Use of Compliant Adhesives in the Large Area Processing of MCM-D Substrates

Jiali Wu, Randy T. Pike, and C. P. Wong, *Fellow, IEEE*

***Abstract*— Large area substrate processing is a key solution for improving the productivity of multichip module deposition (MCM-D) technology. This project is focused on high temperature polymeric adhesives for attachment of silicon tiles to suitable pallets to facilitate large area film processing of MCM structures. Current polymeric high temperature adhesives are predominately polyimide-based that are not reworkable, which places an obstacle to remove the coated substrates and to reuse the high cost pallets. However, an approach will be presented in this paper to address this demand by introducing thermally cleavable links in the thermoset polyimide-amide resin. A series of novel reworkable high temperature (in excess of 350–400 °C) adhesives have been developed, that can meet the requirements of adhesion, viscosity, thermal stability, and reworkability of the MCM-D production. Furthermore, scanning electron microscopy (SEM) microstructure images are presented for intuitive reworkability analysis.**

***Index Terms*— Adhesion, multichip module deposition (MCM-D), polyimide-amide-epoxy, reworkability, thermal stability, thermally cleavable links.**

I. Introduction

THE trend toward high performance and miniaturizing electronic packaging drives the development of multichip module deposition (MCM-D) technology [1]–[3]. However, the high cost production limits the widespread use of MCM-D technology. One approach to overcome this limitation is to expand the existing scale 300 × 300 mm^2 (corresponding to 12 × 12 in^2) of large processing and reuse the costly pallet to achieve cost reduction.

The new MCM-D design technique is to develop a fully operational line for the process of 600 × 600 mm^2 (corresponding to 24 × 24 in^2) carrier. During this process, several silicon tiles 200 × 200 mm^2 (corresponding to 8 × 8 in^2) are to be adhered to a large reusable pallet 600 × 600 mm^2 (corresponding to 24 × 24 in^2), followed by micromechanical 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 tile detachment from the pallet.

Polymeric adhesives are used extensively in present engineering applications in view of their attributes to allow a more uniform stress distribution and a more CTE mismatching material assembly [4]–[10]. Among them, epoxy resin and polyimide are two kinds of widely applied adhesives. Polyfunctional epoxies have labile processibility and can produce cured products having glass transition temperatures (Tg) in excess of 200 °C. However, even the most highly crosslinked epoxies are unable to tolerate the long-term service at temperature at or above 175 °C, owing to their molecular structure [11]. Although polyimide adhesives can resist high temperature environments in excess of 600 °C for short periods, intractability, solvent volatility and byproduct condensation greatly restrict their application. Anyway, neither of these two classic adhesives can meet the MCM-D requirements.

Lincoin Ying *et al*. [12] worked on thermoplastic polyimide-based reworkable die attaching adhesives for hybrid integrated circuit manufacturing. However, this type of thermoplastic material's working temperature window is only from 25 °C to 275 °C.

The thrust of this study is to develop a unique reworkable high temperature adhesive, which is not only reworkable at certain required temperature, but can also resist the severe corrosive environment during the MCM-D substrate fabrication and passivation process. An effective way to address this requirement is to incorporate a kind of cleavable block in the polymerized chains of the adhesive, which allows the thermoset network to be reworkable in a weak acid medium at high temperature [13], [14]. New adhesives have been developed in this study using this approach.

II. Experiment

A. Preparation of Reworkable High Temperature Adhesives

1) Chemical Ingredients of Reworkable High Temperature Adhesives: The chemical formulation studied in this project is based on available commercial adhesive (polyimide-amide, abbreviated as PIA), which is to be modified by incorporating epoxy resin, 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

