Study on preparing single–component flow–type EP underfill adhesive

Li Huilu[1,a], Wei Hongli[1,b], Shao Kangchen[1,c], Zhang Ting[1,d]

[1]College of Materials Science and engineering, Xi'an University of Science and Technology, Xi'an 710054, China;

[a]E-mail: huiluli@sina.com.cn, [b]E-mail: 490829309@qq.com,

[c]E-mail: 781323787@qq.com, [d]E-mail:562864540@qq.com

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Abstract. With EP(epoxy resin) as matrix resin, DCA(dicyandiamide) as curing agent and modified imidazole as curing accelerator, and adding fillers and other additives, a single–component flow–type EP underfill adhesive was prepared. The curing temperature was determined by testing gelation time and characterizing FT-IR(infrared spectroscopy). And the influences of fillers types and proportions on the viscosity, thermal conductivity, dielectric constant and bonding strength of adhesives were discussed. The research results indicated that the adhesive had good combination property and could fully meet the application requirements. when mass ratios of m(EP):m(DCA):m(modified imidazole) was 100:8:5, w(filler)was 60% in EP and m(Al2O3):m(SiO2) was 1:5, and mass fractions of silane coupling agent and dispersing agent were all 0.5% in EP, and curing process was "85°C/30min→120°C/1h"(cured for 30 minutes at 85°C, and cured for 1h at 120°C), Its shear strength was 15.33 MPa, thermal conductivity was 0.793 W/(m.K), and viscosity was 6.06 Pa.S.

Introduction

As the high density package is moving towards miniaturization, high I/O density, better thermal and high reliable system, the conventional wire bonding technology can not satisfy the product need already. The advanced flip chip technology is widely concerned. In flip-chip electronic package, underfill adhesive is used between the chip and the substrate for bonding, which can effectively improve the reliability of the bonding member, reduce interfacial stress of the solder joint and substrate's thermal expansion coefficient difference[1,2]. Therefore, underfill adhesive should have good heat resistance, bonding strength and thermal conductivity etc. Typically, underfill adhesive can be divided into two major categories of flow–type and non-flow type. In this study, with high toughness, strong corrosion resistance, adhesion and insulation with EP (epoxy) as the matrix resin[3,4], and with DCA (dicyandiamide) as the curing agent, modified imidazole as curing accelerator, inorganic filler as strengthening agent and thermal conductive agent, a single–component flow–type EP underfill adhesive of excellent comprehensive performance was expected to be prepared[5,6].

Experimental

Materials. Epoxy resin(EP) and allyl glycidyl ether (AGE) were obtained from the south Asian chemical Company(Guangdong, China), whose brand are respectively GEFR170 and bisphenol F type. Boron nitride(BN) was purchased from Tianyuan chemical Company (Xi'an, China). Aluminum oxide(Al2O3) came from Hua Ya Superfine Powder Company(Foshan, China). Modified imidazole was obtained from Changxing chemical reagent Factory(Guangdong, China). Silane coupling agent(KH-560) was purchased from Jiangsu Chenguang Ltd(Zhenjiang, China); Micro silica powder(SiO2) was from Fuchen chemical reagent Factory(Tianjin, China). Defoaming agent(681F) was from taihe chemical Factory(Xi'an, China). Dispersant(BKY103) was obtained from Germany BYK Chemical Company(Germany). Dicyandiamide(DCA) was from Germany Degussa Company(Germany). The above materials were industrial-grade except that AGE was

chemically pure.

Preparations of underfill adhesives and test samples. the underfill adhesive was obtained by mixing EP, curing agent (DCA), curing catalyst (modified imidazole), fillers and other additives with a certain ratio. A standard injection mold coated with a release agent was filled with the underfill adhesive and the curing process was performed according to a certain curing system. the samples by demoulding, grinding, and being processed into the required size can be determined with certain performance properties.

Characterization. IR spectra of sample was determined with WQF-310 Fourier infrared spectroscopy produced in Beijing second optical instrument Factory. Shear strength of sample was determined with DZE-50 type electronic tension meter produced in Guangdong Zhengye technology Company. Gelation time was determined with gelation time tester by oneself. The Dynamic mechanical analysis(DMA242E) produced in Germany NETZSCH company was adopted to detect sample's dielectric properties according to ASTM D7028-2007. The viscosity of sample was determined with NDJ-5S digital rotating viscometer produced in Shanghai Geology Institute. The thermal conductivity of sample was measured with DRL-type 2 thermal conductivity meter produced in Xiangtan instrument Company according to ASTM D5470-2005 standard,. Dielectric constant of sample was determined with GCSTD-type dielectric constant apparatus produced in Beijing Guance test instrument Company.

