# Characterization of Reworkable High-Temperature Adhesives for MCM-D Application

#### C. P. WONG, JIALI WU, RANDY T. PIKE

School of Materials Science and Engineering & Packaging Research Center, Georgia Institute of Technology, Atlanta, Georgia 30332-0245

Received 28 September 1998; accepted 12 January 1999

ABSTRACT: The need to have a high-temperature adhesive that can withstand temperatures in excess of 350°C for MCM-D silicon substrate process application, yet which can be reworkable at slightly high temperature  $\sim 400^{\circ}$ C for the removal from the glass pallet, is important. A novel, reworkable, high-temperature adhesive based on polyimide-amide-epoxy (PIAE) copolymer was developed and investigated using modulated differential scanning calorimetry (MDSC), thermal gravimetric analysis (TGA), Fourier Transform Infrared Spectroscopy (FTIR) and solid-probe pyrolysis mass spectroscopy (MS). Compared with commercial polyimide-amide (PIA) adhesives, FTIR spectra reveal that the thermally degradative ester groups contribute to the reworkability of the PIAE adhesive at a specific temperature (400°C), yet they remain thermally stable at a lower working temperature (350°C). FTIR spectrum comparison of the residuals of PIAE and PIA are similar after exposure to 400°C. MS spectra of outgassed products identify that the components of radical fragmentation from PIAE are due to polymeric chain degradation at 400°C, while only volatile trace water and N-methyl pyrolidone (NMP) are evolved from the commercial PIA adhesive. TGA results suggest a complementary explanation for the variation of total ion current (TIC) curves on these two adhesives. MDSC curves further verify that the reworkable PIAE adhesive is a copolymer. Furthermore, a reasonable thermal degradation mechanism is presented on the adhesive reworkability. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 997-1005, 1999

**Key words:** reworkable high-temperature adhesives; polyimide-amide-epoxy (PIAE); thermal stability; reworkability; copolymer; thermal degradation

# **INTRODUCTION**

The major driving force today in electronic products is high performance, low cost, and miniaturization. Multichip modules (MCM) technology could be the solution.<sup>1</sup> MCM-D deposition, one of the MCM technologies, can provide the highest performance, wiring density, and silicon efficiency. However, the cost effectiveness of MCM-D technology compared with alternative MCM approaches, such as lamination (MCM-L) and cofired ceramic (MCM-C), greatly prohibits its widespread application. One of the effective approaches to overcome this MCM-D limitation is to expand the exist processing scale of  $300 \times 300$  mm<sup>2</sup> (corresponding to  $12 \times 12$  in<sup>2</sup>) to  $600 \times 600$  mm<sup>2</sup> (corresponding to  $24 \times 24$  in<sup>2</sup>) of large processing and reuse the costly pallet to achieve cost reduction.<sup>2,3</sup>

The new MCM-D design technique is to develop a fully operational line for the process of 600  $\times$  600 mm<sup>2</sup> carrier. During this process, several silicon tiles 200  $\times$  200 mm<sup>2</sup> (corresponding to 8  $\times$  8 in<sup>2</sup>) are to be adhered to a large reusable pallet (24  $\times$  24 in<sup>2</sup>), followed by micromechanical

Correspondence to: C. P. Wong (cp.wong@mse.gatech.edu). Contract grant sponsor: DARPA MCM-D.

Journal of Applied Polymer Science, Vol. 73, 997–1005 (1999) © 1999 John Wiley & Sons, Inc. CCC 0021-8995/99/060997-09

fabrication, thin film passivation deposition, and subsequent detachment of the silicon tiles from the pallet. The total weight of each tile-to-pallet assembly is restricted to 4.5 kg (10 lbs), and the total thickness should be less than 6.25 mm. To achieve this design, a unique high-temperature adhesive is needed that keeps thermally stable at processing temperature (working temperature in excess of 350-400°C) and then thermally degrades at a slightly higher temperature (reworkable temperature) for silicon tiles detachment from the pallet.

Currently, polyimide is an excellent high-temperature adhesive widely used in the microelectronics industry.<sup>4</sup> However, its high modulus and high curing temperature cannot meet the special requirements of MCM-D processing, during which a reworkable adhesive is required to remove the silicon wafers from the glass pallet substrate. An effective way to address this reworkability requirement is to select a specific polyimide–amide resin as a base polymeric system and incorporate special thermally degradable links into the main chain in an attempt to make the copolymeric matrix thermally stable at 350°C, yet thermally degradative, at 400°C for tile detachment.<sup>5</sup>

Pyrolysis mass spectrometry (MS) has been used to study the properties and degradation mechanisms of many common polymeric systems.<sup>6,7</sup> MS, in conjunction with other analytical techniques, including IR spectrometry and thermal analysis, also has been used to study the thermal properties of these polymers.<sup>8</sup>

In this study, modulated differential scanning calorimetry (MDSC), thermogravimetric analysis (TGA), Fourier transform infrared (FTIR) and pyrolysis MS were used to characterize the thermal stability difference between our formulated reworkable PIAE copolymer adhesives and commercial PIA adhesives by comparing their outgassing and residual products composition at specific temperatures. A reworkability mechanism of the PIAE adhesives is also proposed.