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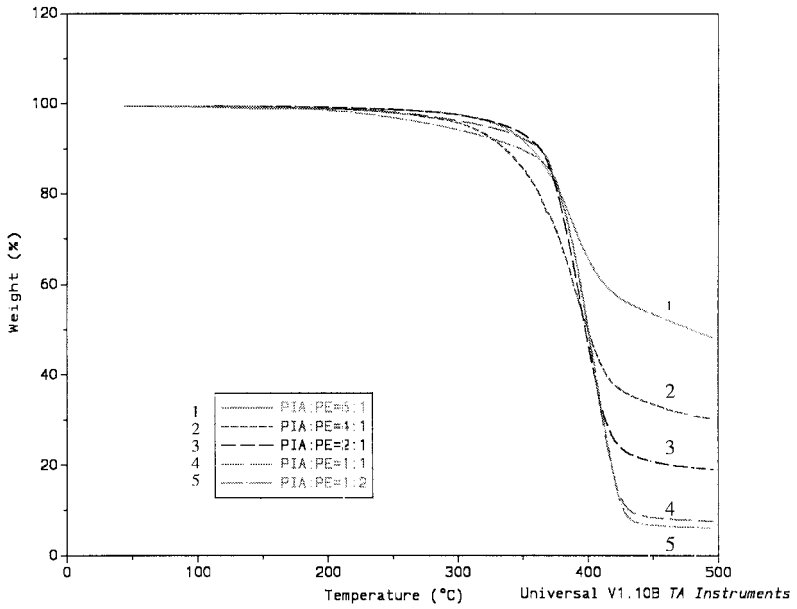

Fig. 1. TGA scan of thermally reworkable adhesives.

is glycerol. These mixtures were stored at −40 °C when they were not immediately used after mixing.

2) Preparation of Adhesive Formulation A quantity of anhydride was mixed with a predetermined amount of epoxy resin and stirred till a homogenous 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 PE). After that, an amount of the above mixed resin was further incorporated with the commercial polyimide-amide adhesive according to the prescribed mixing ratios of PE to PIA. Prior to evaluation, the formulations (the mixture was identified as PIAE) were stored at −40 °C for extending their pot life. However, these stored mixtures must be equilibrated to ambient temperature (25 °C) prior to use.

B. Characterizations

1) Sample Preparation: Samples for TGA analysis were prepared by dispensing liquid formulations into aluminum pans (38 mm diameter). Before curing, the samples were exposed to vacuum for 60 min under 28 mm Hg at 25 °C. Then these samples were transferred to a convection oven and heated to 150 °C at a thermal ramp of 5 °C/min, and held for 30 min. After that the curing temperature was increased to 250 °C at 5 °C/min, and held for 60 min.

2) Thermal Stability Characterization: Studies on thermal decomposition, isothermal stability at set temperatures and times of the series adhesive formulations were performed with a TGA (by TA Instruments, Model 2940). About a 30 mg sample was used for each test. A heating rate of 20 °C/min was applied from 25 °C to 500 °C in a air atmosphere.

3) Viscosity Measurement: A viscosity study was performed with a stress Rheometer (by TA Instruments, Model AR1000N). Measurements were conducted under a certain shear stress mode within shear rate from 1 to 1000 1/s at 25 °C. Regular viscosity variations were obtained on adhesives containing different ratios of PE to PIA.

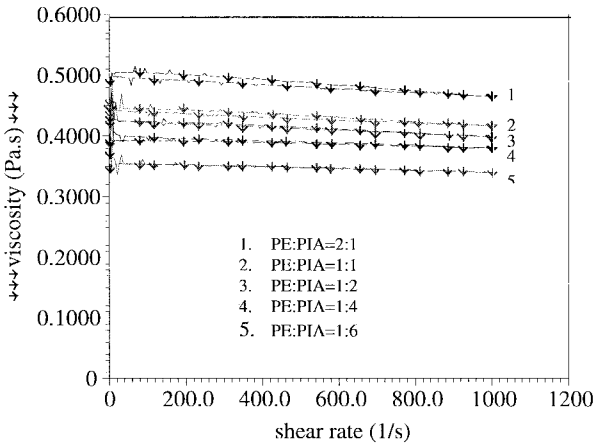

Fig. 2. Plot of viscosity versus shear rate for various PIA to PE ratios.

4) Chemical Compatibility Characterization: Si tiles were attached to glass substrates for wet chemical studies followed by the steps described in Section II-C. (3). Each sample was immersed into acetic acid, hydrochloric acid, acetone, isopropyl alcohol, sulfuric acid, phosphoric acid and nitric acid for 15 min at 25 °C, respectively. Then it was removed for the chemical compatibility test.