Results and discussion

Determination of basic formulation of underfill adhesive. The epoxy value of EP is 0.555~0.588 mol/100g, the relative molecular weight of DCA is 84g/mol [7]. the theoretical dosage of DCA was 11~ 13g when EP and DCA were completely reacted. However, the actual mass ratio of m(EP):m(DCA) was 100: 8 in the process of production, which was lower than the theoretical amount, and FT-IR characterization results showed that they can also be completely cured when mass ratio of m(EP):m(DCA) was 100:8. Therefore, the basic formula of underfill adhesive was: the mass ratios of m(matrix resin):m(curing agent):m(curing accelerator) and m (EP):m(DCA):m(modified imidazole) were also 100: 8:5.

Gelation time of underfill adhesive. Under the premise of other conditions remained unchanged, the effect of different temperature on the gelation time of underfill adhesive was shown in table 1.

Table.1 Gelation time of underfill adhesive

Temperature/°C	Gelation time/min	Temperature/°C	Gelation time/min
85	28	105	19
90	26	110	19
95	25	115	18
100	33	120	13

Table 1 showed that: with the extension of temperature, the gelation time firstly tended to shorten after lenthen progressively when the temperature was 85~120°C; the gelation time was about 30min when the temperature was less than 100°C. So the initial curing temperature of underfill adhesive was 85°C and the holding time was 30min in this study. Because the cross-linking curing reaction of underfill adhesive was not completed at lower temperature, whose exothermic effect was small and can't guarantee the system sufficiently cured, so it is neccesary in extending the system's curing time to make sure the system cured completely. However, system's exothermic effect was serious when the temperature was too high, it would lead to cure excessively, the system would terminate chain extension reaction and reduce the relative molecular weight of the product. Furtherly, the system was prone to appear explosion and make resin brittle; even if the system didn't appear explosion, it would be difficult to control the whole reaction because the curing time was too short.

DMA curves of underfill adhesive. DMA curves of underfill adhesive were shown in figure 1.

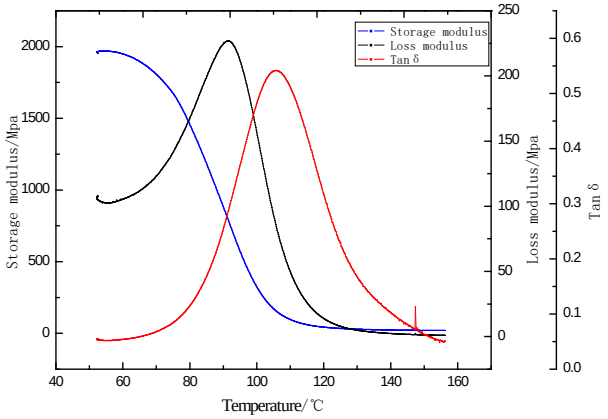

Fig.1 DMA curves of underfill adhesives

Figure 1 showed that: the storage modulus of underfill adhesive decreased when the temperature increased and the elastic properties of the material didn't disappear until the temperature above its Tg; The loss modulus and tanδ increased at first and then decreased when the temperature increased. When the temperature was lower than its Tg, the molecular chain segments inside material can hardly move. When the temperature was higher than its Tg, it was easy to move for molecular chain segments inside material and the interaction forces between molecules were relatively small, so the lost energy was also less. Only when the temperature was close to its Tg, the system's lag effect were most and the loss energy was maximum, so the peak of tanδ curve was sample's Tg. That was to say the Tg of sample was 105.83°C.

FT-IR characterization and analysis of underfill adhesive. When the curing temperature of underfill adhesive was 85°C/30min→120°C/1h. The FT-IR curve of sample were shown Figure 2.

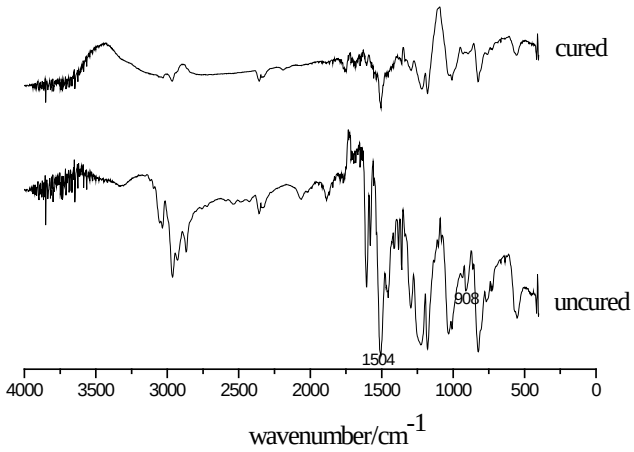

Figure 2 FT-IR curve of sample

Conclusion by figure 2: the peak at 1504cm-1 was characteristic absorption peak of benzene ring, which was extremely strong because the structure of cured EP contained large amounts of benzene ring. The range of 1236~1110cm-1 also appeared strong absorption peak, that was caused by the vibrate composition of—CH, C—C and C—O groups. The absorption peak of epoxy group at 908cm-1 had disappeared, which proved that adhesive had totally cured. So it was suitable that the curing temperature of underfill adhesive was 85°C/30min→120°C/1h.