# **EXPERIMENTAL**

# Chemical Ingredients of Reworkable High-Temperature Adhesives

The chemical formulation of the adhesive studied in this project is based on an available commercial adhesive (polyimide-amide, abbreviated as PIA), which is to be modified by incorporating epoxy, dianhydride, and catalyst. The epoxy resin is 3,4-epoxy cyclohexyl methyl-3,4-epoxy cyclohexyl carboxylate provided by Union Carbide under the trade name ERL-4221E and used as received. The dianhydride is hexahydro-4-methylphthalic anhydride (HMPA) purchased from Aldrich Chemical Company, Inc., and used as received. The catalyst is glycerol. The mixture was stored at  $-40^{\circ}$ C when it was not immediately used after mixing.

## **Preparation of Adhesive Formulation**

A quantity of anhydride was mixed with epoxy resin by mole ratio of 1/1 and stirred until a homogeneous solution was formed. Catalyst was added into the mixture and stirred for 15 min (The mixture containing the above-mentioned three components was identified as EP). After that, an amount of the above mixed resin was further incorporated with the commercial polyimide-amide adhesive according to a 1 : 1 mixing ratio of EP to PIA. Prior to evaluation, the formulation was stored at  $-40^{\circ}$ C for extending their shelf life. However, this stored sample must be equilibrated to ambient temperature (25°C) prior to any using.

# **FTIR Measurement**

Commercially available PIA and our developed PIAE copolymer solutions were used to prepare thin films for FTIR analysis (Nicolet Model 250). All thin film samples were prepared by spin-coating (Specialty Coating Systems, Inc. Model 6708D) adhesives on diced silicon chips  $(20 \times 20 \text{ mm}^2)$ , followed by curing in a convective oven under 150°C for 30 min and 250°C for 60 min at a 5°C/min heating rate, respectively. After FTIR analysis, all these samples were further exposed to 350°C for 60 min and then 400°C for 60 min. FTIR analysis was performed immediately after each thermal process.

## **MS Measurement**

Samples for solid-probe pyrolysis MS analysis were prepared by dispensing both adhesives into aluminum pans, followed by curing under the same process listed above. The MS data presented in this article were obtained with a VG 70-SE 2-sector magnetic mass spectrometer. The MS analyzer in this system is a solids probe with a



**Figure 1**  $T_g$  from the MDSC curve.

range of 4-1000 atomic mass unit (amu). Ionization was performed by 70 eV electron impact, and the ion source temperature was at 200°C.

Adhesive samples were heated from 25 to 400°C at a 2°C/s heating rate; and at 250, 350, and 400°C, temperature stages were isothermally remained for 2 min, respectively. At each temperature stage, the samples were bombarded using Xenon atoms of 8000 V energy (in a saddle field ion gun) under vacuum of  $10^{-7}$  Torr.

## **TGA Measurement**

Thermogravimetric scanning analysis was conducted using a thermogravimetric analysis (TGA) analyzer (TA Instruments, Model 2940). Sample preparation is the same as above. Thermal scanning was performed at a 10°C/min heating rate, with an air purge at 12 cc/min X-axis and 70 cc/min Y-axis flow rates. The residual weight percentage was recorded in an air atmosphere from 25 to 500°C.

#### **MDSC Measurement**

Glass transition temperature  $(T_g)$  was determined utilizing a MDSC analyzer (TA Instruments, Model 2920). Approximately 10 mg of each commercial PIA adhesive, EP, and reworkable PIAE adhesive was placed into a DSC cell and

cured with the same curing process as described.  $T_g$ 's of the cured samples were obtained by heating the samples at 5°C/min to specific temperatures, which were slightly higher than their respective glass transition temperatures.

#### **RESULTS AND DISCUSSION**

#### **MDSC** Analysis

MDSC is an effective method to identify whether a fully cured matrix is an alternating copolymer or a block copolymer. Modulated curves in Figure 1 show the  $T_g$  points of the reworkable PIAE, EP, and commercial PIA adhesives. The presence of a single  $T_g$  transition in the MDSC curve indicates that the PIAE adhesive is an alternating copolymer.