C. Reworkability Tests

1) Surface Treatment of Si Tiles and Boro-float Glass Substrates: Si titles and Boro-float glass substrates were degreased by boiling for 15 min in a strong base solution of NH_3H_2O:H_2O_2: DI (18 MΩ) water at 1:2:5. After rinsing with DI water, these silicon tiles and substrates were further degreased with ultrasonic cleaning in acetone and anhydrous alcohol for 5 min, respectively, then dried with compressed air. All the Si tiles and Boro-float glass substrates needed a UV/ozone treatment at 50 °C for 5 min before adhering Si tiles on top of Boro-float glass substrates.

TABLE I
RESULTS OF CHEMICAL COMPATIBILITY TEST

Sample	Acetic acid 100%	Hydrochloric acid 36-38%	Nitric acid 90%	Acetone	IPA	Sulfuric acid 96.4%	Phosphoric acid 85%
Commercial adhesive	No	No	Λ	No	No	No	No
Developed PIAE adhesives							
PIA:EP = 6:1	No	No	Δ	No	No	No	No
PIA:EP = 4:1	No	No	Δ	No	No	No	No
PIA:EP = 2:1	No	No	Λ	No	No	No	No
PIA:EP = 1:1	No	No	Δ	No	No	No	No
PIA:EP = 1:2	No	No	Δ	No	No	No	No

*No: no obvious change after immersion in the solution for 15min
Δ: dissolved the edge after immersion in the solution for 15min

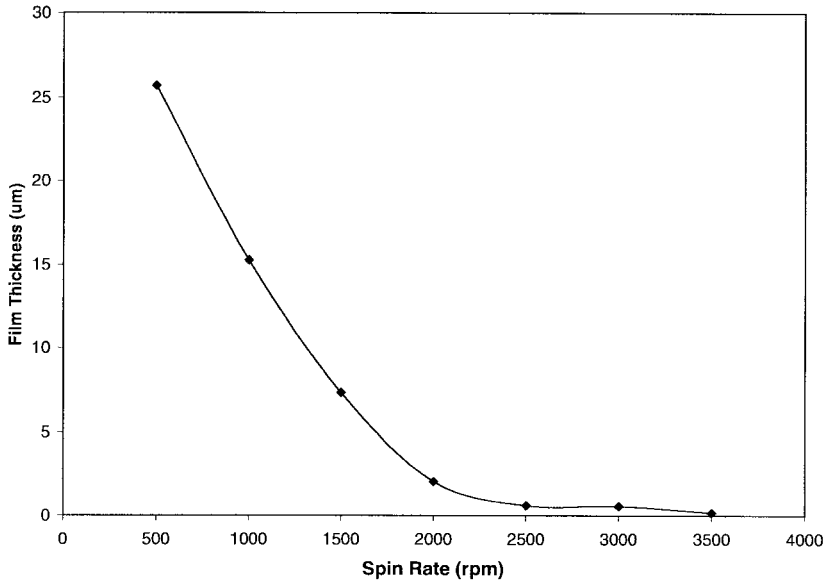

Fig. 3. Plot of adhesive thickness versus spin rate of developed adhesive with PIA:PE ratio of 1:1 (spin time = 30 s).

2) Film Thickness Control and Measurement: Uniform adhesive layers were coated on top of Boro-float glass substrates (pallets) by a spin coater (by Specialty Coating Systems, Inc. Model 6708D). Thickness of these layers was controlled by adjusting spin speed with respect to time. A Dektak Model 3030 Surface Profiler was used to measure the film thickness.

3) Si Tiles on Boro-float Glass Pallets Assembly: Following the adhesive coating, Si diced chips (tiles) of size 2×3 mm^2 were placed directly onto the top of the Boro-float glass substrates using PIAE as adhesives and a light pressure was applied onto the silicon chips to remove entrapped air. The assembled samples were then placed into a vacuum oven for 60 min at 28 mm Hg at 25 °C. Finally they were transferred to a convection oven and cured at 150 °C for 30 min, then 250 °C for 60 min.

