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Effects of Silica Filler and Diluent on Material Properties of Non-Conductive Pastes and Thermal Cycling Reliability of Flip Chip Assembly

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Abstract: In this paper, thermo-mechanical and rheological properties of NCPs (Non-Conductive Pastes) depending on silica filler contents and diluent contents were investigated. And then, thermal cycling (T/C) reliability of flip chip assembly using selected NCPs was verified. As the silica filler content increased, thermo-mechanical properties of NCPs were changed. The higher the silica filler content was added, glass transition temperature (T_g) and storage modulus at room temperature became higher. While, coefficient of thermal expansion (CTE) decreased. On the other hand, rheological properties of NCPs were significantly affected by diluent content. As the diluent content increased, viscosity of NCP decreased and thixotropic index increased. However, the addition of diluent deteriorated thermo-mechanical properties such as modulus, CTE, and T_g. Based on these results, three candidates of NCPs with various silica filler and diluent contents were selected as adhesives for reliability test of flip chip assemblies. T/C reliability test was performed by measuring changes of NCP bump connection resistance. Results showed that flip chip assembly using NCP with lower CTE and higher modulus exhibited better T/C reliability behavior because of reduced shear strain in NCP adhesive layer.

Keywords: Non-Conductive Paste(NCP), Filp chip, Stud bump, Termal Cycling reliability

1. Introduction

As electronic packaging technology trends move toward lower cost, fine pitch, higher electrical performance and better reliability, flip chip technology gains popularity as one of the best chip packaging candidates to meet these trends.

Although flip chip assembly using solder balls is in the main stream of flip chip technology, flip chip assemblies using polymer conductive adhesives such as isotropic conductive adhesives (ICAs), anisotropic conductive films (ACFs), and non-conductive pastes (NCPs) have been under development because of their potential advantages compared with solder flip chip assemblies such as lower processing temperature, lower cost due to fewer assembly processing steps, and cheaper bumping method, and green process (no lead, no flux, and no cleaning solvent).

Among these conductive adhesive flip chip technologies, flip chip with NCPs and gold stud bumps is one of the promising method for certain applications. Therefore, it is necessary to investigate thermo-mechanical properties and rheology of NCPs. The thermo-mechanical properties such as modulus, CTE, and T_g are important for good flip chip assembly reliability, and rheological properties such as viscosity and thixotropy are important for good NCPs dispensability.

It is previously observed that flip chip adhesives on organic substrates fails during the thermal cycling test mainly due to high CTE of adhesive layer$^{1)}$. Therefore, silica (SiO_2) fillers are added to reduce CTE for good T/C reliability. However, NCP's viscosity increases as silica filler content increases resulting in a poor dispensability. To solve dispensability problem, diluent is added.

In this study, effects of silica fillers and diluent on NCP properties are investigated. Finally, the relationship between thermo-mechanical properties of NCPs and T/C reliability of NCP flip chip on organic substrates will be discussed.

2. Experiments

2.1 NCP Materials

NCPs are composed of bisphenol-A type liquid epoxy, latent curing agent, silica filler, and diluent. Various amounts (0 wt%, 10 wt%, 20 wt% and 30 wt%) of silica filler were mixed with liquid epoxy to investigate effects of silica filler on NCP material properties. And, to investigate effects of diluent on NCP material properties, various amounts (2.1 wt%, 4.2 wt%, 6.2 wt%, and 8.0 wt%) of diluent were also added with the same silica filler content. Fig. 1 shows the chemical structure of HDGE (1,6-Hexanediol diglycidyl ether) diluent. NCPs were mixed for 2 minutes for uniform dispersion in epoxy matrix and degassed for 30 seconds to remove bubbles out. The differential scanning calorimeter (DSC) was performed to investigate curing behaviors of NCPs. NCPs were cured in a mold at 165°C for about 30 minutes and were ground into proper size for the thermo-mechanical characterization such as dynamic mechanical analysis (DMA), and thermo-mechanical analysis (TMA). Rheological behaviors of NCPs were also investigated using a rheometer and viscometer.

