Development of Polyester-Modified Epoxy Resins for Self-Organization Soldering

Shinji Fukumoto, Keisuke Yoshida, Yosuke Mizokami, Michiya Matsushima and Kozo Fujimoto

Graduate School of Engineering, Osaka University, Suita 565-0871, Japan

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Materials Transactions, Vol. 60, No. 6 (2019) pp. 858 to 864
Special Issue on Frontier Researches Related to Interconnection, Packaging and Microjoining Materials and Microprocessing for Such Materials -Part II-

Key words: viscosity, self-organization, compatibility, solder, electronics packaging, thermoset resin, thermoplastic resin, hybrid resin

1. Introduction

Internet technology has spread rapidly in recent years and the importance of information in society is increasing. Thus, mobile information terminals such as smartphones must be further miniaturized and achieve higher speeds and systematization. The development of high-density packaging of the IC (Integrated Circuit) chip has allowed for the miniaturization of electronic devices along with decreased solder bump size of electronic components and narrowed pitch between the electrodes. In general, an IC chip is mounted on a substrate using small solder bumps and thermal stress is the electrodes. Therefore, various underfill materials were developed to protect the solder joints in small electronic devices that are exposed to harsh environments including falling impacts and high temperature.

The required properties for the underfill resins before curing differ from those after curing. Capillary flow type underfill resin must have low viscosity and low thixotropic properties because the resin is injected into narrow gaps between electrodes or between the chip and substrate before curing. Many studies on the capillary flow phenomenon, viscosity, thixotropic properties, and wettability have been reported. However, because the capillary flow type encapsulate technology requires a large number of processes, pre-mount-type no-flow underfill resin materials have been developed. Shape retention ability on the substrate is essential for the no-flow underfill resins. It is necessary to optimize the viscosity so the resin does not spread out on the substrate before chip mounting when using no-flow underfill resins. Self-organization soldering technology using a thermoset resin containing fine solder particles has also been developed to reduce the number of processes and accommodate the packaging of smaller devices. This method is also a pre-mount-type process in which a resin-based solder paste is stencil-printed onto a substrate using a stencil mask. Because of the self-organization behavior of the molten solder particles, the electrodes are spontaneously bonded through the coalesced solder and the periphery of the solder joint can be sealed simultaneously with the cured resin. The resin-based solder paste for the self-organization assembly should exhibit viscosity characteristics such that the printed shape is maintained before heating and the fine solder particles in the resin coalesce during heating. Therefore, the control of resin viscosity before curing is key for the self-organization assembly process. For example, it has been reported that when the thermoset resin viscosity before curing is not properly controlled, the solder particles in the resin settle on the substrate during heating before the curing reaction begins, resulting in an inhomogeneous dispersion.

Because the thermal stress due to the difference in the coefficient of thermal expansion between the chip and substrate is loaded on the solder bonds described above, excellent adhesion, high strength, and high toughness are required in the thermoset resin after curing. Although high toughness is required to reinforce the solder joints, it is desirable that the resin exhibit a low Young’s modulus at high temperature to reduce thermal stress on the chip. To control the toughness and Young’s modulus of the thermoset epoxy resin, compounding technologies have been developed including modification with elastomer particles and modification with thermoplastic engineering plastics. For example, reported that when the reactive elastomer is compatibilized with the epoxy resin, the elastomer is dispersed in an island-like pattern in the epoxy resin matrix, improving the toughness of the epoxy resin. However, since the elastomer and epoxy resin are only marginally compatible with each other, the elastomer-modified epoxy resin often becomes brittle as a result of phase separation. Therefore, it is necessary to modify the epoxy underfill resin with a resin exhibiting good compatibility.

In this study, a thermoplastic polyester-modified thermoset epoxy resin (hybrid resin) was developed for self-organization soldering. The change in chemical structure of the hybrid resins before and after curing, curing reaction, and mechanical properties were investigated. The adaptability of the developed resins for self-organization soldering was also examined.

2. Experimental

2.1 Materials

The thermoset epoxy resin (Fujikura Kasei Co., Ltd.) consisting of bisphenol-A epoxy resin-50 mass% phthalic
Phthalic anhydride and imidazole were used as a curing agent and accelerator, respectively. Hereafter, the thermoset epoxy resin is referred to as the XB1005 resin. Various commercial supersaturated copolymerization polyester resins (Unitika Co. Ltd. elitel® UE series) were used as thermoplastic resins, as shown in Table 1. Hereafter, each polyester resin is referred to as the polyester-A to -E resin. The XB1005 thermoset resin was modified with the polyester resins and the resulting material is defined as the Hybrid resin in this paper. Hybrid resins A to E (HR-A to HR-E) were fabricated by adding each polyesters-A to -E to the XB1005 resin. The polyester resin mixture ratio was varied from 5 to 40 mass%. Depending on the type and content of the polyester resin, the name of the resin is expressed in terms of HR-type(mass%). For example, the hybrid resin containing 10 mass% of polyester-A is referred to as HR-A(10%).