4) Shear Strength Study of Cured Samples: Shear strength test was performed with an adhesion analyzer (by Royce Instruments System 552) at room temperature. Testing was conducted with a vertical offset of 49 μm (0.002 in). Shear strength results are listed in Fig. 5.

5) Shear Strength Study on Samples Exposed to Working Temperature (350 °C for 1 h) and Reworkable Temperature (400 °C for 1 h): After step 3, all these samples were continued to expose to 350 °C and 400 °C for an hour, respectively. Shear strength measurements were conducted as described in step 4. Results are listed in Fig. 4.

D. Microstructure Analysis on Reworkability

Microstructural variations of the cross-section of the samples exposed to different thermal processes were observed with a scanning electrion microscope (SEM) (by Hitachi Model S-800). SEM samples were prepared the same way as those prepared for reworkability testing. Small strips were diced across the Si/glass interface using a diamond saw, and mounted on SEM sample stubs. Finally the samples were polished, cleaned, and gold sputtered for 5 min before SEM analysis. Cross section microstructures of commercial PIA and developed PIAE adhesives are shown in Fig. 7.

III. RESULTS AND DISCUSSION

A. Evaluation of Thermal Stability

Thermal stability is critical to adhesives for MCM-D applications. Thermal stability analysis by TGA was performed on these samples, and the results are shown in Fig. 1. Weight losses corresponding to different ratios of PIA to PE show a

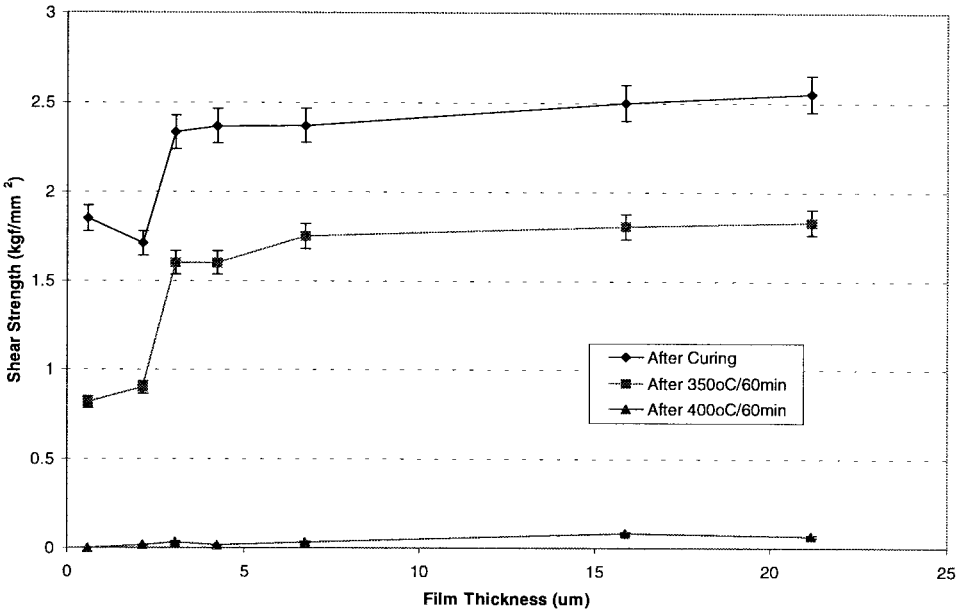

Fig. 4. Shear strength versus film thickness for adhesives (PIA:PE = 1:1) exposure to various thermal process.