2.2 Characterization

2.2.1 Differential Scanning Calorimeter (DSC)

DSC experiments were performed to determine curing profiles of NCP materials with various filler content and diluent content. Aluminum pans containing 5~7 mg NCP were heated from 50°C to 200°C at a heating rate of 10°C/min under nitrogen environment.

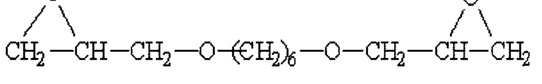


Fig. 1. Chemical structure of HDGE (1,6-Hexanediol diglycidyl ether) diluent.

2.2.2 Dynamic Mechanical Analysis (DMA)

2×5×20 mm cured NCP was prepared for the DMA analysis. The measurement was performed by a 3-point bending method under 1 Hz sinusoidal strain loading with heating from 0°C to 300°C using 10°C/min heating rate. Storage modulus (*E'*) and loss tangent were obtained.

2.2.3 Thermo-Mechanical Analysis (TMA)

Coefficients of thermal expansion (CTEs) of cured NCPs with various silica filler content and diluent content were measured using TMA. 2 mm thickness and 10 mm diameter samples were heated from 25°C to 200°C at a heating rate of 5°C/min, and detected dimensional change with 100 mN compression load.

2.2.4 Rheology Analysis

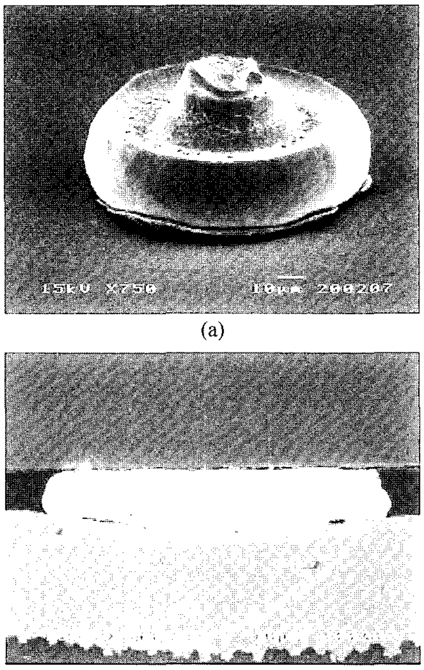
Rheological properties of NCPs were measured using a rheometer. NCP mixture was sheared between a cone and plate at shear rates from 0 sec^{-1} to 100 sec^{-1} for 2 minutes. After shear rate reached to a maximum value, shearing force was removed. Also, thixotropic index (=viscosity at 0.5 rpm/viscosity at 5 rpm) was obtained using a viscometer.

2.3 Stud bump formation

It is necessary to form bumps on I/O pads of chips to be interconnected on substrates using NCPs. Gold stud bumps were formed on each I/O pads of chips. Total 34 peripheral bumps were formed on dog-bone patterns of chips. Fig. 2 shows SEM image of stud bump and stud bump joint in flip chip assembly.

2.4 Flip Chip Assembly using NCPs

Substrates used for flip chip assembly were 1.2 mm thick PCB (FR-4 substrate). The specifications of test chips and test boards were summarized in Table 1. There are three processing steps for NCP flip chip assembly on an organic substrate. First, gold stud bumps on chips and I/O pads on test substrates were aligned. Then NCPs were dispensed on a substrate to interconnect chips. Finally, bonding pressure of 130N was applied to bond a chip on a substrate at 180°C for 70 seconds. As a result, chips



(a)

(b)

Fig. 2. (a) SEM image of stud bump formed on chips, (b) Cross-sectional image of stud bump joint.

were electrically interconnected between PCB pads and stud bumps due to mechanical contact.