<table>
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<tr>
<th>Resin (type)</th>
<th>Model: elitel®</th>
<th>Molecular mass</th>
<th>( T_g (^{\circ}C) )</th>
<th>Softening temperature ((^{\circ}C))</th>
<th>Specific weight</th>
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<td>Polyester-A</td>
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<tr>
<td>Polyester-B</td>
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<tr>
<td>Polyester-C</td>
<td>UE-3200</td>
<td>16000</td>
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<td>165</td>
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<tr>
<td>Polyester-D</td>
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<td>20000</td>
<td>65</td>
<td>165</td>
<td>1.25</td>
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<tr>
<td>Polyester-E</td>
<td>UE-3500</td>
<td>30000</td>
<td>35</td>
<td>145</td>
<td>1.23</td>
</tr>
</tbody>
</table>

Fig. 1 Schematic illustration of land grid array (LGA) substrates, (a), and self-organization soldering process on LGA substrate, (b).

2.2 Self-organization soldering

Figure 1 shows the geometry of the land grid array (LGA) substrate and a schematic illustration of the self-organization soldering process. Resin-based solder pastes were printed on the substrate with the LGA matrix using a 0.15 mm thick stencil mask. The aperture size of the stencil was 11 × 11 mm and the diameter of the Cu electrode land was \( \phi \)400 µm with a pitch between lands of 400 µm. Before heating, the fine solder particles were homogeneously dispersed in the resin on the LGA substrate. During the reflow process, molten solder particles moved and coalesced to form larger particles and wetted the electrodes. Finally, solder bumps formed on the electrodes and were sealed with the cured resin. The reflow process was performed according to the temperature profile shown in Fig. 2. The profile has three main stages; the first holding stage at 120°C is designed to reduce the surface oxide film on the solder particles, the second holding stage
at 165°C is necessary for self-organization of the solder particles, and third holding stage at 215°C was performed to cure the thermoset resin. Further details of the self-organization soldering process have been reported in Refs. 6–8).

2.3 Evaluation
The viscosity of the XB1005 and HR resins was measured using a rheometer (HAAKE MARS III, Thermo Fisher Scientific Inc.). The curing reaction and resin structural analysis were evaluated using a differential scanning calorimeter (DSC; DSC7000X, Hitachi High-Technologies Co., Ltd.) and Fourier transform infrared spectrophotometer (FT-IR; PerkinElmer Inc.), respectively. The heating and cooling rates in the DSC analysis were 10 and 30°C/min, respectively. The compression test was performed at 25 and 80°C to evaluate the mechanical properties of the cured resins under a cross-head speed of 0.05 mm/s. The specimen was a φ5 mm × 4 mm cylinder.

3. Results and Discussion

3.1 Viscosity
Figure 3 shows the changes in viscosity upon heating of the hybrid resins from 20°C to 150°C (HR-A(10%)) to HR-E(10%) containing 10 mass% of polyesters-A to E, respectively.15) The XB1005 resin viscosity is shown for reference. The viscosity of the XB1005 resin prepared with conventional bisphenol-A epoxy decreased with increasing temperature and reached a minimum of approximately 15 mPa·s at 140–150°C, which is higher than the melting point of the Sn–58 mass%Bi solder. All hybrid resins showed 2–8 times higher viscosity than the XB 1005 resin at 20°C and showed similar viscosity changes as that of XB1005 as a function of temperature. The minimum viscosity of the hybrid resins was higher than that of XB1005. During self-organization soldering, since the molten Sn–58 mass%Bi particles coalesce at temperatures slightly higher than the melting point, the resin viscosity above the melting point of solder is important. The viscosities of HR-A(10%) to HR-E(10%) at 145°C were plotted against the molecular mass of the blended polyester resin (Fig. 4). The viscosity at 145°C was almost directly proportional to the molecular mass of the constituent polyester resin. As a representative example, the viscosity of the HR-A containing different amounts of polyester-A was measured. The viscosity of HR-A at 145°C as a function of the polyester-A content is shown in Fig. 5.15) The viscosity of HR-A increased with increasing polyester-A content. Thus, the viscosity of the hybrid resin at temperatures ranging between 20°C to the SnBi melting point was controlled by the content and molecular mass of the blended polyester resin.