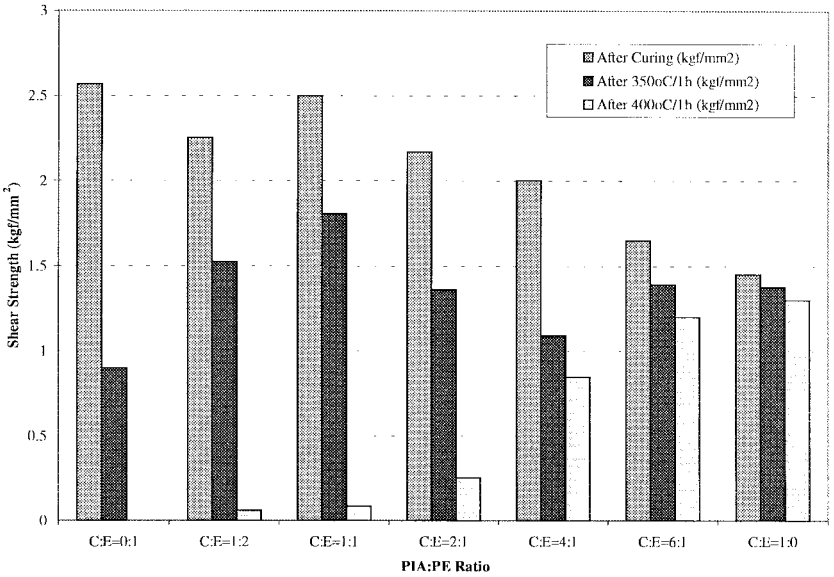

Fig. 5. Shear strength versus PIA to PE ratio for adhesives exposure to various thermal processes.

regular variation. It is determined that as the ratio increases, the weight loss decreases. The decomposition temperatures in air for different ratio adhesives, except for the original commercial one, are approximately 350 °C. Dramatic weight loss takes place within the temperature range of 350 °C to 400 °C due to thermal degradation of the ester group. We deduce that as the adhesives fill in a tiny gap (5–30 μm) between Si tiles and glass substrate, the thermal oxidative stability is enhanced compared to that performed under atmosphere. So the significant weight loss variation temperature (onset point) of bulk adhesives will shift a little bit to the higher temperature region.

B. Viscosity Improvement

Aside from intractability, high viscosity limits application of the polyimide-amide adhesives. To lower their viscosities, a high percentage of solvent, such as NMP (N-Methyl-pyrrolidinone) and DMAC (N,N-Dimethylacetamide), was used as a diluent. A drawback associated with solvent addition is void formation inside the material. In this study, the addition of an extremely low viscosity epoxy resin results in ease of processing and enhanced adhesion. Fig. 2 shows the viscosity curves change with the shear rates for five different ratio of PAI to PIAE materials at 25 °C. Within the 1–1000 1/s shear rate range, all materials show Newtonian behavior.

C. Chemical Compatibility Characterization

Chemical compatibility studies focused on acidic and organic solvents used in MCM-D fabrication. Wet chemical studies indicate that the studied adhesives show excellent resistance to acetic acid, hydrochloric acid, acetone, iso-

propyl alcohol, sulfuric acid and phosphoric acid. However, all interfacial modified adhesives show loss of adhesion upon immersion in 90% nitric acid. Detail results are listed in Table 1.

D. Film Thickness Control and Relation of Shear Strength versus Film Thickness

Using spin coater to dispense adhesives on Boro-float glass substrates is a easy way to get uniform thin films. Through adjusting spin rate and time, different desirable thickness of adhesive layer can be obtained. Relation between thickness of adhesive film and spin rate of PIAE with PIA to PE ratio of 1:1 is illustrated in Fig. 3. Shear strength as a function of the adhesive film thickness varies with thermal loading processes. Fig. 4 shows the relation between shear strength and film thickness after samples (PIA:EP = 1:1) were exposed to different thermal processes. Results indicate that when the adhesive film is thicker than a certain thickness, shear strength remains almost unchanged with variation of adhesive layer thickness. A comparison of shear strength after various thermal loading for a specific thickness, such as 15 μm, reveals that the shear stress changes from 2.45 kgf/mm^2 after curing to 1.78 kgf/mm^2 after exposure to working temperature of 350 °C for 1 h, and then reaches almost zero after exposure to reworkable temperature of 400 °C for 1 h. In addition, adhesive cohesion reduction always results in shear delamination, so an over-thick adhesive layer will inversely lead to weaker shear strength.