## **FTIR Analysis**

FTIR is an effective way to determine the uncertain chemical structure qualitatively.<sup>9</sup> Hoshino and coworkers<sup>8</sup> used FTIR, combined with TGA and GC–MS to characterize the thermogravimetric behavior of perfluropolyether. FTIR spectra results of our developed reworkable PIAE adhesives, after various thermal processing cycles, are shown in Figure 2. Strong methylene asymmetric and symmetric stretch absorption on cyclohexyl



**Figure 2** IR absorption of the developed PIAE adhesives exposed to different thermal processes: (a) curing temperature, (b) 350°C/60 min, and (c) 400°C/60 min.

ring appear at 2945 and 2854  $\text{cm}^{-1}$  for the cured sample, and these absorption bands become weak after the sample exposure to 350°C for 60 min. When the PIAE sample was further exposed to 400°C for 60 min, all these IR functional absorption bands vanish. Characteristic absorption bands at 1405, 1170, and 1100  $\text{cm}^{-1}$  are attributed to the typical symmetric carboxylate (C=O) stretch and C-O asymmetric vibration in C—C(=O)—O mode of cyclic anhydride groups. The results indicate that after the samples were exposed to 350°C for 60 min, the IR spectrum still displays a comparatively weak absorption at these regions; however, upon exposure to 400°C for 60 min, the IR absorption bands become extremely weak. Spectral variations confirm that the polyester blocks, which contain all the cyclohexyl groups, can fully and thermally degrade at 400°C, and a small amount of anhydride can exist in the matrix network until at least 350°C.

Compared with the PIAE adhesive, the FTIR spectra of commercial PIA adhesives (see Fig. 3) only illustrate a comparatively weak variation of absorption intensity of imide group at  $1770 \text{ cm}^{-1}$ . As the exposure temperature is enhanced, the intensity of the characteristic absorption band of imide carbonyl groups CO—NH at  $1770 \text{ cm}^{-1}$  increases a little bit.

Comparison of Figure 2 with Figure 3 indicates that the spectra of these two adhesives are identical after the samples were exposed to 400°C for 60 min. The major component of residual products of the reworkable adhesive is primarily carbon-rich polyimide–amide.

## Stepwise Low-Temperature MS and TGA Analysis

MS is widely applied for determining chemical composition. Dussel and coworkers<sup>6</sup> used pyrolysis field-ionization MS to identify characteristic fragments of several polyamides and proposed mechanisms for their degradation. Johnson evaluated the properties of polyimide films under various curing conditions.<sup>7</sup> In this study, stepwise pyrolysis MS was used as a way for identifying the outgassing products from the PIAE and commercial PIA adhesives. The samples were placed into a quartz tube in the direct-insertion solids probe. Samples were heated sequentially in the mass spectrometer ion source to 250, 350, and 400°C at a heating rate of 2°C/s and were held for 2 min at each temperature.

Mass spectral results of direct insertion probe experiments are shown in Figure 4. It is evident that the total ion current (TIC) is a function of time when the probe temperature was ramped from ambient temperature to 250, 350, and 400°C for a typical commercial PIA adhesive or a developed PIAE adhesive. The corresponding temperatures are shown in the lower part of the same graph. It can be observed that there are more outgassing products from the commercial PIA adhesive than from the developed PIAE adhesive under 250°C, but less within 350-400°C.

An attempt of direct measurement of mass weight loss during pyrolysis in MS analyzer is not



**Figure 3** FTIR absorption of commercial PIA adhesives exposed to different thermal processes: (a) curing temperature, (b) 350°C/60 min, and (c) 400°C/60 min.



**Figure 4** Thermogravimetric analysis on the reworkable PIAE and commercial PIA adhesives from 25 to 500°C at 10°C/min.

feasible since the measurement requires measuring a weight change in mass that is smaller than the precision of the available balance. TGA can be used as a complementary method for accurate weight loss evaluation. An estimation of weight loss percentage at each temperature point utilizing thermal scanning from 25 to 500°C is shown in Figure 5. At an initial thermal stage, below 250°C, that is, 200°C, the weight loss of commercial PIA adhesive is 0.52%, whereas the studied PIAE adhesive is only 0.21%. This result is identical to that of the TIC graph (Fig. 4) below 200°C, while it seems that there is a contradiction within 200-250°C. This is possibly caused by the variation of pyrolysed fragments.

