanes, additives for reduced modulus, were synthesized and added into the curable epoxy resins. The modulus and the coefficient of thermal expansion (CTE) were also measured to investigate the thermal stress and to see whether the epoxy functional siloxane adversely affects the CTE or not.

As a result, around 26% to 72% of thermal stress reduction was observed with no adverse effect on CTE.

Keywords : *siloxane, epoxy, hydrosilylation, thermal, stress*

1. Introduction

Epoxy resins are widely used in the electronics industry because of their high impact resistance and excellent adhesion property and mechanical strength. Epoxy resins are also used as adhesives and encapsulants protecting the semiconductor chips. Semiconductor chips encapsulated with epoxy resins are called semiconductor packages.

The performance and the life time of semiconductor packages are evaluated by reliability test. Reliability test is performed under the harsh test conditions such as thermal cycle test, pressure cooker test and reflow test. Semiconductor packages sometimes resulted in crack or delamination during the reliability test due to the thermal stress.

Thermal stress is a function of the modulus and the coefficient of thermal expansion (CTE) according to the following thermal stress relationship.

$$\sigma = \frac{E\alpha\Delta T}{1-\nu}$$

σ = thermal stress (MPa)
E = modulus (MPa)
α = CTE ($^{\circ}C^{-1}$)
ν = poisson's ratio
T = temperature ($^{\circ}C$)

Epoxy resin encapsulants are excellent in impact resistance but weak in stress reduction because they transfer the stress directly to the semiconductor chips and

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components due to their rigid or high modulus natures. This is why semiconductor packages encapulated with epoxy resins often fail in reliability test caused by crack or delamination.

Low modulus materials or organic rubbers such as carboxyl terminated butadiene acrylonitrile (CTBN) or amine terminated butadiene acrylonitrile (ATBN) rubber are often added to epoxy resins to reduce the modulus for thermal stress relief. These organic rubbers, however, are not thermally stable and sometimes adversely affect the physical properties of the epoxy resins. Siloxane polymers are sometimes chosen as low modulus additives for epoxy resin encapsulant in replacement of organic rubbers due to their thermal stability and low modulus. But epoxy functionality or compatibility is required for the siloxane polymer for the reaction with epoxy resins since siloxane polymers are usually not compatible with epoxy resins.

In this study, epoxy pendant block siloxane polymers were synthesized, and added into epoxy resin composition to verify decrease in modulus, which is a major driving force for reduced thermal stress. Coefficient of thermal expansion (CTE) was also measured to see if the addition of epoxy functional siloxane increases CTE with adverse effect on the thermal stress. Finally thermal stress was calculated and verified by thermal stress relationship using the modulus and the CTE data measured above.

Functional siloxanes with low epoxy content were also synthesizedto see if further stress reduction is achievable. For the synthesis of functional siloxane with low epoxy content, allyl polyether was introduced in place of some portion of the allyl glycidyl ether.

2. Experimental

2.1. Reagents

For the synthesis of epoxy functional siloxane, allyl glycidyl ether (AGE, 114 g/mol) was purchased from Sigma-Aldrich. Methyl hydrogen polysiloxane (MHPS, 748 g/mol, SiH 0.76%) was obtained from Dow Corning. Hydrosilylation catalyst, hexachloro platinic acid (HCPA, 30% Pt), waspurchased from Alfa Aesar, and diluted with isopropyl alcohol into 0.3% Pt solution for the precise control of the catalyst dosage. MA-200 allyl polyether (APE, 240 g/mol) obtained from NOF Corp. was also used in combination with allyl glycidyl ether to synthesize functional siloxane with low epoxy content.
For the preparation of epoxy curable composition, DER-332 diglycidyl ether of bisphenol A (DGEBA, 384 g/mol) was obtained from Dow Chemical. HN-2200, methyl tetrahydro phthalic anhydride (MTHPA, 166 g/mol) obtained form Kukdo Chem was used as curing agent. For epoxy ring opening catalyst, triethanol amine (TEA, 98%) purchased from Sigma-Aldrich was used.

2.2. Synthesis of Glycidoxypropyl Polysiloxane

17.8 g (23.8 mmol) of MHPS, 15.53 g (136.1 mmol) of AGE and 0.06 g of HCPA were introduced into 1 L round bottom flask equipped with thermometer and nitrogen purge gas. The mixture was heated at 80 ℃ for 2 hours under nitrogen atmosphere using Rota mantle. The reaction mixture was then vacuum evaporated at 100 ℃ for 1 hour after the reaction was completed to obtain the glycidoxypropyl polysiloxane (GPPS).