2.5 Reliability Test

T/C reliability test was performed for three selected NCPs. To investigate the effect of silica filler, no silica filler added NCPs and 30 wt% silica filler added NCPs were used. In addition, to investigate effect of diluent on T/C reliability, no diluent contained NCPs and 4.2 wt% diluent contained NCPs (with same silica filler content, 30 wt%) were used. To investigate the reliability of NCP flip chips on organic substrates, analysis of the contact resistance of a single interconnect is important. Failure was defined when connection resistance increased more than 100%. Typical Pb/63Sn solder reflow process was carried out two times before -55°C (15 min) ~125°C (15 min) thermal cycling reliability test.

Table 1. Specifications of test chips and organic substrates for NCP flip chip assembly

Specification	Substrate
Material	FR-4
Size (mm×mm)	34×37
Final metallization	Cu/Ni/Au
Specification	**Test IC**
Size (mm×mm)	14.7×8.6
I/Os	32
Pitch (μm)	800
Pad size (μm diameter)	400
Bumps	Au stud bumps

3. Results and Discussion

3.1 Effects of silica fillers on NCP properties

To improve thermo-mechanical properties of NCP composites, silica fillers were added. In this chapter, effects of silica fillers on NCP material properties such as CTE, modulus, T_g and viscosity, etc. were described.

3.1.1 DSC result

Table 2 shows summary of DSC results as a function of silica filler content. Addition of silica filler content slightly increased the curing onset and peak temperature, which was reported elsewhere[1]. However, exothermic amount of heat per actual epoxy resin was almost the same.

Table 2. Summary of DSC results as a function of silica filler content

Silica filler content (wt%)	Curing onset temp. (°C)	Curing peak temp. (°C)	Exothermic heat per pure epoxy resin (J/g)
0	119.62	129.17	428
10	119.93	129.46	423
20	120.43	129.80	435
30	121.10	129.29	428

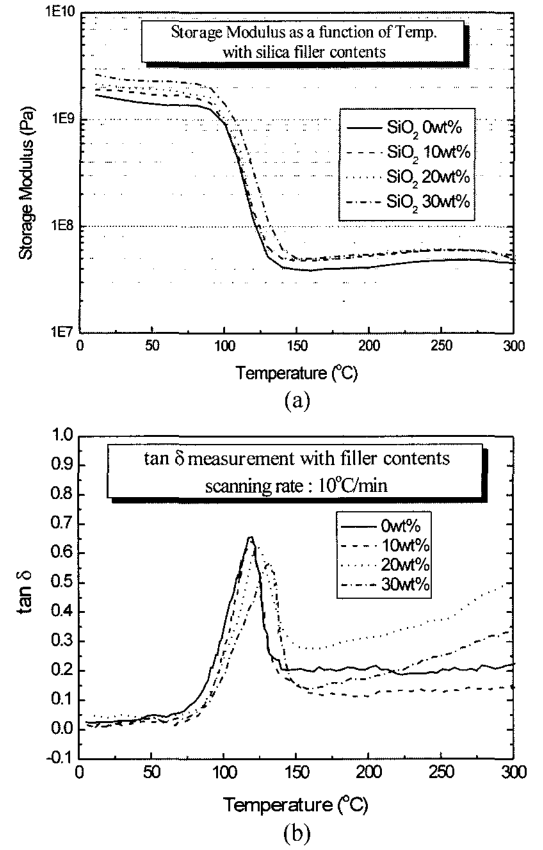


Fig. 3. (a) Storage modulus curve, (b) tan δ curve of NCPs with 0-30 wt% silica filler content.

3.1.2 DMA result

Fig. 3 shows curves of the storage modulus and loss tangent of NCPs with various silica filler content at various temperature. The storage modulus of cured NCPs increased as silica filler content increased at room temperature. The glass transition temperature (T_g^{DMA}), characterized by the maximum value of loss tangent, increased as silica filler content increased. These behaviors are due to the increase of polymer/filler interaction in NCPs. If silica filler content increases continuously, the internal friction due to the increase of polymer/filler interface will rise quickly, resulting in hindering the movement of the polymer molecules. This increase in friction made T_g higher as silica filler content increased[2]. This "stiffening effect" is presumably due to large specific surface area of silica fillers.