3.2 Curing reaction
The phase transformation of HR-A(10%), XB1005, and polyester-A resins was investigated by thermal analysis (DSC) and the results are shown in Fig. 6. In the polyester-A resin DSC curve, an endothermic peak showing a glass transition at approximately 10°C and an exothermic peak indicating cold crystallization at approximately 70°C were observed. The XB1005 resin underwent an exothermic reaction corresponding to the curing, and the curing
temperature \( (T_c) \) was approximately 150°C. The HR-A(10\%) composed of the polyester-A and XB1005 resins exhibited both small and large exothermic peaks at 70 and 180°C, respectively. The former peak corresponds to the cold crystallization of the polyester resin and the latter corresponds to the curing reaction of the XB1005 resin. The glass transition was not detected in the DSC curve of HR-A since the amount of polyester resin in the HR-A was small resulting in a negligible endothermic quantity. However, since cold crystallization due to the polyester resin was observed in the HR-A, glass transition of the polyester resin could also occur in the HR-A. The curing temperature \( (T_c) \) of the HR-A shifted to a temperature higher than that of XB 1005 since the epoxy molecules mixed with polyester molecules and the epoxy resin curing reaction slowly progressed. The phase transformations derived from both the XB1005 and polyester-A resins occurred in the HR-A. Even when the polyester and epoxy resins were mixed the phase transformations of the individual components were largely unaffected.

### 3.3 Self-organization of the solder particles in the hybrid resin

The hybrid resin and XB1005 resin-based solder pastes were printed onto the substrate, and heated according to the temperature profile shown in Fig. 2. Figure 7 shows the results of self-organization soldering using the XB1005- and HR-A(15\%)-based solder pastes. The resin-based solder paste was prepared with reducing agent in each resin at concentrations of 10 and 30 mass\%. Although the fine solder particles coalesced to form solder bumps on the Cu electrodes in all pastes, some differences in terms of resin spreading and residual solder particles were observed. For the XB1005-based solder paste containing 10 mass\% reducing agent, fine solder particles successfully coalesced to form a solder bump on each electrode and the entire LGA matrix area was

![Fig. 5 Viscosity at 145°C of HR-A as a function of content of polyester-A resin.](image1)

![Fig. 6 DSC curves of HR-A(10\%), XB1005, and polyester-A resin.](image2)

![Fig. 7 Formation of solder bumps on LGA substrate via self-organization soldering using resin-based Sn-58 mass\%Bi solder pastes.](image3)
covered with cured resin, although many small particles remained between the electrodes (Fig. 7(d)). However, since XB1005 exhibits very low viscosity at high temperatures, as shown in Fig. 3, the printing area spread and fine solder particles flowed to the periphery (Fig. 7(a)). For the HR-A-based solder paste containing 10 mass% reducing agent, since the viscosity of HR-A(15%) at high temperatures is higher than that of XB1005, the printed area nearly maintained the initial shape before heating (Fig. 7(b)). However, since the viscosity of HR-A is higher than that of XB1005 due to the polyester mixture, the mobility of the solder particles decreased and solder particles with insufficient coalescence remained between the electrodes. To improve the coalescence of solder particles in the hybrid resin-based solder paste, the reducing agent content was increased to 30 mass%. The printed area of the solder paste was nearly maintained and the fine solder particles coalesced on each electrode to form a solder bump with decreased residual solder particles (Figs. 7(c) and 7(f)). Thus, deterioration of coalescence due to increased resin viscosity can be improved by adding an appropriate amount of reducing agent.

### 3.4 Properties of the cured hybrid resins

The compression properties of the cured XB1005, HR-A(15%), and HR-A(40%) samples are shown in Fig. 8. A maximum compression strength of 130 MPa was obtained for the XB1005 resin at 25°C. As the amount of polyester resin in the mixture increased, the compression strength of the hybrid resin decreased, but the elongation characteristics were improved. The elongation increased as the polyester resin content increased. The initial gradient of the stress-strain curves, that is the quasi-Young’s modulus, decreased as polyester resin content increased. This trend became more prominent as the temperature was raised. Since the hybrid resin exhibited better elongation characteristics than the conventional epoxy resin, it is expected to reduce the thermal stress generated in the electronic components and substrate when used as an underfill resin.

