Effect of Filler Content and Coupling Agent on Mechanical Properties of Underfill Material

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Abstract
Effects of filler content and coupling agent on mechanical properties of underfill (UF) were investigated using standard UF materials which are composed bisphenol F-type epoxy resin and spheroidal SiO₂ filler. For the effect of filler content, elastic modulus of UF increased and fracture strain decreased with increasing the filler content. On the contrary, the effect on tensile strength was negligible. When the temperature was above T_g, elastic modulus decreased and fracture strain increased remarkably. Fracture mainly occurred in matrix resin below T_g and in the interface between matrix resin and filler above T_g. Moreover, it was confirmed that tensile strength and fracture strain were decreased by aging treatment. For the effect of coupling agent, elastic modulus and tensile strength of UF were increased by coupling treatment. Fracture strain was increased at R.T., but was decreased at 80°C and 120°C by coupling treatment. Tensile strength depends on the interfacial state of matrix resin and fillers. Peeling of fillers from matrix resin was suppressed by coupling treatment at the temperature under 80°C. Fracture mode of UF with coupling treatment changed from matrix fracture to interfacial fracture in the boundary of T_g.

Keywords: Underfill, Filler, Aging Treatment, Coupling Agent, Tensile Properties

1. Introduction
Recently, miniaturization and high performance of electronics have been promoted. To achieve these requirements, area array packages such as ball grid array, chip size package and flip chip have been spread.[1] In the solder joint of area array package, thermal stress which is caused by co-efficient of thermal expansion (CTE) mismatch between package and substrate materials is loaded. In particular, thermal fatigue fracture has been a major issue in the flip chip joint.[2] Then, UF has been applied for the flip chip joint to release the thermal stress loaded to the joint.[3] Material properties of UF strongly affect on the solder joint reliability. It was reported that the thermal fatigue life of solder joint degrades compared with that of the original solder joint unless suitable UF is applied.[4, 5] Thus, investigation of material properties of UF is very important to design the solder joint reliability.[6] Current UF materials include many kinds of additives such as a curing agent, filler, a coupling agent, a coloring agent and so on. Since the details of such additives are not revealed, the effects of additives on material properties and mechanical properties of UF are not clear.[7, 8] The purpose of this study is to investigate the effects of filler content and coupling agent on mechanical properties of UF. In this study, standard UF materials which are composed of clear additives were prepared and mechanical properties of them were investigated.

2. Experimental Procedure
Table 1 shows the specification of UF materials to investigate the effect of filler content. Bisphenol F diglycidyl ether
ether and Bis (4-amino-3-ethylphenyl) methane were used as a matrix and a curing agent, respectively. Spherical SiO2 filler with 1.98 μm average particle size was added in the matrix. The particle size is conventional one for flip chip applications. 3-glycidoxypropyltrimethoxysilane was applied as a coupling agent for SiO2 filler. Three types of UF, which filler contents were changed from 0 to 49.9 wt%, were prepared. UF materials were poured into a Teflon mold on the hot plate heated to 80°C. Curing of UF was conducted at 80°C for 2 h and sequentially at 150°C for 4 h. The glass transition temperature (Tg) of UF materials after curing were measured by differential scanning calorimetry (DSC). The Tgs of A1, A2 and A3 were investigated to be 108.2°C, 109.2°C and 108.4°C, respectively.

Table 2 shows the specification of UF materials to investigate the effect of coupling agent. Two types of coupling treatment, which are dry treatment (C_d) and wet treatment (C_w), were investigated in this study. Although the specification of C_d used here is the same one of UF as A3 shown in Table 1, production lots of them were different. C_w is expected to have a superior coupling effect to C_d because the coupling treatment was conducted in a wet process. UF material without coupling agent (C_0) was also prepared for comparison. The Tgs of C_d, C_w and C_0 were investigated by DSC measurement to be 108.4°C, 108.5°C and 109.1°C, respectively.

Figure 1 shows shape and dimensions of the tensile specimen fabricated with the Teflon mold. The tensile specimen is based upon JIS No. 7 specimen with 5 mm width and 1 mm thickness. The gage length and the parallel length were 8.9 mm and 10 mm, respectively. To investigate the effect of aging treatment, aging was carried out for 250 h, 500 h, and 1,000 h at 120°C using a heating furnace. Tensile test was conducted at strain rate of $8.3 \times 10^{-3}$ s$^{-1}$ at three temperatures of R.T., 80°C and 120°C. Three specimens were tested in each tensile condition. Fracture surfaces were observed with a scanning electron microscope (SEM). Viscoelasticity of UF materials were investigated by dynamic mechanical analysis (DMA). The specimen with $32 \times 5 \times 1$ mm size was prepared for DMA (refer to Fig. 1 (b)).