Examination of mass spectra taken during the analysis provides the identification of the various PIA and PIAE segments as they are degraded and explains the possible reason of TIC curves variation. Figure 6 shows PIAE and PIA adhesives mass spectra taken under each of the three specified temperatures. In Fig. 6(a) and (b), the mass spectra at 250°C show that the evolution of water and NMP in 6(a) is less than that in 6(b), which is identical with the result drawn from Figure 5. The commercial PIA adhesive contains 90% of NMP and 10% polyimide–amide, while the developed PIAE adhesive only contains 45% NMP, 5% polyimide–amide, and 50% epoxy. So the amount of outgassing mainly containing NMP and  $H_2O$ 

(trapped in the crosslinking network or escaped from hydrocarbon thermal oxidation) from the PIA adhesive is much more than that from the PIAE adhesive at 250°C. The mass spectra in Figure 6(c) and (d) illustrate wider fragment ranges of ion abundance evolved from the PIAE adhesive, while a trace amount of water and NMP were evolved from the commercial PIA adhesive at 350°C. The mass spectrum at 400°C [see Fig. 6(e)] shows a severe breakdown of the PIAE adhesive, along with characteristic fragments of the polyimide-amide-epoxy copolymer structure appearing in the mass spectrum (see Table I). In regard to the commercial adhesive, only a trace of water comes from the sample. All the above results demonstrate that the commercial PIA adhesives can keep comparatively thermal stability at 400°C, whereas the reworkable PIAE adhesives will be severely thermal degraded at 400°C.

Major fragmentation of the developed PIAE adhesive, determined from the mass spectrum, is listed in Table I according to the mass units in Figure 7. These pyrolysis fragments identified during MS measurement are the radical fragments appeared at the backbone of polyimide– amide–epoxy copolymers.

## Curing Mechanism and Thermal Reworkability

The curing mechanism of PIAE adhesive that consists of epoxy, anhydride, catalyst, and polyim-



**Figure 5** Total mass spectrometer ion current for (a) reworkable PIAE adhesive and (b) commercial PIA adhesive. The sample temperature is ramped from ambient to 250, 350, and 400°C.



**Figure 6** Mass spectra taken during stepwise pyrolysis of studied and commercial adhesives: T = (a) 250, (c) 350, and (e) 400°C for studied adhesive; T = (b) 250, (d) 350, and (f) 400°C for commercial adhesive.



Table IPyrolysis Fragments of Studied ReworkableAdhesive  $(T = 400^{\circ}C)$ 

ide–amide has not been reported so far. However, similar work has been studied on a polyepoxide– anhydride–polyimide–amide system by C. J. Lee,<sup>10</sup> but there is no further explanation regarding thermal reworkability. Based on our reworkable PIAE adhesive system, we proposed the following possible mechanism (Scheme 1). The commercial polyimide–amide adhesive as received is an anhydride-ended amide acid monomers or oligomers dissolved in NMP with pH value of 5.3. First, the PIA mixture will be heated at 150°C for 30 min to remove most of the solvent, followed by raising its temperature to 250°C for 60 min in order to complete solvent removal and the conversion to polyimide. Generally, the imidization will start at 200°C and accomplish the polyimide con-



**Figure 7** Mass spectra of pyrolysis products for studied PIAE adhesives pyrolyzed at 400°C for 2.0 min.



version at 250°C for 60 min.<sup>1</sup> Regarding the PIAE system, since there is cycloaliphatic epoxy mixed in, it will definitely react with the carboxylic functionality on the ring-unclose o-carboxy-phthalamide. So a competition between imidization and esterification takes place inside the PIAE mixture. The carboxyl connected to the phthalamide has an equivalent reactivity toward the epoxy group, as does the anhydride. However, the anhydride has two carbonyl functionalities, whereas the o-carboxy-phthalamide only has one functionality. It is reasonable to calculate the requirement of epoxy for reaction with anhydride and o-carboxy-phthalamide, based on the equivalent epoxy-to-carboxylic acid ratio [see eq. (1) and (2) in Scheme 1]. It is necessary to have this ratio equal

to 1/1, not considering the amount of carboxy consumed for conversion to phthalimid, in order to obtain void-free polyimide-amide-epoxy thermoset products. The rationale behind this requirement is that the overloading of anhydride will be caused by the reaction between epoxy and o-carboxy-phthalamide since the equivalent of cycloaliphatic epoxy and anhydride formulated in the PIAE system is 1/1. That means the polyimide-amide-epoxy copolymer used in the process of this project is prepared by using a molar deficient of cyclic aliphatic epoxy resin compared stoichiometricaly with that of carboxylic acid in ocarboxy-phthalamide and anhydride. So, the overloading anhydride will be hydrolyzed in the trace water generated from hydrocarbon oxidation and accelerate the polyester complete degradation within 350–400°C.

## **CONCLUSION**

The experiments reported here have demonstrated the use of FTIR and solid probe pyrolysis-MS techniques to differentiate commercial polyimide amide adhesive and developed PIAE reworkable adhesives under different thermal processing conditions. Residual solvent and volatile polymerization products were effectively measured by pyrolysis MS at working (350°C) and thermally degradable temperatures (400°C). Residues from left in the adhesive after specified thermal processing were reasonably detected by FTIR. TGA results suggest a compatible explanation. All results illustrate that the reworkability of the studied PIAE adhesive is due to thermal degradation of polyester functional group of developed PIAE.

The support from DARPA MCM-D consortium is greatly appreciated.

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