WETTABILITY STUDIES OF A REFLOWABLE UNDERFILL

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ABSTRACT

A series of novel reflowable underfill materials have been developed. Various curing profiles were determined via differential scanning calorimeter (DSC). Wettability was demonstrated through solder sphere wetting test. Fourier transmission infrared spectroscopy (FTIR) was used to detect the interactions that occurred among functional groups during simulated reflow process; while the viscosity change was characterized via heating-programmable rheometer. In addition, the effect of reflow profile on wettability was evaluated as well, for example, the variation of overall acid number under several reflow profiles was monitored via titration with standard sodium hydroxide (NaOH) solution. The results showed that wettability was substantially enhanced with the addition of certain amounts of wetting precursor. The reaction that occurred between wetting precursor and hardener at elevated temperature was also observed. The curing degree of the material prior to solder bump melt increased with extending the duration in the temperature range of 150^{o}-183^{o}C. As a result, the overall reaction gave rise to the decrease of overall acid number that translated into lower wettability. Rheological results showed that viscosity started to ramp up earlier during reflow given that the material has been aged at ambient temperature for a certain period of time. On the other hand, material with lower wettability can prevent the solder bump from over-reflow, as such, maintain a certain standoff from the standpoint of higher reliability.

Key words: Flip-Chip, underfill, wettability, reflow.

INTRODUCTION

As the trend toward miniaturization and compact products continues in the electronics industry, lighter, smaller, thinner, and faster electronics packaging are critically demanded. The use of Flip-Chip has inherent advantages over other methods for electronic packaging due to its high-density and short-signal propagation pass [1]. However, the difference of the thermal expansion coefficient between the chip and the substrate causes significant reliability problem [2]. Although this can be resolved by dispensing the underfill material between the chip and board, this additional process will take longer time and increase the overall cost. Elimination of assembly steps will enable high throughput, and reduce process complexity and capital equipment requirement.

To implement the high throughput, a novel process that is compatible with SMT assembly has been proposed, as shown in Figure 1.

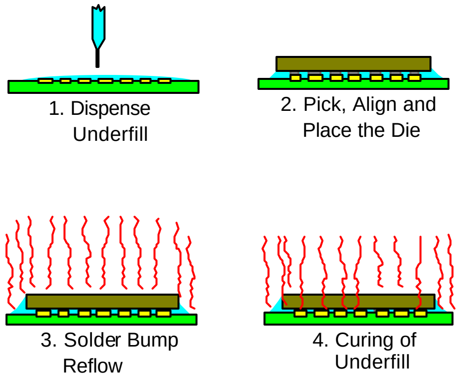


Figure 1. Schematic diagram of Flip-Chip assembly with reflowable underfill.

The overall process begins with dispensing the underfill onto the bond pads on the substrate. Then the bare chip was picked, aligned via a vision system and placed on the substrate. The whole parts were subsequently transferred into reflow oven where solder bump reflow and material cure occurred simultaneously. Finally, off-line postcure was conducted according to different underfill specification.

Several companies have explored reflowable underfill and a few commercial products have become available. Georgia Tech has performed substantial studies in this area and reported on it extensively [3-6]. Shi et al has developed several reflowable underfill formulations and the effect of various constituents on material properties has been substantially addressed [3]. Daniel F. Baldwin et al has simulated this compression flow chip placement process via commercially available polymer fluid flow analysis software [5]. Some reliability studies were also reported in their work. As reflowable underfill was an integration of epoxy and fluxing agent, it was endowed with self-fluxing characteristics. On the other hand, the fluxing capability is likely to become weakened if the material formulation and assembly process parameters were not finely tuned, due to the trade-off between epoxy curing reaction and fluxing action. As such, the wettability of reflowable underfill plays a critical role in determining the success of this novel Flip-Chip process.

In this work, the wettability studies were presented in three aspects: material formulation, reflow profile and substrate surface conditions. Our goal is to gain in-depth understanding of reflowable underfill performance during reflow process, and consequently establish the guide for material formulation as well as the process parameters to suit different packages.

