Springer

KSME

Journal of Mechanical Science and Technology 24 (2010) 311~314
www.springerlink.com/content/1738-494x
DOI 10.1007/s12206-009-1145-2

Characterization for coating processes of imidazole powders using an ultrasonic atomizer†

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(Manuscript Received May 4, 2009; Revised September 30, 2009; Accepted October 16, 2009)

Abstract

Imidazole-curing accelerator powders were coated with stearic acid to increase the pot life of anisotropic conductive adhesive (ACA) formulations. To accomplish an efficient coating process, the coating was tested using an ultrasonic atomizer after mixing imidazole powders with a molten coating agent. Design of experiments analysis was organized to elucidate the effect of process parameters and to determine the most crucial parameter. The final formulation incorporating well-processed imidazole loaded powders indicated longer pot life, higher shear strength, and excellent highly accelerated stress test (HAST) reliability. Results show that the coating process using an ultrasonic atomizer is effective in increasing the pot life of ACA formulations.

Keywords: RFID chip bonding; ACA (anisotropic conductive adhesive); Snap curing; Pot life; Powder coating; Ultrasonic (US) atomizer

1. Introduction

The rapidly enlarged radio frequency identification (RFID) industry and the interest in low-temperature bonding materials in the electronic interconnection technology have recently induced technical improvements in the polymer-based conductive adhesives [1-5]. Although the conductive adhesives reveal relatively poor reliability in comparison to solder joints, it is estimated that the adhesive materials will be adopted more widely in low cost interconnection processes due to their low bonding temperature, fast bonding speed, and other advantageous characteristics. The formulation of conductive adhesive materials is one of the core technologies in the RFID assembly industry as high-speed chip bonding is very beneficial in the reduction of assembly cost.

In previous studies, the author demonstrated the research results regarding low cost formulations having high-speed (snap) curing properties as a chip bonding material for the assembly of RFID inlays [6, 7]. The formulations were optimized to demonstrate high-speed curing properties in such that the bonding process would be completed within several seconds using regular RFID chips. The suggested formulations consisted of Bisphenol-F resin, anhydride-based curing agent (~80 % of resin in molecular weight), imidazole curing accelerator (~15 % of resin in molecular weight), spherical Ag fillers, and others.

However, pot life of the suggested formulations was relatively short, approximately 90 min. This means that the formulations created a considerable problem for industrial applications. Several ideas have been considered to extend pot life of the formulations with regard to the curing accelerator. One proposal is using imidazole derivatives as the curing accelerator; another is to coat the accelerator with non-reactive material [8]. The cause of pot life increase in the latter case could be considered as a barrier effect by the coating material. A curing accelerator serves to promote cross-linking between the base resin and curing agent or between resins. Therefore, the curing reaction could be restrained at room temperature when the curing accelerator powders are coated with specific agents that do not contribute in the cross-linking reaction. Meanwhile, the coating agent melted and dissolved into the formulation and uniformly through the convection during the ramping when the bondline temperature was increased to 150~170 ^{o}C in the bonding process for an RFID chip. Ultimately, the curing accelerator was exposed and reacted with the mixture of resin and curing agent. Consequently, the high-speed curing properties of the final formulation were not greatly affected by coating the curing accelerator powders. Therefore, this research aims to improve pot life of anisotropic conductive adhesive (ACA) formulations by applying simple coating methods on curing accelerator powders.

† This paper was presented at the ICMDT 2009, Jeju, Korea, June 2009. This paper was recommended for publication in revised form by Guest Editors Sung-Lim Ko, Keiichi Watanuki.

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2. Experimental procedure

2.1 Overview

Imidazole-curing accelerator powders (melting temperature: 88~92°C) were coated with stearic acid having a melting temperature of 69~70°C. To prepare the mixture of imidazole-curing accelerator powders and stearic acid, imidazole powders were sprinkled into the molten stearic acid while stirring. The heated flowing mixture was poured onto the oscillating surface (sonotrode) of an ultrasonic (US) atomizer, as described in Fig. 1 [9, 10]. On the sonotrode, the flowing mixture was broken by US vibration into fine droplets that freely fell and were solidified by cooling at room temperature (RT). The imidazole loaded microparticles were collected in a chamber at RT.