For underfill materials in case of solder flip chip assembly, high modulus is needed to effectively redistribute the solder joints stress to the chip and substrate through the assembly warpage[3]. Similarily, since NCP materials assembled on an organic substrate function as both underfill and die adhesive, higher modulus by adding high content of silica filler is needed. Therefore, higher content of silica filler is preferred, unless the viscosity of NCP is too high to be used during the dispensing process.

3.1.3 TMA result

Fig. 4 shows CTE values of NCPs with various silica filler content measured in TMA. Higher silica filler content causes the decrease of CTE due to stiffening effect of composite materials with larger interface area between silica filler and epoxy resin as discussed in DMA results. The CTE of NCPs below T_g defined as α_1 and the CTE above T_g defined as α_2, are important parameters in determining the reliability of NCP flip chip assembly. From DMA and TMA results, higher content of silica filler is desirable for the reliability improvement of NCP flip chip assembly.

3.1.4 Viscosity and Thixotropy

The rheological analysis was performed to evaluate viscosity of NCP composites. At room temperature, apparent viscosity increased generally as silica filler content increased as shown in Fig. 5. Viscosity decreased as shear rate increased for one sample.

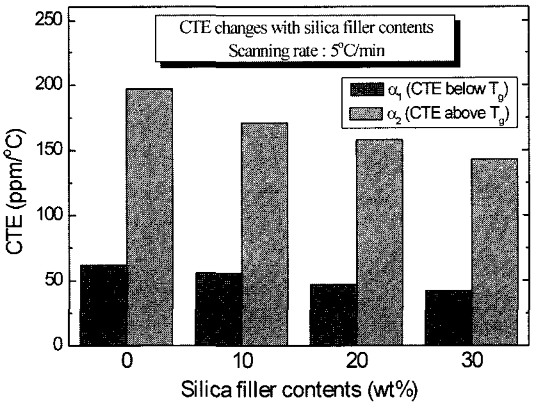


Fig. 4. CTE changes with various silica filler content.

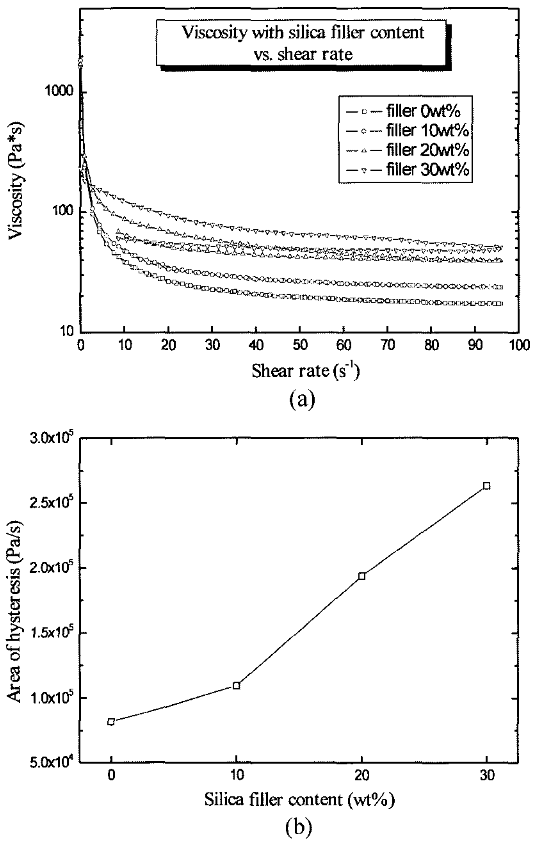


Fig. 5. (a) Viscosity with silica filler content vs. shear rate, (b) area of hysteresis as a function of silica filler content.