3. Results and Discussion

3.1 Effect of filler content

3.1.1 Tensile properties

Figure 2 shows the effect of filler content on tensile properties of UF. Elastic modulus increases with increasing the filler content. The result means that the composite effect of SiO2 filler is effective on elastic modulus. Tensile strength is relatively stable at R.T. and gradually increases with increasing the filler content at 80°C and 120°C. Fracture strain reduces with increasing the filler content. Since SiO2 filler is stiff material, the increase of filler content causes the reduction of fracture strain.

For the effect of temperature on tensile properties, elastic modulus and tensile strength diminish and fracture strain improves with increasing temperature. Tensile strength decrease due to localized plastic deformation at 80°C because localized micro-Brownian motions can be gradually promoted in the polymer matrix even at temperatures below Tg.[9] The difference of fracture strain at R.T. and 80°C is negligible. Moreover, elastic modulus decreases and fracture strain increases remarkably when the temperature is above Tg which is approximately 110°C. This is probably due to the micro-Brownian motion. Since the motion of the polymer chain is improved at a temperature above Tg, ductility is greatly improved. On the contrary, an abrupt change in the tensile strength is not observed when the temperature changes across the Tg. At a temperature above Tg, the polymer chains are oriented in the tensile direction so that the tensile strength would increase slightly. As the result, the abrupt decrease of tensile strength would be inhibited.

3.1.2 Fracture surfaces

Figure 3 shows fracture surfaces observed with a SEM.
In fracture surfaces of A1 at R.T. and 80°C, it was confirmed that there are radial cracks. The origin of the cracks corresponds to the crack generation point. At 120°C, no crack was observed in the fracture surface of A1. In this study, fracture strain investigated by measuring the specimen butted two fractured pieces after tensile test was approximately a few %. Therefore, the fracture surface would change from the ones as observed at R.T. and 80°C to that at 120°C by viscositic recovery of UF.

In the fracture surfaces of A2 and A3, similar microstructures were observed regardless of the filler content. At R.T., rather elongated microstructures were observed in the fracture surfaces. SiO₂ filler were scarcely observed in the fracture surfaces. This means that fracture occurs in matrix resin itself. At 80°C, several SiO₂ filler were observed in the fracture surfaces which show rather elongated microstructures. At 120°C, SiO₂ filler were observed in the whole fracture surfaces. Moreover, many tracks where SiO₂ filler separate from matrix resin were also observed in the fracture surfaces. As described above, since the $T_g$ of UF was approximately 110°C, the test temperature of 120°C is the temperature above the $T_g$. As shown in fracture surfaces of A2 and A3 in Fig. 3, main fracture mode was changed from fracture of matrix resin itself to that of interface between matrix resin and filler when the test temperature increases above $T_g$ of UF. It seems that the coupling effect of SiO₂ filler with 3-glycidoxypropyltrimethoxysilane degrades at the temperature above $T_g$ of UF. The degradation of coupling effect of SiO₂ filler strongly affects on the reduction of elastic modulus (refer to Fig. 2 (a)).

### 3.2 Effect of aging treatment

#### 3.2.1 Tensile properties

Figure 4 shows the effect of aging treatment on tensile properties of UF which were estimated at R.T. Elastic modulus increases with increasing the aging time in all filler content investigated, although the increase rate is relatively low in A1 compared with A2 and A3. This means
that the composite effect of SiO\textsubscript{2} filler on elastic modulus is effective even after aging. On the contrary, tensile strength and fracture strain decrease with increasing the aging time. The effect of filler content on both properties becomes to be small with increasing the aging time.

Figure 5 shows the Fourier-transform infrared spectroscopy (FT-IR) analysis results of aged A3 specimens. The new peak near 1,700 cm\textsuperscript{-1} attributable carbonyl compounds was observed with increasing aging time. Carbonyl group is a functional group derived from the degradation of epoxy resin. On the basis of the FT-IR analysis, it was confirmed that oxidative degradation by aging treatment proceeds. Upon aging, cleavage of the polymer chain by oxidative decomposition occurs so that the degree of crystallinity is increased by rearrangement of intermolecular. The increase of the degree of crystallinity seems to make elastic modulus increase as shown in Fig. 4 (a). On the other hand, cleavage of the polymer chain causes the degradation of tensile strength and fracture strain.