2.2 Ultrasonic atomizer

Traditional atomizers (e.g., rotary, pressure, and others) are characterized as having low efficiency because, generally, only a small amount of generated energy is used to shatter the liquid. Meanwhile, the US atomizer has been considered as an alternative powder fabrication technology in pharmaceutical or other industrial fields with high energy efficiency exceeding 85 % [9-11]. The high energy efficiency means low defect generation rate in the surface or interior of microparticles.

Fig. 1 shows the schematics of a US atomizer used for the current lab-scale study. The US atomizer consists of three parts: a heated dispenser, a US piezoelectric generator/sonotrode, and a collector.

Temperature and hydrostatic pressure in a thermostated reservoir of the liquid mixture to be atomized affects the feeding rate onto the surface of sonotrode. Matching between the feeding rate and US control parameters determine the quality of imidazole-loaded microparticles. The US atomizer was operated at a constant frequency of 20 kHz and at varied power (maximum power output of 1.5 kW). Therefore, the process parameters considered for this study were mixing ratio (wt. % of coating agent), reservoir temperature, air pressure in the reservoir, drop distance, US power and US angle (Table 1).

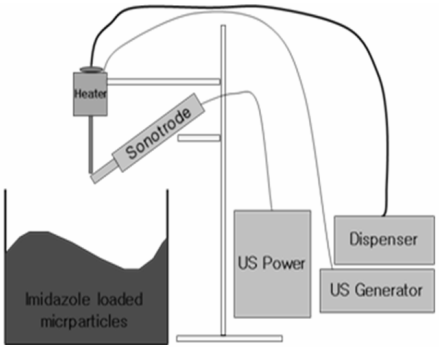

Fig. 1. Schematic representation of the coating processes of powders using an ultrasonic atomizer.

2.3 Materials

Imidazole (Samchun Chemical, Korea) and stearic acid (Samchun Chemical, Korea) were used for preparing of the mixture.

Fabricated imidazole-loaded microparticles were again mixed with the Bisphenol F/anhydride-based curing agent. Fillers were not added in the current study.

2.4 Particle observation

The size distribution, overall shape, and surface morphology of imidazole loaded microparticles were observed using scanning electron microscope (SEM).

Table 1. Design of experiments and pot life results to select main parameters.

Mixing ratio (wt. % of coating agent)	Reservoir temp. (°C)	US power (kW)	US angle (°)	Drop distance (mm)	Air pressure (kPa)	Pot life at R.T. (hr)
23.0	80	0.33	30	20	10	42
37.5	80	0.33	30	100	10	30
23.0	100	0.33	30	100	50	30
37.5	100	0.33	30	20	50	30
23.0	80	0.68	30	100	50	60
37.5	80	0.68	30	20	50	30
23.0	100	0.68	30	20	10	60
37.5	100	0.68	30	100	10	60
23.0	80	0.33	60	20	50	60
37.5	80	0.33	60	100	50	42
23.0	100	0.33	60	100	10	60
37.5	100	0.33	60	20	10	42
23.0	80	0.68	60	100	10	42
37.5	80	0.68	60	20	10	42
23.0	100	0.68	60	20	50	60
37.5	100	0.68	60	100	50	60

*Pot life was determined as the time when the viscosity increases by 2 times.

Table 2. Design of experiments using main parameters.