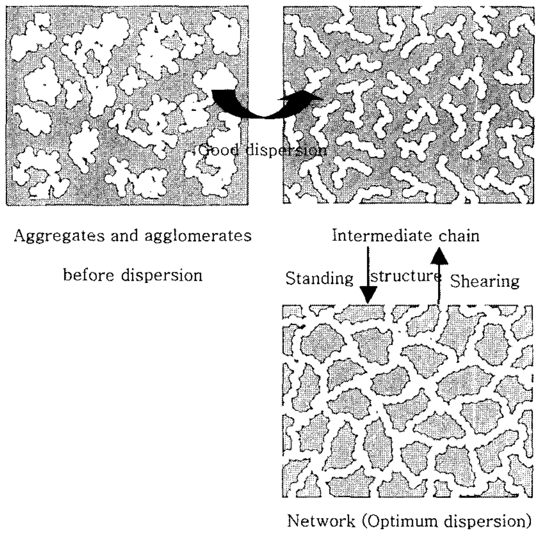


Fig. 6. Model of levels of silica network formation as a function of level shearing during mixing.

And thixotropy increased as silica filler content increased. Because silica fillers act as an obstacle to make fluids difficult to flow, more stress is needed to flow as silica filler content increases. Thixotropy can be qualitatively known by the area of hysteresis in shear rate vs. shear stress curve. As silica filler content increased, the area of hysteresis increased. The result can be understood by a model as shown in Fig. 6. The increase in thixotropy with silica filler content is due to van der Waals force among particles. The particles form network structure at stand-by state and the network results in increase in viscosity. If shear force is applied to the mixtures, the shear force breaks down the network structure. This results in lowering in viscosity. Higher filler content is preferable to reduce CTE because of thermo-mechanical reason. Therefore, in rheological point of view, excess silica fillers make to high viscosity resulting in worse dispersion.

3.2 Effects of diluent on NCP properties

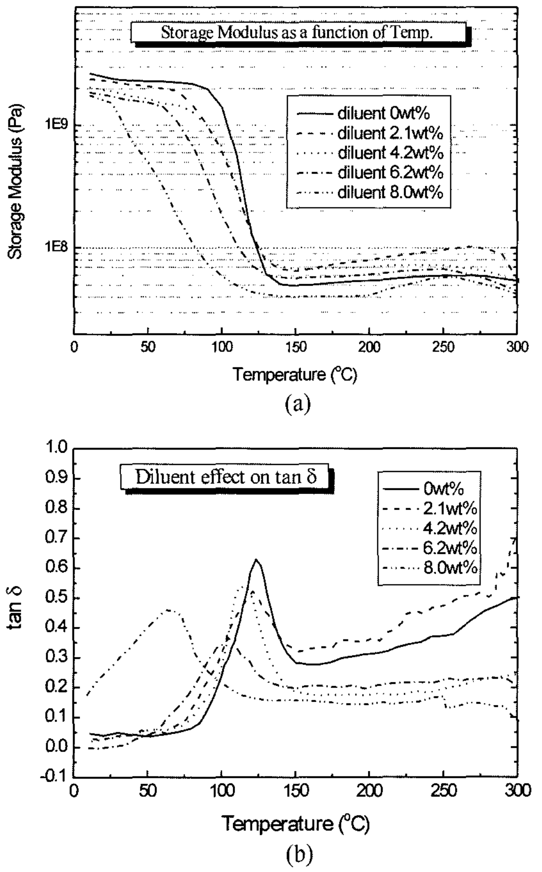
Dispensing problem due to high viscosity can be solved by using diluents (monomers). Effects of diluents on NCP properties were described with the same silica filler content, 30 wt%.

3.2.1 DMA result

Fig. 7 shows the variation of the storage modulus and loss tangent of NCPs with different diluent content as a function of holding temperatures. The storage modulus of cured NCPs at room temperature decreased. And maximum value of tan d decreased as diluent content increased, because diluent has linear molecular structure. Molecular chain mobility increases, as diluent content increases. This phenomenon makes cured NCPs softer. When diluent was added 8.0 wt%, glass transition temperature decreased down to about 65°C. Excessive amount of diluent can cause a serious detrimental effect on thermo-mechanical properties of NCPs, especially T_g.