EXPERIMENTAL

Chemicals

The epoxy resin, hardener, catalyst and wetting precursor were purchased from commercial sources and used as received.

Characterization

DSC studies were performed via a modulated DSC (TA Instruments, Model 2920). Approximately 10 mg of sample was used for each run. For curing profile determination, the ramping rate was kept at 10^{o}C/min for all the samples. For reflow process simulation, three heating profiles were programmed according to different real reflow profile calibrated by SlimKIC™, and were defined as shown in Table 1.

Table 1. Reflow profile specifications

	Time Between (s)		
	25/150	150/183	183/230
Reflow 1	107	73	53
Reflow 2	107	30	64
Reflow 3	107	142	61

For solder sphere wetting test, approximately 20mg reflowable underfill material was dispensed on top of a fresh copper foil, and then two 30 mil eutectic Sn/Pb (63/37) spheres were placed into the material. Ensure that there is physical contact between the two solder spheres before the copper foil is transferred into reflow oven (Heller 1800W) that is running under a certain reflow profile. After reflow, solder joints were inspected via microscopy to evaluate the wettability.

A FTIR (Bio-Rad) was used to detect the interactions among various constituents in the formulation. About 30mg underfill material was heated in the DSC cell under Reflow 1, and quickly taken out after the temperature reached the pre-set value. The sample was then prepared via KBr pellet.

A rheometer (TA Instruments, Model AR 1000N) was used to monitor the viscosity variation during reflow. Reflow1 was used as heating profile for this study, and the shear rate was kept at 0.17 1/s.

For the overall acid number measurement, approximately 30mg sample was heated in DSC cell under Reflow1, Reflow 2 and Reflow 3, respectively. After being heated to the pre-determined temperature, the sample was taken out quickly and subsequently dissolved into acetone while standard NaOH solution was used for titration. The overall acid number was designated as NaOH [mmol]/sample [mg].

Substrate surface conditions

Two types of substrates were evaluated: one is solder mask defined with Ni/Au finishing; another type contains just Ni/Au coating without solder mask.

RESULTS AND DISCUSSION

Material formulation

Figure 2 shows the curing profiles of three reflowable underfill. It can be seen that two major reactions demonstrated by two exothermic peaks at about 155^{o}C and 205^{o}C, respectively, are probably involved in the overall curing reaction of underfill A and underfill B. While for underfill C, only one exothermic peak at about 180^{o}C was observed. In addition, underfill C possesses fast curing characteristics illustrated by its relatively lower exothermic peak temperature. The results of corresponding solder sphere wetting test are shown in Figure 3. Obviously, underfill A and underfill C exhibit better wettability demonstrated by the formation of a round solder joint after reflow. Theoretically, wettability of reflowable underfill is inversely proportional to its curing rate, or in another word, underfill C should show the lowest wettability. This discrepancy suggests that wettability may not be exactly in agreement with its curing rate.

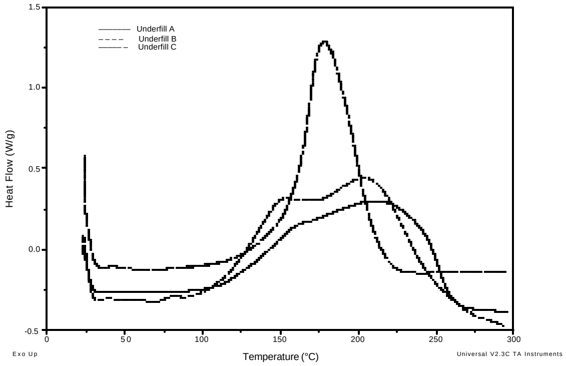
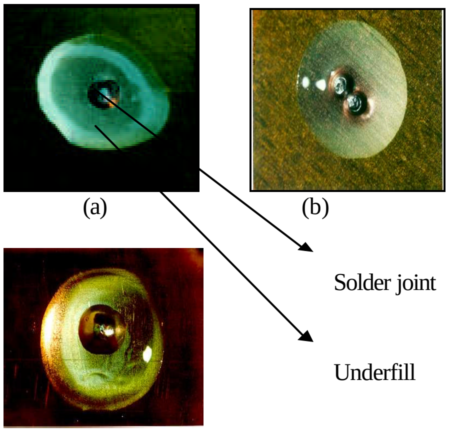