Process condition #	Mixing ratio (wt.% of coating agent)	Air pressure (kPa)
1	27.2	37.3
2	42.1	37.3
3	27.2	72.7
4	42.1	72.7
5	23.1	55.0
6	44.4	55.0
7	35.5	30.0
8	35.5	80.0
9	35.5	55.0

2.5 Characterization of imidazole loaded powders

Through various US atomization attempts, including those in Table 1, two main process parameters were initially selected from the pot life at RT analyzed by MATLAB: mixing ratio (wt. % of coating agent) and air pressure in the liquid reservoir. The second design of experiments was organized more minutely with regard to the main parameters (Table 2). During the second experiment, reservoir temperature, drop distance, US power, and US angle were optimized as 80°C, 30 mm, 0.45 kW and 45°, respectively. The best final coating processes were also investigated through the measuring of accelerated pot life at 60°C.

Shear strength, as a function of the atomization process, was measured to check the bonding quality. Fig. 2 shows the schematics of the flip-chip bonding process for measuring

shear strength of Si chip. The substrate was a printed circuit board (PCB). The flip chip bonder (Fineplacer®, Finetech, Germany) picked up the Si chip and arrayed the pads of the substrate with the bumps of the Si chip. Prior to contact, a dispenser applied about 15 ml of formulation as a glob-top shape on the substrate. A thermo-compression then created a bondline. Initial temperature of the bottom plate under the antenna pattern was set to 120°C and that of the hot bar to press the chip was set to 150 °C. The maximum temperature for the bottom plate and hot bar was set to 150°C and 180°C, respectively. The chip dimension was 5.2 × 7.2 mm. To reduce bonding time, the bonder was designed to rapidly increase temperature from the initial to the maximum temperature. Therefore, the bonding time was very short, approximately 20 s. Compressive pressure during the flip-chip bonding process was set to 40 N. Shear bonding strength was measured on the bonded die using a shear tester (Dage 4000, Dage, U.S.). The bottom of the shearing tool was located 50 μm above the substrate and the speed of the shearing tool was 167 μm/s. Shear strength was checked twice: at bonging and after highly accelerated stress test (HAST). The HAST samples were stored for 96 h in a chamber set as 85 % relative humidity (RH) at 130 °C.

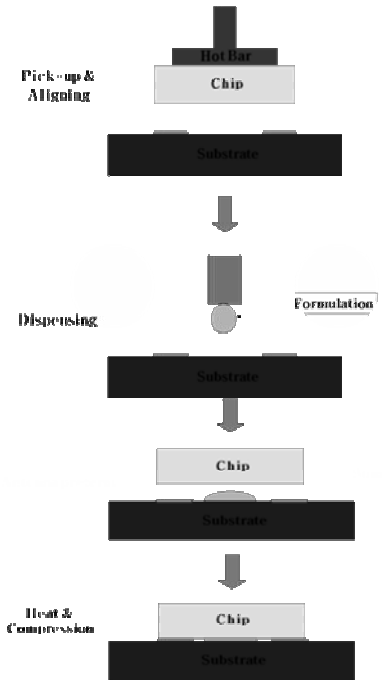

Fig. 2. Schematics of flip-chip bonding process for the measuring shear strength of Si chip.

3. Results and discussion

3.1 Microparticles characterization

Fig. 3 shows the SEM micrographs as a function of process conditions. Depending on the process parameters, the particle size distribution of imidazole-loaded spherical micro particles can be described as a Gaussian curve. Nevertheless, several process conditions (#4, 6, 2, 7) represented much wider particle size distribution. In these conditions, imperfect spherical particle shape was also observed more frequently. A number of particles gathered from conditions #4 and 6 [Fig. 3(f) and (h)] showed surface defects mainly caused by the exposure of raw imidazole surface morphology due to extremely thin coating.