3.2.2 TMA result

Fig. 8 shows CTE values of NCPs with various



(a)

(b)

Fig. 7. (a) Storage modulus curves, (b) tan δ curves of NCPs with different diluent content.

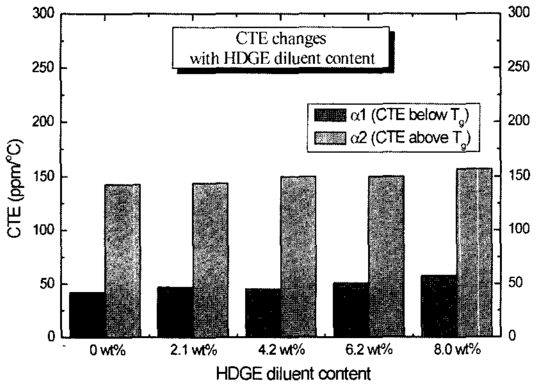
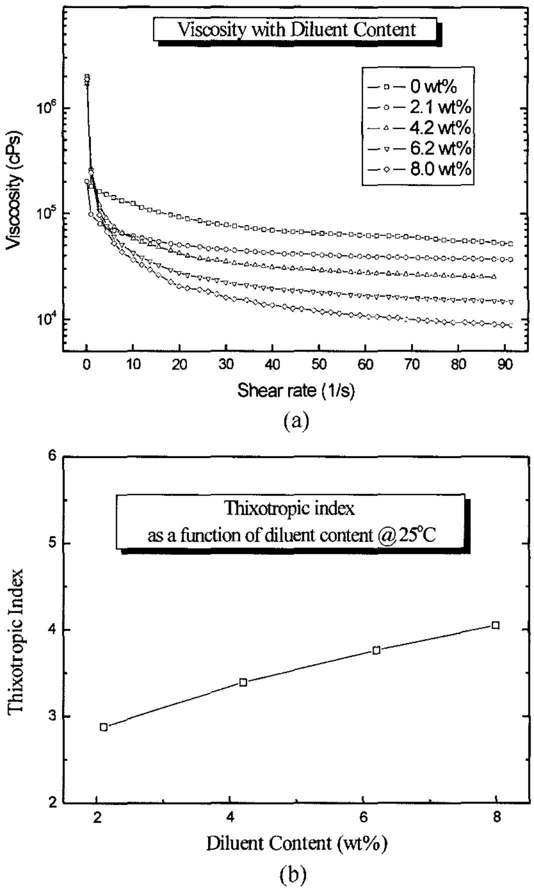


Fig. 8. CTE changes of NCPs as a function of diluent amount.

diluent contents. In microscopic view, shorter chains of polymer molecules can move more easily than longer chains as discussed in 3.2.1.



(a)

(b)

Fig. 9. (a) Viscosity with various diluent content vs. shear rate, (b) Thixotropic Index as a function of diluent content.

3.2.3 Viscosity and Thixotropy

The main purpose of adding diluents is to improve dispensability by lowering viscosity. Fig. 9 shows viscosity and thixotropic index changes as a function of diluent content. Viscosity decreased clearly as diluent content increased. In addition, thixotropic index increased from 2.8 to 4.1. It is presumably due to particles can move more easily in matrix and particle interactions increases relatively higher as diluent content increases. Changes of thermo-mechanical properties and dispensability by adding diluents are contrary to each other. Therefore, trade-off is needed in optimizing diluent amounts.