Figure 2. Curing profile of reflowable underfill

The effects of wetting precursor on the curing profile and wettability of underfill A are shown in Figure 4 and Figure 5, respectively. As shown in Figure 4, an increase in the heat flow of first reaction was observed upon increasing the amount of wetting precursor, which indicates that the wetting precursor has participated in the overall curing reaction. As shown in Figure 5, the wettability of underfill A is substantially enhanced as the amounts of wetting precursor increased from 0.5% to 5%.



(a) (b)

(c)

Figure 3. Microscopy graph showing wettability of (a) Underfill A (b) Underfill B and (c) Underfill C.

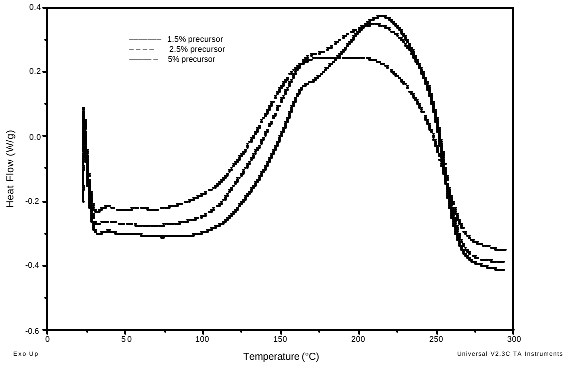
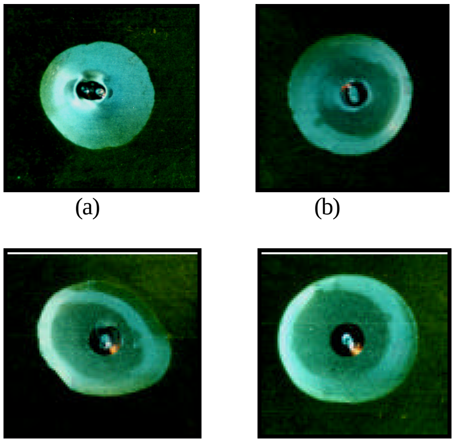


Figure 4. Curing profile of underfill A containing various amounts of wetting precursor.

The same investigation has been carried out for underfill C and similar results are obtained, as illustrated in Figure 6 and Figure 7. However, the effects of precursor on both curing profile and wettability of underfill C are not well pronounced in comparison with underfill A.



(a) (b)

(c) (d)

Figure 5. Microscopy graph showing wettability of Underfill A containing various concentrations of wetting precursor (a) 0.5% (b) 1.5% (c) 2.5% (d) 5%.

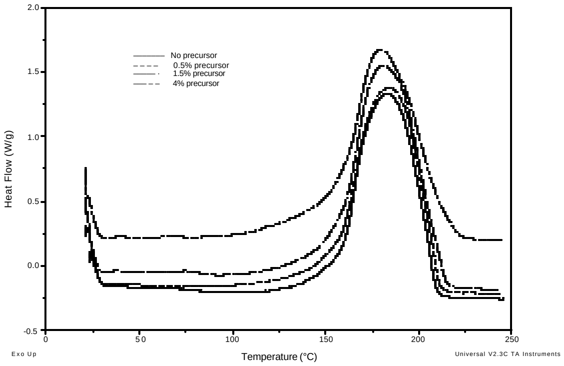
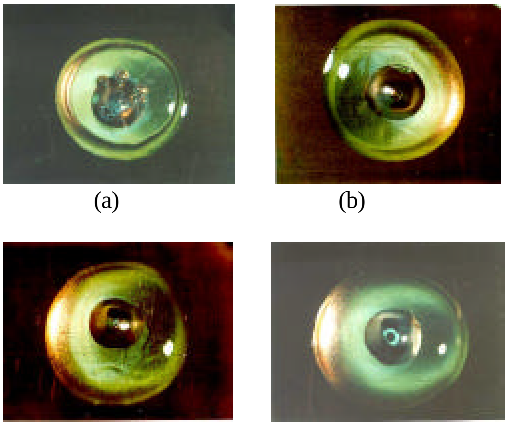