### 4. Discussion

When hybrid resin-A was heated to 230°C for the DSC analysis, the phase transformations of both the bisphenol-A epoxy and polyester resins were detected, corresponding to the curing reaction of the former resin and cold crystallization of the latter resin, as shown in Fig. 6. It was previously reported that a mixture of bisphenol-A epoxy and oxetane resins can function as a plasticizer to the polyester resin.\textsuperscript{16)\textcircled{1}} Therefore, the epoxy and polyester resins must be compatible in the hybrid resins before curing. On the other hand, the cured HR-A exhibited larger elongation than the XB1005 resin, as shown in Fig. 8. The chemical structure of the polyester resin was maintained in the cured hybrid resins. FT-IR analyses were performed to identify the chemical structures of XB1005, polyester, and hybrid resins before and after heating.

The FT-IR spectrum of the XB1005 resin before curing is shown in Fig. 9. The XB1005 resin contains bisphenol-A epoxy resin, phthalic anhydride and imidazole.
polyester resins. Figure 11 shows the FT-IR spectra of HR-A(10\%\) to HR-E(10\%\) before curing, which contain XB1005 resin (bisphenol-A epoxy resin, phthalic anhydride, and imidazole), and various polyester resins. Characteristic absorption peaks arising from the epoxy ring, benzene ring, and C=O groups in the epoxy resin and phthalic anhydride were observed. Peaks originating from the C=O, C(O)O, and CH groups in the polyester resins were detected in all hybrid resins. Additionally, no significant peaks were observed other than those derived from each resin. In other words, the spectra of the hybrid resins were simply sums of the spectra of the epoxy and polyester resins. The epoxy resin is known to act as a plasticizer in thermoplastic resins.\(^{16,17}\) It is likely that the hybrid resins before curing adopt a compatible state in which the epoxy molecule can pass through the gap between polymer chains of the polyester resins.

The chemical structure of the cured hybrid resins was investigated by FT-IR analyses. The spectrum of the cured HR-A(10\%) was typical of hybrid resins and is shown in Fig. 12 along with the spectra of the cured XB1005 and polyester-A resins for comparison. Figure 13 shows the curing reaction of the bisphenol-A epoxy resin with phthalic anhydride. The epoxy ring is opened by phthalic anhydride and the epoxy resin is cured via polymerization.\(^{15}\) The absorption peaks arising from the epoxy ring and the phthalic anhydride C=O group at 914 and 1770 cm\(^{-1}\) observed before curing disappeared in both cured XB1005 and HR-A due the curing reaction shown in Fig. 13. On the other hand, the polyester-A resin spectral peaks arising from C=O, C(O)-O, and CH– remained in HR-A even after curing. Thus, the cured hybrid resins are expected to exhibit thermoplasticity. Thermal analyses were performed on a HR-A(10\%) and Fig. 14 shows the results of DSC analyses of three thermal histories of HR-A(10\%).\(^{15}\) As shown in Fig. 6, the cold crystallization of the polyester resin and the curing reaction of the epoxy resin were detected on the 1st heating cycle at approximately 70°C and 180°C, respectively. On the 2nd and 3rd heating cycles, no peaks corresponding to the curing reaction was observed, but the exothermic peak arising from the cold crystallization was observed at approximately 70°C. Therefore, it is clear that the hybrid resins exhibited thermoplastic properties due to the polymer chains of polyester resin in the cured epoxy resin.
5. Conclusions

Polyester-modified epoxy resins were developed as under-fill resins for the self-organization soldering process. The major results and conclusions of this study can be summarized as follows:

1. The hybrid resin containing the bisphenol-A epoxy and polyester resins showed higher viscosity than the epoxy resin from room temperature to the melting point of Sn-58 mass%Bi. The minimum viscosity of the hybrid resin depended on the content and molecular mass of the polyester resin in the hybrid.

2. Since the hybrid resin exhibited a higher viscosity than the epoxy resin at the melting temperature of the SnBi solder, self-organization soldering with reduced spreading of the printed area was achieved. The addition of a reducing agent into the solder paste improved the coalescence behavior of the solder particles.

3. The hybrid resin before curing adopted a chemical structure in which the bisphenol-A epoxy resin was compatible with the polyester resin. The curing reaction of the epoxy resin and the cold crystallization of the polyester resin occurred in the hybrid resins upon heating.

4. The hybrid resins retained the chemical structure of the polyester resin even after curing and exhibited thermoplastic properties during heating cycles.

Acknowledgements

The materials used in this study were supplied by Fujikura Kasei Co., Ltd. and Senju Metal Industry Co., Ltd. The authors would like to express their appreciation for the crucial contributions by Takeshi Kan, Minoru Ueshima, and Daisuke Minakuchi. This research was partially supported by the Fujikura Foundation.

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