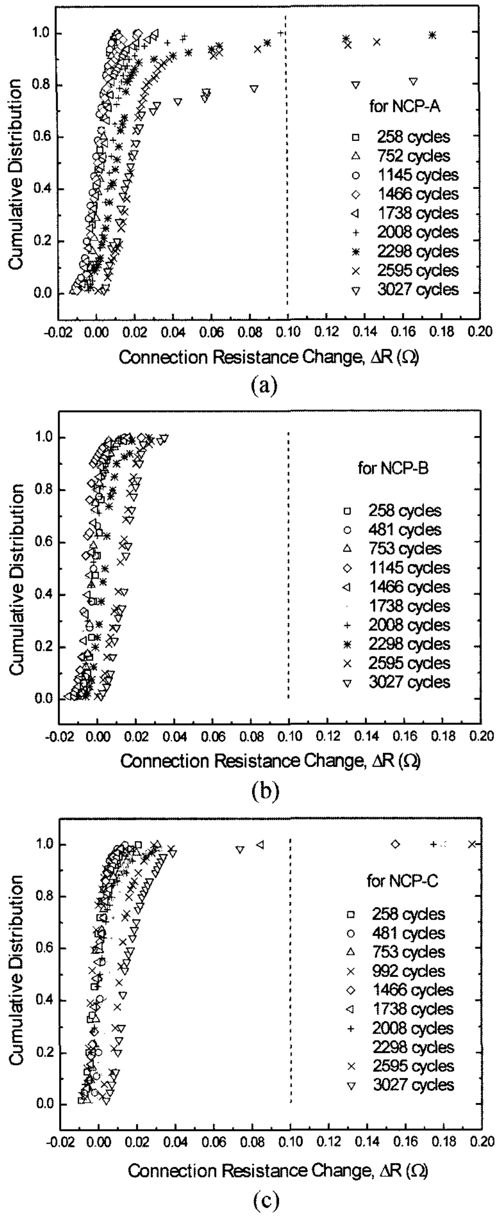


Fig. 10. Cumulative distributions of connection resistance changes for flip chip assembly using (a) NCP-A, (b) NCP-B, (c) NCP-C in thermal cycling test.

3.3 Thermal cycling reliability

Fig. 10 shows cumulative distributions of connection resistance changes of NCP flip chip during 55°C (15 min)~125°C (15 min) thermal cycling condition. For NCP-A (without silica filler and diluent) flip chip assembly, first fail occurred after 2008 cycles. Also for NCP-C (with silica filler and diluent) flip chip assembly, first fail occurred after 1466 cycles. However, NCP-B (with silica filler and no diluent) flip chip assembly passed 3000 cycles without fail. Failure accelerated more rapidly for NCP-A than two other samples. These results of the thermal cycling test indicate that thermo-mechanical properties of NCP composites have noticeable effects on the reliability of NCP flip chip assembly on an organic substrate. The higher content of silica filler in NCPs causes lower CTE and higher storage modulus resulting in a higher reliability of NCP flip chip assembly on an organic substrate during thermal cycling test[4].

It was already reported that as the induced shear strain in adhesive layer reduced, thermal cycling reliability of flip-chip assembly was improved. This is due to the more rigid mechanical constraints between the chip and the board[5]. Accordingly, the modification of mechanical properties due to the silica filler addition results in improvement of thermal cycling reliability[4].

Induced shear strain was calculated for used three NCPs. One-dimensional analytical solution of stress and strain in a trilayer composite structure which is allowed to bent freely was published by Suhir[6]. Schematic diagram of trilayer structure was shown in Fig. 11. From Suhir's model[7], the shear deformation of the second layer, in this case the NCP composite, can be explained as

$$\gamma_{zx}(x) = \kappa\frac{2\Delta\alpha\Delta T\sinh kx}{3G_2\lambda\cosh kl} \tag{1}$$

The parameters are defined as follows:

x	Distance from chip center
$2l$	Chip length
t_i	Thickness of layer i
E_i	Elastic modulus of layer i
υ_i	Poisson ratio of layer i
$G_i = E_i/2(1+\upsilon_i)$	Shear modulus of layer i
$D_i = E_i t_i^3/12(1-\upsilon_i^2)$	Flexural rigidity of layer i
$D = D_1+D_2+D_3$	Flexural rigidity
$t = t_1+t_2+t_3$	Assembly thickness

$$\lambda=\frac{(1-\upsilon_1)}{E_1t_1}+\frac{(1-\upsilon_3)}{E_3t_3}+\frac{t^2}{4D}\quad \text{Axial compliance}$$