Figure 6. Curing profile of Underfill C containing various amounts of wetting precursors.



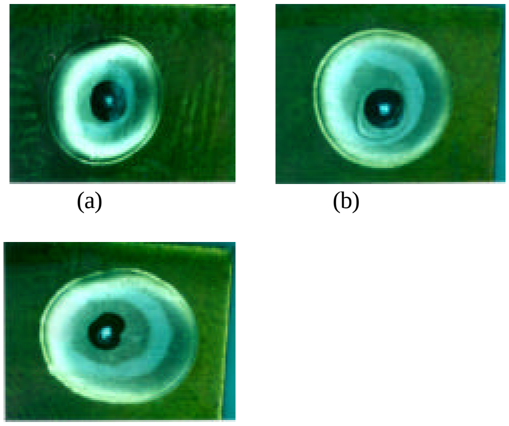
(a) (b)

(C) (d)

Figure 7. Microscopy graph showing wettability of Underfill C containing various concentrations of wetting precursor (a) 0% (b) 0.5% (c) 1.5% (d) 4%

Reflow profile

Figure 8 shows the effect of reflow profile, more accurately the duration between 150°C and 183°C, on wettability of underfill A containing 2.5% wetting precursor. As shown in Figure 8, Reflow 3 gives rise to relatively poor wettabilty as demonstrated by the formation of a small irregular shaped solder sphere after melting. The fact demonstrates that extending duration between 150°C and 183°C could deteriorate the wettability of reflowable underfill.


(a) (b)

(c)

Figure 8. Microscopy graph showing wettability of Underfill A under various reflow profiles (a) Reflow 1 (b) Reflow 2 (c) Reflow 3.

To gain in-depth understanding of material property changes during reflow, DSC is used to simulate the reflow oven operating environment, in which underfill sample and a solder sphere are put into the crucible together. Figure 9 and Figure 10 clearly depict the epoxy curing characteristics before and after solder melt under various reflow profiles for underfill A and underfill C, respectively. In either Figure 9 or Figure 10, it is observed that underfill curing extent before solder melt, which is represented by integration of heat flow in the temperature range up to solder melt, decreases as the aforementioned duration shortens. In the present case, Reflow 1 and 2 give rise to lower curing degree than Reflow 3. The less-cured underfill material will not hamper the solder sphere melt, thus, Reflow 1 and 2 show better wettability compared to Reflow 3. Meanwhile, the overall acid number at various temperatures is determined via NaOH titration and labeled in the corresponding curing curve, as shown in Figure 9 and Figure 10 again.

It can be readily observed that the overall acid number, in terms of standard NaOH solution volume consumed by per milligram of underfill, decreases as the reaction proceeds under each profile. For example, the number reduces from 0.375 to 0.306 ml NaOH/mg in the temperature range of 125°C to 190°C under Reflow 1. The reflowable underfill typically includes anhydride as hardener that affords some level of flux action. Anhydride can hydrolyze to carboxylic acids that are the key ingredients for flux to remove the metal oxide from the solder bump surfaces. On the other hand, anhydride is involved in the epoxy curing reaction as well such that the acidity of the formulation will decrease as the curing reaction proceeds further.