2.3. Synthesis of Glydoxypropyl Polyethersiloxane

Functional siloxane with low epoxy content was also synthesized by incorporating APE in combination with AGE. 14.07 g (18.8 mmol) of MHPS, 5.93 g (52.0 mmol) of AGE, 13.33 g (55.6 mmol) of APE and 0.06 g of

HCPA were introduced into 1 L round bottom flask equipped with thermometer and nitrogen purge gas. The mixture was heated at 80 ℃for 2 hours under nitrogen atmosphere using Rota mantle. The reaction mixture was then vacuum evaporated at 100 ℃ for 1 hour after the reaction was completed to obtain glycidoxypropyl polyethersiloxane (GPPES).

2.4. Preparation of Epoxy Resin Composition

5 g of epoxy functional siloxane synthesized above was mixed with 55 g of DGEBA, 39 g of MTHPA curing agent and 1 gof TEA catalyst using Thinky® mixer at 2000 rpm for 30 seconds. Then the mixture was de-aired at -650 mmHg for 10 minutes and poured into the 0.5 mm thick Teflon® mold with Teflon®release film and then clamped and cured at 175 ℃ for 1 hour to measure the elastic modulus. The mixture was also cured in 5 mm thick silicone rubber mold with Teflon® release film and then clamped and cured at 175 ℃for 1 hour to measure the coefficient of thermal expansion (CTE).

Epoxy resin composition with no addition of epoxy functional siloxane was also prepared for comparison. 58 g of DGEBA was mixed with 41 g of MTHPA and 1 g of TEA catalyst and cured in the same manner as described above.

2.5. Material Characterization

The structure of synthesized epoxy functional siloxane, GPPS, was analyzed by Nicolet FT-IR and the molecular weight and the yield were analyzed by Waters GPC. Elastic modulus was measured with TA Instrument ARES Rheometer and CTE was measured with Seiko Instrument thermal mechanical analyzer (TMA) at the temperature ranging from 29 ℃ to 150 ℃.

3. Result and Discussion

3.1. Analytical Result

Synthesized GPPS and GPPES were analyzed by Nicolet FT-IR as shown in the Figure 1 and 2. Epoxy functional peak and the unreacted SiH functional peak were detected at around 3060 cm^{-1} and 2155 cm^{-1} respectively. Ethylene oxide peak was observed at around 1460 cm^{-1}.

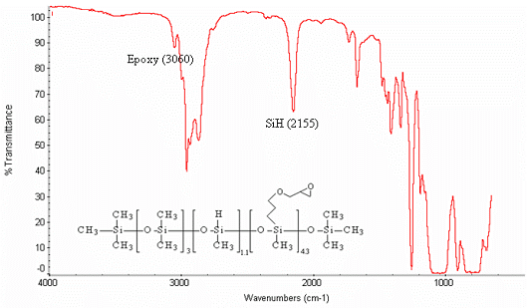

Fig. 1. FT-IR spectrum of glycidoxypropyl poly siloxane.

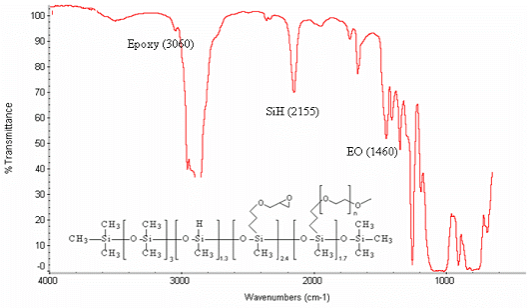

Fig. 2. FT-IR spectrum of glycidoxypropyl polyether siloxane.

Molecular weight and the yield were also analyzed by Waters GPC system as shown in the Figure 3. Molecular weights of the synthesized GPPS and GPPES were measured by GPC and the resultswere 1,400 and 1,900 while theoretical molecular weights were 1,170 and 1,480. The yields were around 89.3% and 89.5% respectively measured by GPC.

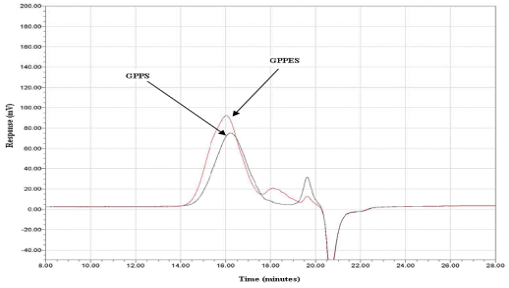

Fig. 3. GPC chart of glycidoxypropyl polysiloxane and glycidoxypropyl polyethersiloxane.

5% of synthesized GPPS and GPPES were added into the epoxy resin with anhydride curing agent and cured at 175℃for the measurement of elastic modulus and CTE using Rheometer and TMA respectively. Elastic modulus and CTE were measured below and above glass transition temperature (T_g) because modulus and CTE are dependent on T_g. Modulus and CTE of epoxy resin composition with no addition of epoxy functional siloxane was also measured for comparison.