$$\kappa=\frac{t_1}{3G_1}+\frac{2t_2}{3G_2}+\frac{t_3}{3G_3}\quad \text{Interfacial compliance}$$

$$k=\sqrt{\lambda/\kappa}$$

Assuming that the stud bumps deform along with the NCP composite layer, (1) can be used as an estimation of the induced shear strain in stud bumps. Calculated shear strain as a function of x was plotted in Fig. 12. Material properties were summarized in Table 3 for shear strain analysis. Poissons ratio of NCP composite was assumed as a typical value for a cured rigid epoxy system, 0.34[8].

As shown in Fig. 12, calculated shear strain dramatically increased along x-axis. It is presumably understood that interconnection resistance increase occurred at chip edge side may be related to the shear strain. The difference in the three shear strain curves is due to the modulus characteristics of each adhesive layer. As shown in previous results, it is understood that high modulus NCP results in small shear strain and results in good T/C reliability.

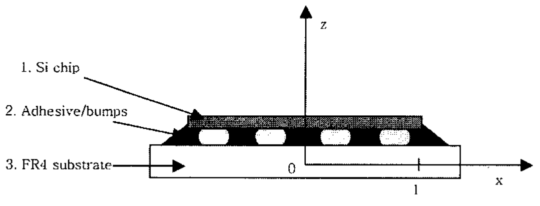


Fig. 11. Schematic diagram of a trilayer structure flip-chip on a board.

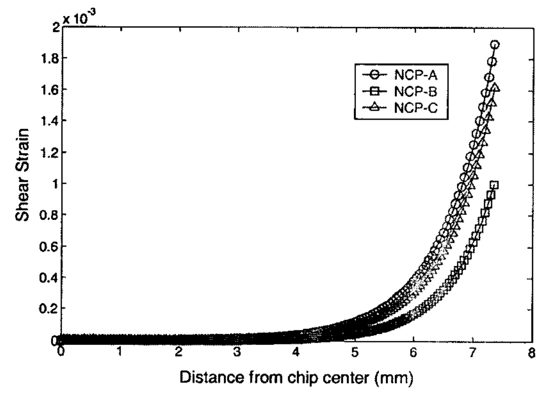


Fig. 12. Calculated shear strain for 3 NCPs.

4. Conclusion

In this paper, thermo-mechanical and rheological properties of NCPs depending on silica filler contents and diluent contents were investigated. And then, T/C reliability of flip chip assembly using selected NCPs was verified.

The content of silica filler was the key factor which controls thermo-mechanical properties of NCPs such as CTE, modulus, and T_g. As the content of silica filler increased, T_g and storage modulus increased. At the same time, the CTE decreased. However, the content of diluent was the key factor to improve the dispensability of NCPs. As diluent content increased, viscosity decreased and thixotropy increased, but thermo-mechanical properties such as CTE, modulus, and T_g were deteriorated. In order to verify relationship between thermo-mechanical properties of NCPs and flip chip reliability, three kinds of NCPs were compared. NCP-B (with silica filler and

Table 3. Sumary of properties of NCPs used in shear strain analysis

		Chip	NCP-A	NCP-B	NCP-C	FR-4 Substrate
Thickness (μm)		700	60	60	60	1200
CTE (ppm/°C)	α1	2.8	62	42	45	15.8
	α2	-	197	143	150	20.0
Modulus (GPa)		160	1.57	2.41	1.74	17.2
Poisson's ratio		0.27	0.34	0.34	0.34	0.15
Glass transition temperature (°C)		-	119	128	114	-

no diluent) flip chip assembly could pass 3000 cycles without fail, but NCP-A and NCP-C flip chip could not pass 2000 cycles. Definitely, lower CTE and higher modulus NCP flip chip assembly improved the T/C reliability.

For better T/C reliability, high content of silica filler is preferred, unless the viscosity of NCP composite is too high to be dispensed. To obtain the optimum properties of NCPs, trade-off between thermo-mechanical properties and dispensability is needed.

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