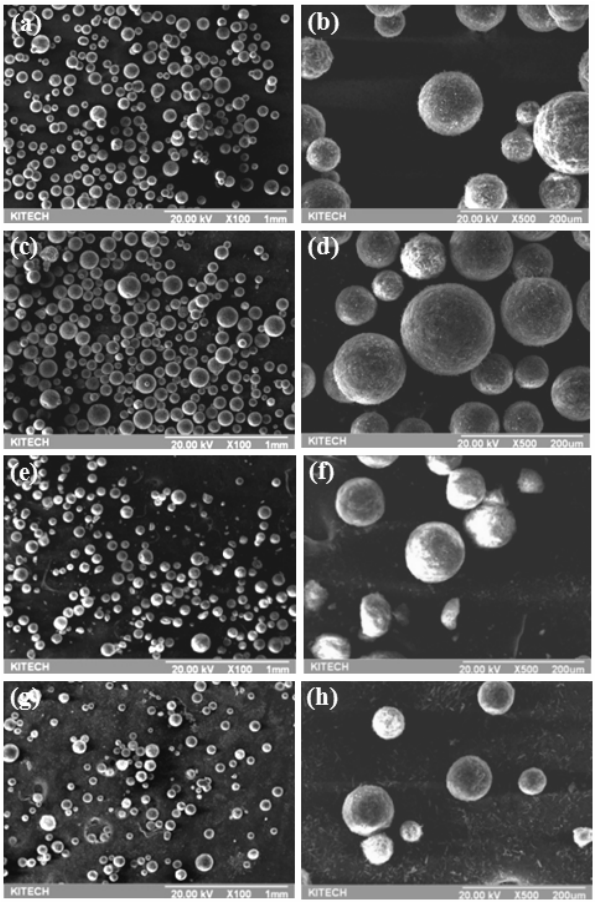

Fig. 3. SEM micrographs as a function of process conditions: (a)/(b), (c) /(d), (e)/(f) and (g)/(h) were fabricated by the process condition 5, 3, 4 and 6, respectively.

Table 3. Experimental results showing the characteristics of formulation and the joint.

Process condition #	Pot life at 60ºC (hr)	Shear strength /unit area (N/mm^2)	Shear strength /unit area (after HAST) (N/mm^2)
1	4.0	32.32	19.17
2	2.5	-	-
3	4.0	31.20	34.49
4	1.0	-	-
5	4.0	45.33	44.08
6	1.0	-	-
7	2.5	21.74	18.09
8	3.0	30.99	28.11
9	3.5	30.73	28.68

3.2 Characterization of pot life and fabricated joints

Table 3 summarizes the experimental results showing the characteristics of the formulation and the joint. Regarding the pot life, it was judged that process conditions indicating narrow size distribution and high spherical-shaping ratio present longer pot life. A more interesting fact is that the process conditions indicating low mixing ratio (i.e., wt. % of coating agent) result in longer pot life in the fixed US operating condition. This means that conditions indicating low mixing ratio present a wider process window with regard to the air pressure in a reservoir. Increase of the mixing ratio resulted in more detrimental effect in the pot life, irrespective of the air pressure (i.e., feeding rate). Consequently, from this experiment, the mixing ratio could be considered as the most critical process parameter characterized as a fixed US operating condition. Surplus molten stearic acid seems to be transferred into fine powders not containing imidazole particle(s) during non-optimized atomization.

Samples indicating longer pot life showed higher average shear strength values, not only after as-reflow, but also after HAST. Highest shear strength value of condition #5 might coincide with the least amount of stearic acid. We did not compensate for the inadequacy produced by the coating agent. Sufficient amount of the curing accelerator is beneficial to increase cure density and bonding strength. Condition #5 showed excellent properties with regard to water absorption, the most menacing problem in the polymeric bondline.

4. Conclusions

To increase the pot life of ACA formulation, imidazole curing accelerator powders were coated with stearic acid using a ultrasonic atomizer. Designs of experiments testing were organized to elucidate the effect of process parameters, the most critical of which was the mixing ratio (wt. % of coating agent). The final formulation incorporating well-processed imidazole-loaded powders indicated longer pot life, higher shear strength, and excellent HAST reliability. Results show that the coating process using an ultrasonic atomizer was effective in increasing pot life of ACA formulations.

Acknowledgment

This work was supported by the Seoul R&BD Program (10848) and the Ministry of Commerce, Industry and Energy (MOCIE) of Korea (10031777).

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