Elastic modulus reduced by 20% below T_g(42% above T_g) when 5% of GPPS was added and 35% below T_g(72% above T_g) when 5% of GPPES was added. It was alsofound that there was relatively little change in CTE when epoxy functional siloxanes were added.

Elastic modulus and CTE measured from 29 ℃ to 150 ℃ are shown in the Figure 4, 5, 6 and 7.

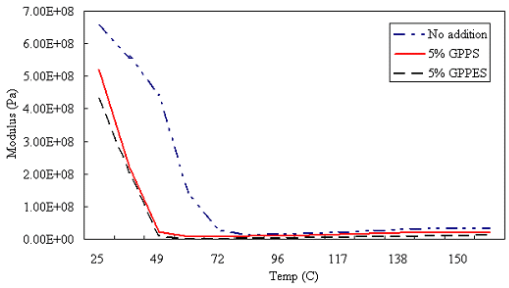

Figure 4. Elastic modulus comparison chart.

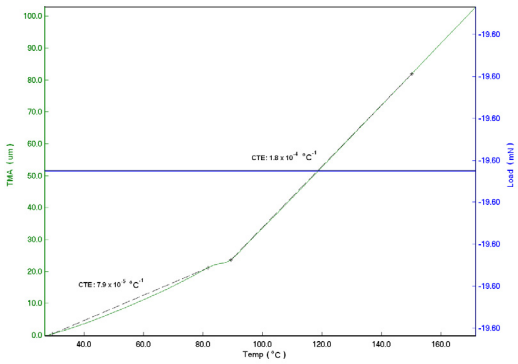

Fig. 5. CTE and T_g of epoxy resin composition with no addition of epoxy functional siloxane.

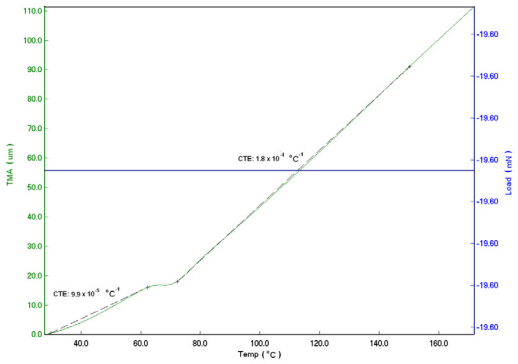

Fig. 6. CTE and T_g of epoxy resin composition with addition of 5% GPPS.

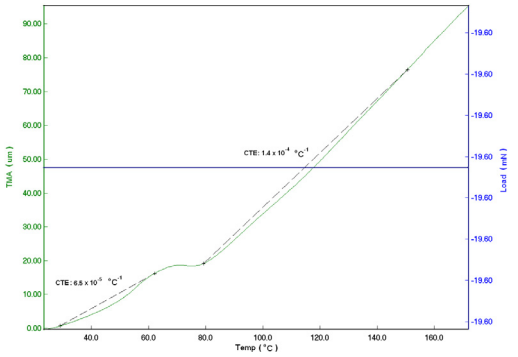

Fig. 7. CTE and T_g of epoxy resin composition with addition of 5% GPPES.

3.2. Thermal Stress Estimation

Based on elastic modulus and CTE data, thermal stress was calculated by thermal stress relationship described in the introduction section.

As shown in the Table 1 and 2, reduction of the thermal stress was estimated when epoxy functional siloxane was incorporated into the epoxy resin composition. Further reduction of the thermal stress was also possible with functional siloxane with low epoxy content according to the calculation. This stress reduction may be attributed to shock absorption effect of the low modulus or rubbery properties of epoxy functional siloxanes incorporated in the epoxy resin composition.

Table 1. Thermal Stress Estimation below T_g

Below T_g	No addition	5% GPPS	5% GPPES
CTE (α), $^oC^{-1}$	7.9×10^{-5}	9.9×10^{-5}	6.5×10^{-5}
Thermal stress, MPa	2.41	1.49	1.26

Table 2. Thermal Stress Estimation above T_g

Above T_g	No additives	5% GPPS	5% GPPES
CTE (α), $^oC^{-1}$	1.8×10^{-5}	1.8×10^{-5}	1.4×10^{-5}
Thermal stress, MPa	0.47	0.35	0.13

4. Conclusion

It is known that the addition of low modulus materials into epoxy encapsulants reduce the thermal stress during the reliability test. In this study, epoxy functional siloxanes was synthesized and added into the epoxy resin composition to measure the modulus. CTE was also measured because CTE also can affect the thermal stress. Thermal stress reduction effect was calculated using modulus and CTE data measured and followings are conclusions of this study.

Thermal stress reduction effect was estimated by introducing the elastic modulus and CTE data to thermal stress relationship. It was found that estimated thermal stress reduced by 26 to 72% with the addition of the epoxy functional siloxanes. With the functional siloxane with low epoxy content such as GPPES, further reduction of the thermal stress was attainable by thermal stress relationship.

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