E. Shear Strength versus PIA to PE Ratios

Since adhesion strength of PE is much higher than PIA, shear test results of mixtures involved various PIA to PE ratios show an interesting variation after samples being exposed to different thermal processes. Fig. 5 shows the relation of shear strength and PIA/PE ratio combined with different thermal processes (adhesive film thicknesses of all the samples are approximately 15 μm). Samples' shear strength after thermal cuing decreases with PIA/PE ratio increasing. This is mainly due to the high adhesion strength of PE. While shear strength of samples after exposure to 350 °C for 1 h, initially increases with the PIA/PE ratios increasing, then decreases a little bit. This illustrates a combination contribution of both polyimide-amide and epoxy to the adhesion strength of an adhesive mixture. Although part of the epoxy resin is thermally degraded (further analysis will be presented in a later paper), the remaining part still plays a major role of adhesion strength. However, after samples exposure to 400 °C for 1 h, the shear strength increases with the increase of PIA/PE ratios because polyimide can endure higher temperature than epoxy. In addition, as the temperature increases, thermal mismatch between adhesives and tile or pallet becomes greater due to the difference in thermal expansion coefficient of adhesive and silicon or glass. This is another reason for adhesion reduction. Subsequently, this chart can be used to select the exact PIA/PE ratio of adhesives to meet specific application requirements.

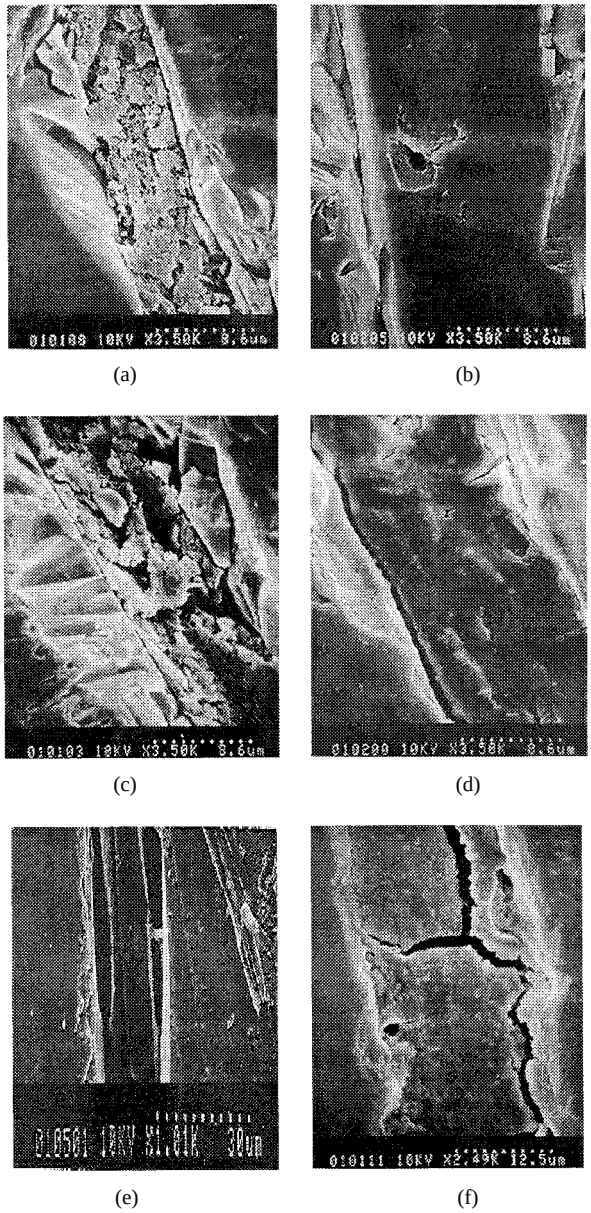

Fig. 6. SEM microstructure cross section analysis. (a), (c), (e) are the developed PIAE adhesives (PIA:PE = 1:1) exposed to curing temperature, 350 °C/1 h, and 400 °C/1 h, respectively. (b), (d), (f) are the commercial PIA adhesives exposed to curing temperature, 350 °C/1 h, and 400 °C/1 h, respectively.