3.2.2 Fracture surfaces

Figure 6 shows fracture surfaces after aging treatment. In the A1 specimen, it was confirmed that the fracture surface is smooth with increasing aging time. The viscoelastic properties of matrix resin are lost by aging treatment and thus the growth of the hubbly surface is inhibited. In the fracture surfaces of A2 and A3, it was confirmed that fracture mainly occurs in matrix resin regardless of aging time. Considering from the tensile strength measurement result shown in Fig. 4 (b), the strength of matrix resin itself is reduced by aging treatment. As described above, oxidative degradation by aging treatment causes the degradation of the strength of matrix resin.

3.3 Effect of coupling agent

3.3.1 Tensile properties

Figure 7 shows the effect of coupling agent on tensile properties. Elastic modulus was increased by coupling treatment at the temperature range investigated, although the effect is relatively small at 80°C and 120°C. Coupling agent promotes bonding of matrix resin and filler and strengthens the combined effect. The difference of the type of coupling treatment in elastic modulus is negligible. From Figs. 2 and 7, it was found that elastic modulus of C\textsubscript{d} are slightly smaller than those of A3 at all temperatures investigated although the specifications of both A3 and C\textsubscript{d} were identical. As described above, the specifications of both were the same but production lots of them were different. Thus the difference in elastic modulus seems to be caused the filler size distribution, the adhesion amount of the coupling agent and so on. Dispersion by dry processing is also a concern.

Tensile strength was also increased by the coupling effect although the effect is reduced at high temperatures. It seems to be due to the strong coupling force by 3-glycidypropyltrimethoxysilane. When the strong coupling interface was formed between matrix resin and filler by coupling treatment, such interface bears tensile force and thus tensile strength increases. Tensile strength of UF with wet coupling treatment is a little higher than that of UF with dry treatment. Moreover, the effect of the type of coupling treatment on tensile strength is greater than that on elastic modulus. Tensile strength was evaluated in the plastic region of a few percent strain although elastic modulus was done in the elastic region with extremely small strain. Thus detection of the difference of coupling treat-
ment becomes remarkable in tensile strength than elastic modulus.

Fracture strain of UF with coupling treatment decreased with increasing temperature compared with that of UF without coupling treatment. This means that the deformation of resin is suppressed by the restraint at the coupling interface at high temperatures. Fracture strain rapidly increased at 120°C. Since macromolecular chains start macro-Brownian motion at the temperature over $T_g$ of UF, matrix resin transitions from a glassy state to a rubbery state. Matrix resin has fluid nature at the temperature over $T_g$ and thus fracture strain greatly increases. Although fracture strain was slightly increased by coupling treatment at R.T., it was slightly decreased by coupling treatment at 80°C and 120°C. The discussion for this result is conducted in 3.3.2.

### 3.3.2 Fracture surfaces

Figure 8 shows fracture surfaces after tensile test. At R.T., fracture occurs in the matrix in all UF materials. Figure 9 shows the fracture surface in the vicinity of the fracture origin in the UF material with wet coupling treatment (C_w). The exposure of fillers is observed in the vicinity of the fracture origin. This means that the interface between matrix resin and filler became the starting point of fracture. When the coupling force is strong, interfacial fracture does not occur easily. Thus tensile strength and fracture strain at R.T. were improved by coupling treatment as shown in Figs. 7 (b) and (c).

At 80°C, the exposure of fillers are observed in the fracture surface of UF material without coupling treatment. Fracture occurred in both matrix resin and the interface between matrix resin and filler. On the contrary, the exposure of fillers is not observed in the fracture surfaces of UF materials with coupling treatment and fracture occurred in matrix resin. It was confirmed that peeling of fillers from matrix resin was suppressed by coupling treatment.

At 120°C, the exposure of fillers is observed in all UF materials regardless of coupling treatment. Fracture occurred in the interface between resin and filler. It was
confirmed that the interfacial strength decreases and fracture mode changes from matrix fracture to interfacial fracture when the coupling force reduces at 120°C which is the temperature higher than $T_g$. Fracture is governed by the coupling force between resin and fillers so that tensile strength was increased and fracture strain was decreased by coupling treatment as shown in Fig. 7.