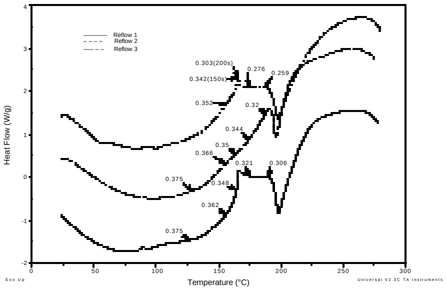


Figure 9. Curing profile of Underfill A simulated under three reflow profiles, respectively, to monitor overall acid number in terms of [NaOH] (ml)/[Underfill A] (mg) at various temperature.

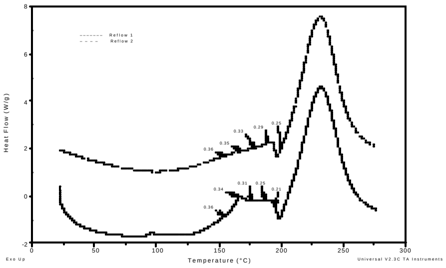


Figure 10. Curing profile of Underfill C simulated under two reflow profiles, respectively, to monitor overall acid number in terms of [NaOH] (ml)/[Underfill C] (mg) at various temperature.

It can also be noticed that Reflow 2 that has shortest duration between 150°C and 183°C gives rise to highest overall acid number at the same temperature in comparison with another two reflow profiles. For example, the overall acid number of Underfill A at 175°C are 0.321(Reflow1), 0.344(Reflow2) and 0.276(Reflow 3), respectively. In addition, the number decreases dramatically from 0.342 to 0.303 ml NaOH/mg after being maintained at 166°C for 50s, as shown from Reflow3 that has longest dwell time between 150°C and 183°C. The plausible explanation is that part of anhydride as well as its hydrolyzed counter part organic acid have been incorporated into the epoxy network even before the solder started to melt, and the immobilized anhydride and/or acid have less reactivity toward NaOH. This fact manifests that acidity of this particular reflowable underfill will substantially become weak and deteriorate the fluxing activity in the case of prolonged duration between 150°C and 183°C. The similar trend can be found for Underfill C, as shown in Figure 10. In addition, relatively smaller acid number at the same temperature as that for Underfill A are observed for Underfill C that has faster curing characteristics, in particular when temperature is near to solder reflow point. As a result, relatively shorter time in the aforementioned period is preferred during reflow process from the standpoint of wettability, especially for fast curing material like Underfill C. On the other hand, more voids have been found if the ramping rate before solder melt becomes drastic. Accordingly, there is a trade-off between wettability and void issue concerning reflow process control (to be published later). Considering these two circumstances, Reflow 1 was adopted as reflow profile for assembly process.

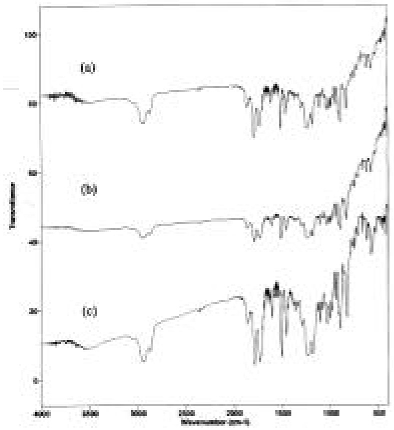


Figure 11. FTIR spectrum of Underfill A showing the interaction that occurred during the reflow process. (a) Pristine (b) heating to 175°C and (c) heating to 214°C.

FTIR is used to detect the functional group changes associated with reflow process. Figure 11 shows the FTIR spectra of Underfill A that has been heated to different temperatures under Reflow 1. As the reflow proceeds, it can be observed that the peak at 3500cm^{-1} becomes wider and another two peaks at about 1750cm^{-1} nearly turns into equal height compared to the pristine one. This observation implies that acid group has been generated, probably arising from the reaction between anhydride and wetting precursor.

Viscosity variation during reflow is another critical factor to affect the wettability of reflowable underfill, in particular the onset temperature of viscosity ramping up. Thus, the reflow process was accordingly simulated via rheometer under a certain heating profile to determine the onset temperature. Figure 12 shows the rheological curves of Underfill A being carried out under Reflow 1 after aging at ambient temperature for different period of time. The viscosity starts to ramp up at 195°C for the fresh formulation, while the onset temperature decreases to around 190°C and 180°C after the fresh material has been kept at ambient temperature for 8h and 28h, respectively.