F. Microstructure Analysis on Reworkability

SEM is an effective technique for microstructure analysis. Fig. 6 reveals a cross-sectional SEM photomicrographs of the modified PIAE (PIA:PE = 1:1) and commercial PIA adhesives after exposure to different thermal processes. A photomicrograph (a) of modified PIAE adhesive developed after curing displays a heterogeneous structure. This may be dependent upon the characteristic copolymer structure, i.e., polyimide-amide-epoxy block copolymer. Conversely, commercial adhesive (b) displays a homogeneous structure. Both interfaces show excellent adhesion. SEM photomicrographs of (c) and (d) display cross-sectional structures of the two adhesives after exposure to 350 °C for 1 h. The microcavities in modified PIAE adhesive (c) become larger, this possibly due

to thermal cleavage or oxidation of ester group. Graphs (e) and (f) display morphological variation of adhesives after exposure to 400 °C for 1 h. Severe delamination takes place at the interfaces between modified PIAE adhesives and glass/silicon (e), due to complete degradation of epoxy resin matrix and oxidation of both polyimide and epoxy resins. This is the basis of thermal reworkability. Although SEM analysis of the polyimide-amide adhesive reveals severe cracks occurring inside the materials due to CTE mismatch and high temperature oxidation, the adhesion at the interface is still maintained. These cross-sectional photomicrographs correlated well with the adhesion results.

IV. Conclusion

Reworkable high temperature (350–400 °C) adhesives are uniquely suited for MCM-D fabrication. Polymeric copolymers of PIA and PE appear to be a simple method to meet various temperature requirements. The new adhesives presented in this paper provide low viscosity, good thermal stability, high shear strength at working temperature (350–400 °C), yet they are rapidly reworkable after exposure to slightly higher rework temperature for 1 hour. These properties ideally meet the requirements of large scale MCM-D technology. In addition, this research also addresses possible adhesive materials for other potential microelectronic assembly applications [15].

References

[1] C. P. Wong, Ed., *Polymers for Electronic and Photonic Applications*. San Diego, CA: Academic, 1993.
[2] G. L. Van and P. Ludlow, "MCM-D Consortium," in *Proc. 1995 Int. Conf. Multichip Modules*, SPIE, 1995, vol. 2, pp. 249–252.
[3] MCM-D Consortium World-wide Web page: http://eto.sysplan.com/Eto/El-Packaging/Projects/Trp/mcm-d.html.
[4] P. M. Hergenrother, "High-temperature adhesives," *Chemtech*, vol. 14, pp. 496–502, 1984.
[5] S. J. Shaw and A. J. Kinloch, " High-temperature adhesives," in *Proc. Int. Adhesion Conf.*, 1984, pp. 3.1–3.4.
[6] S. J. Shaw, "Adhesives in demanding application," *Polym. Int.*, vol. 41, pp. 193–207, 1996.
[7] S. Tamai and M. Ohta, "Polyimide and high-temperature adhesive thereof," U.S. Patent 4 931 531, 1990.
[8] T. K. Dougherty, "Low temperature vulcanizing carborane siloxane adhesive," U.S. Patent 5 290 897, 1994.
[9] H. Oikawa and M. Ohta, "High-temperature adhesive polyimide from 2,6-bis (3-aminophenoxy) pyridine," U.S. Patent 4 797 466, 1989.
[10] M. R. Bowditch and S. J. Shaw, "Adhesive bonding for high performance materials," *Adv. Perform. Mater.*, vol. 33-4, pp. 324–342, 1996.
[11] K.-M. Chen, T.-H. Wang, and J.-S. King, "Effect of imidizaton temperature on properties of polyimide films," *J. Appl. Polymer Sci.*, vol. 48, pp. 291–297, 1993.
[12] L. Ying, "A reworkable high reliability thermoplastic die attach adhesive," in *Proc. Int. Symp. Microelectron.*, 1986, pp. 621–631.
[13] S. L. Buchwalter and L. L. Kosbar, "Cleavable epoxy resins: Design for disassembly of a thermoset," *J. Polym. Sci., A: Polym Chem.*, vol. 34, pp. 249–260, 1996.
[14] A. Afzali-Ardakani, S. L. Buchwalter, J. D. Gelorme, L. L. Kosbar, B. H. Newman, and F. L. Pompeo, "Cleavable diepoxide for removable epoxy compositions," U.S. Patent 5 560 934, 1996.
[15] C. P. Wong, "Novel high temperature adhesives," U.S. patent pending.

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