### 3.3.3 Viscoelastic properties

Figure 10 shows viscoelastic properties of UF materials. The data of UF without filler are also plotted for comparison. The master curve for each UF material was created using the reference temperature of 109°C ($T_0$) which corresponds to $T_g$. From Fig. 10, it was found that coupling treatment makes the relaxation time of storage modulus shift to the longer side. This means that the relaxation of elastic modulus is suppressed when matrix resin is bound to fillers by coupling treatment. Thus coupling treatment affects on the relaxation behavior of elastic modulus of UF. The relaxation behavior of UF without coupling treatment shows similar one of UF without fillers. It was clarified that the relaxation behavior of UF depends on the properties of matrix resin unless coupling treatment is conducted.

### 4. Conclusion

The effects of filler contents and coupling treatment on mechanical properties of UF have been examined using standard UF materials which are composed of bisphenol F-type epoxy resin and spheroidal SiO$_2$ filler. The obtained results are summarized as follows.

1. Elastic modulus of UF increases and fracture strain decreases with increasing the SiO$_2$ filler content. Moreover, elastic modulus decreases and fracture strain increases at a temperature above $T_g$. Fracture mainly occurs in matrix resin below $T_g$ and in the interface between matrix resin and filler above $T_g$. The change seems to be caused by degradation of the coupling effect of SiO$_2$ filler at a temperature
above Tg.

(2) Elastic modulus of the UF increases and tensile strength and fracture strain decrease with increasing aging time. In the case of UF without filler, since the viscoelastic properties of resin are lost by aging, the growth of the bubbly surface is inhibited. In the case of UF with filler, fracture mainly occurs in matrix resin regardless of aging treatment.

(3) Elastic modulus and tensile strength of UF was improved by coupling treatment. Fracture strain was improved at R.T., but was decreased at 80°C and 120°C by coupling treatment. Peeling of fillers from matrix resin was suppressed by coupling treatment at 80°C. The fracture mode of UF with coupling treatment changed from matrix fracture to interfacial fracture between matrix resin and fillers in the boundary of Tg. Coupling treatment affects on the relaxation behavior of elastic modulus of UF and makes the relaxation time of storage modulus shift to the longer side.

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References

[1] E. Higurashi, “Flip Chip Bonding Technology to Realize Highly Functional MEMS,” Journal of Japan Institute of Electronics Packaging, Vol. 11, pp. 456–460, 2008.

[2] H. Mitsugi, I. Shohji, S. Koyama, and S. Kitagoh, “Effect of Coupling Agent on Mechanical Properties of Underfill for Flip Chip Bonding,” Proc. of Mate2014, pp. 279–282, 2014.

[3] Y. Sun, Z. Zhang, and C. P. Wong, “Study on Mono-dispersed Nano-size Silica by Surface Modification for Underfill Applications,” Journal of Colloid and Interface Science, Vol. 292, pp. 436–444, 2005.

[4] I. Shohji, K. Yoshizawa, M. Nishimoto, and T. Kawano, “Thermal Stress Relief in Lead-free Solder Joint for Chip Size Package with Encapsulant Material,” Smart Processing Technology, Vol. 1, pp. 175–178, 2006.

[5] I. Shohji, K. Yoshizawa, M. Nishimoto, and T. Kawano, “Effect of Properties of UF Materials on Thermal Stress Relief in Lead-Free Solder Joint of Chip Size Package,” Key Engineering Materials, Vol. 353–358, pp. 2029–2032, 2007.

[6] Y. He, “Thermomechanical and Viscoelastic Behavior of A No-flow Underfill Material for Flip-chip Applications,” Thermochimica Acta, Vol. 439, pp. 127–134, 2005.

[7] S. Kitagoh, H. Mitsugi, S. Koyama, and I. Shohji, “Effect of Filler Content on Tensile Properties of Underfill Material for Flip Chip Bonding,” Proc. of IEMT2012, IEMT2012-P150, 2012.

[8] S. Kitagoh, H. Mitsugi, I. Shohji, and S. Koyama, “Effect of Filler Additive Amount on Mechanical Properties of Underfill for Flip Chip Bonding,” Proc. of Mate2013, pp. 171–176, 2013.

[9] H. Yoshida, “Enthalpy Relaxation of Polymeric Glasses,” Netsu Sokutei, Vol. 13, pp. 191–199, 1986.