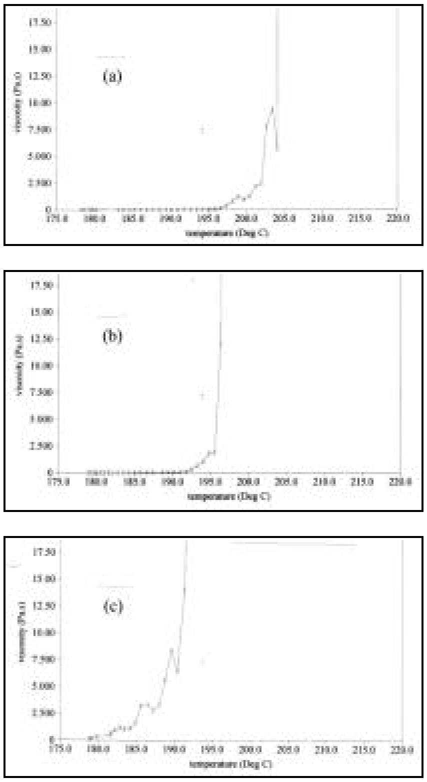


Figure 12. Rheological curves showing the onset temperature of viscosity ramping up in reflow process after aging at ambient temperature for (a) 0h (b) 8h (c) 28h, respectively.

This phenomenon probably resulted from the interactions that even occurred during room temperature storage. This pre-reaction will accelerate epoxy curing in the subsequent reflow process and cause earlier appearance of the onset temperature. For Flip-Chip assembly, the solder bump cannot collapse and form the joint with bond pad on the substrate side in the case that the underfill viscosity has already become too high before the temperature reaches the solder melting point. This is also a useful window to observe the pot-life effect on reflowable underfill wettability.

In a summary, the overall reaction that occurred prior to solder melt will result in significant property changes of the reflowable underfill during reflow process, which will consequently affect the wettability. Meanwhile, those changes are also affected by different formulation, reflow condition as well as the aging time. Despite the complexity, good wettability can be achieved via discreet consideration and integration of material formulation and process control. All these need the closed collaboration between material specialist and process engineer.

Substrate surface finishing

Nowadays, non-solder mask defined substrate, which is mainly aimed for cost saving, has come out. However, solder bump will flow all the way along the circuitry if this kind of substrate was used for flip-chip assembly. This will make the control of solder bump stand-off becomes tough, which will bring out the reliability concern and even result in bridging between the adjacent bumps.

This problem is mainly resolved via either changing bump structure or controlling reflow profile. For example, a certain height of non-fusible constituent in the bump will maintain the stand-off up to a certain level, and the proper control of reflow peak temperature and reflow time will also assist to prevent the solder from over reflow. On the other hand, it is reasonable to control the solder reflow from the underfill point of view.

Figure 13 shows the bump cross-sections of two chips assembled on non-solder mask defined substrates with Underfill A and Underfill B, respectively. As shown in Figure 13 (a), Underfill B that has lower wettability enables to prevent the solder bump from over-reflow and consequently maintain a higher stand-off. However, for the unit assembled with Underfill A, the solder bump has extremely flowed out after reflow, causing the bond pad on substrate side to almost touch the chip surface.

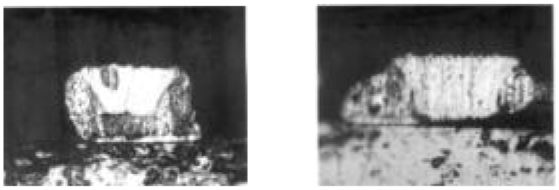

(a) (b)

Figure 13. Bump cross-sections of units assembled on non-solder mask defined substrate with (a) Underfill B and (b) Underfill A.

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