Effect of fillers contents on viscosity and shear strength of underfill adhesive. To meet the application requirements, underfill adhesive must have good liquidity and good heat conduction performance, the mass fraction of fillers must be more than 35%. When mass ratio of m(EP):m(DCA):m(modified imidazole) was 100:8:5, the effect of different fillers contents on viscosity and shear strength of underfill adhesive was shown in table 2.

Table.2 Effect of fillers contents on viscosity and shear strength of underfill adhesive

Number	1	2	3	4	5	6	7
Percent contents of fillers/%	35	40	45	50	55	60	70
Viscosity/(Pa.S)	2.48	3.24	4.40	4.46	5.32	6.06	8.20
Shear strength/MPa	18.79	15.69	15.60	15.58	15.48	15.33	13.44

Table 2 showed that: with the contents of fillers increasing, the viscosity of underfill adhesive increased while its shear strength declined. When fillers contents were more than 60%, the viscosity of underfill adhesive increased and the shear strength decreased significantly.

Effect of filler contents on thermal conductivity of underfill adhesive. When the other conditions remain unchanged, the effect of fillers contents ,fillers types and proportions on thermal conductivity of underfill adhesive was shown in table 3 and table 4.

Table.3 Effect of fillers contents on th ermal conductivity of underfill adhesive

Number	1	2	3	4	5	6	7	8
Percent contents of fillers/%	35	40	45	50	55	60	65	70
Thermal conductivity/W/(m.K)	0.35	0.38	0.40	0.52	0.55	0.69	0.68	0.66

As can be seen from Table 3, with the total mass of the filler increasing, the thermal conductivity of underfill adhesive firstly tended to increase after slightly reduce, because increasing the filler content lead to the increasing of filler inside ratio per unit mass of epoxy resin. However, when the filler content was greater than 60%, the proportion of epoxy groups would fall, so that the thermal conductivity would decrease slightly, so only when filler content was in the middle, its thermal conductivity was the most, So the paper choose that filler content was 60%.

Table.4 Effect of different proportion of SiO2 and Al2O3 on thermal conductivity of underfill adhesive

m(SiO2):m(Al2O3)	10:50	20:40	30:30	40:20	50:10
Thermal conductivity/W/(m.K)	0.616	0.623	0.677	0.703	0.793

We can see from table 4: with mass ratio of m(SiO2):m(Al2O3) increasing, the thermal conductivity of underfill adhesive increased progressively, its heat conduction performance was gradually getting better. Although the total quality of silicon dioxide was the same as aluminium oxide, its volume fraction in EP increased when mass fraction of silicon dioxide increasing in m(SiO2):m(Al2O3) because of silicons dioxide with small particle size. Therefore, the greater the mass fraction of silicon dioxide in m(SiO2):m(Al2O3), the more conductive filler in EP, it would lead to the number of thermal network chain in EP going up. As a result, the heat conduction performance of underfill adhesive got better. So the most appropriate choice of the mass ratio of m(SiO2):m(Al2O3) was 50:10.

Effect on dielectric properties. When the other conditions remained unchanged, influence of different formula on the electrical properties of underfill adhesive was shown in table 5.

Table.5 Dielectric properties of underfill adhesive with different formulas

The percent content of Al2O3/%	35	40	45	50	55	60	70
Relative permittivity/εr	5.4	5.7	6.0	6.6	7.4	7.2	7.2

The relative permittivity of EP is 3.8 ~ 4.5, and the aluminium oxide was 9.0[8]. As shown in table 5, with increasing of Al2O3 content, the relative permittivity of underfill adhesive firstly rose rapidly and then dropped slowly. That was due to the fact that the insulation performance of the

inorganic filler was better than EP, so the more inorganic filler presented in system, the higher the dielectric constant of EP system. However, when the filler content was excessive, the agglomeration phenomena between fillers would result in the dielectric constant of EP system decreasing slightly.

Conclusion

When mass ratios of m(EP):m(DCA):m(modified imidazole), m(BN):m(Al2O3) and m(Al2O3):m(SiO2) were 100:8:5, 4:5 and 10:50 respectively, mass fractions of silane coupling agent and dispersing agent were all 0.5% in EP, and curing process was "85°C/30min→120°C/1h", the flow-type underfill adhesive selected by single factor test can be well prepared and had good combination property: larger shear strength (15.33MPa), maximum heat conduction coefficient [0.793W/(m.K)] and moderate viscosity (6.06Pa.s), which can meet the application requirements of high mobility, good bonding property and thermal conductivity completely.

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