International Research Journal of Advanced Engineering and Science
ISSN (Online): 2455-9024

Auger Electron Spectroscopic Analysis of Filler Densification-Induced Interfacial Fracture in Polymer Particulate Composite System

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***Abstract*—** *Component failure due to the interfacial adhesion loss is a serious concern in advanced semiconductor packages. Herein, we report the systematic failure analysis performed on a system where one component detaches from the assembly due to the adhesion loss between the base material and the glue. Surface analysis of the fractured surface via scanning electron microscopy – energy dispersive X-ray spectroscopy (SEM-EDS) elemental mapping and Auger electron spectroscopy (AES) revealed that the component failure is due to the densification of the filler in the epoxy-based polymer particulate adhesive. AES depth profiling indicate softening of the base material surface during thermal treatment and/or the mutual solubility with the glue causing the localization of $CaSiO_3$ at the interface. The densification resulted in the creation of an epoxy-rich meta-stable zone and a filler-rich layer, which reduces the resistance of the composite interface to mechanical stress. The metastable layer becomes the fracture plane resulting in the failure observed in the system.*

Keywords *Auger electron spectroscopy, adhesion, interface, filler, epoxy.*

I. Introduction

The creation of interfaces between two materials is central to many industrial applications such as in the microelectronics, automotive and aerospace industries. The adhesive joint formation and its integrity determine the reliability of the resulting product [1].

Dispersed metallic or non-metallic particles in organic or inorganic matrices constitutes particulate polymer composites (PPCs) [2], which are important materials used in adhesion science and engineering. The high stiffness, strength and glass transition temperature of thermosets make them ideal materials for PPC, as compared with thermoplastics [3]. Thermosets of epoxy-based polymers are used for structural composites due to their relatively lower cost and ease in processing. However, the relative brittleness of thermosets results in structural damage due to the poor crack growth resistance [4]. The incorporation of secondary phases, as filling polymers with particles of different size-scale, aspect ratio, stiffness, and filler-matrix interfacial strength could improve the PPCs tolerance to thermomechanical damage [5].

Herein, we report the systematic analysis of the observed component failure due to the glue-to-base material adhesion loss. Surface analysis via SEM-EDS and AES revealed the filler densification creating an epoxy-rich fracture plane resulting in the component failure.

II. Experimental Details

Component assembly was performed using optimized parameters established using elaborate design of experiment (DOE) that is outside the scope of this report. Two surfaces were attached using a non-conductive glue (NCG) as shown in Fig. 1. Detachment of the two surfaces was observed in several components, wherein the fracture was observed along the base material and glue region. A systematic failure analysis was conducted using Philips XL30 scanning electron microscopy - energy dispersive X-ray spectroscopy (SEM-EDS) elemental mapping and JEOL JAMP-9500F Field Emission Auger Microprobe Auger electron spectroscopy (AES).

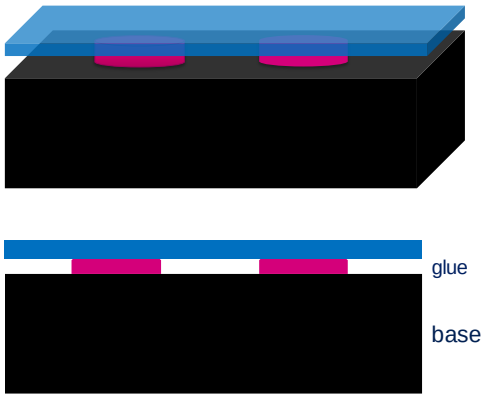

Fig. 1. Schematic representation of the attachment of two surfaces using epoxy glue.

III. Results and Discussion

The component failure due to the adhesion loss along the glue and base material region causes a serious concern on the functionality of the assembly. A systematic failure analysis was performed to understand the failure mechanism, and to establish a corrective action to prevent the failure from recurring. The material components of the glue and the base material were evaluated using their material safety data sheet (MSDS). Using the unique numerical identifier assigned by the Chemical Abstracts Service (CAS), the structures of the components were summarized in Fig. 2. These components were tabulated in an attempt to identify a distinctive marker representative of the material that will guide the analysis.

Ian Harvey Arellano and Dexter delos Santos, Auger Electron Spectroscopic Analysis of Filler Densification-Induced Interfacial Fracture in Polymer Particulate Composite System) *International Research Journal of Advanced Engineering and Science*, Volume 4, Issue 2, pp. 421-423, 2019.

International Research Journal of Advanced Engineering and Science
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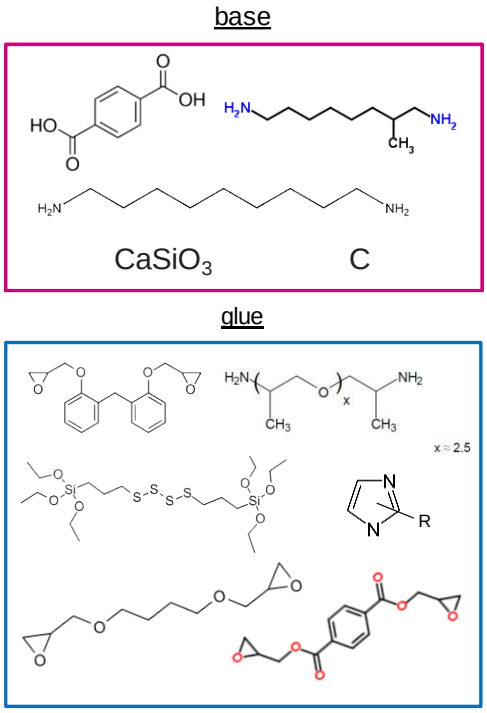

Fig. 2. Chemical structures of the glue and base material components.

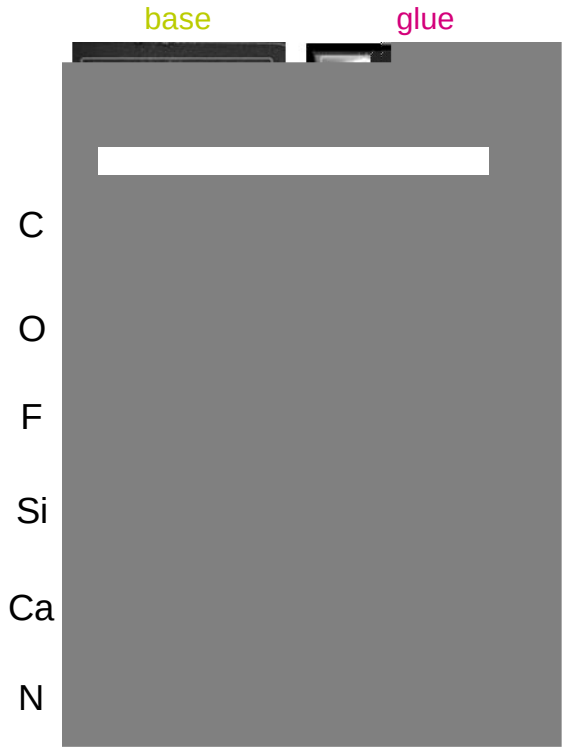

Fig. 3. Elemental mapping of the detached surface on the base material side (left) and the glue side (right).

Based on the document review, the base material is a PPC comprising of Wollastonite ($CaSiO_3$)-filled polyamide pre-formed material. The glue material contains epoxy backbone with amine crosslinkers, and polysulfide and polysiloxane moieties.

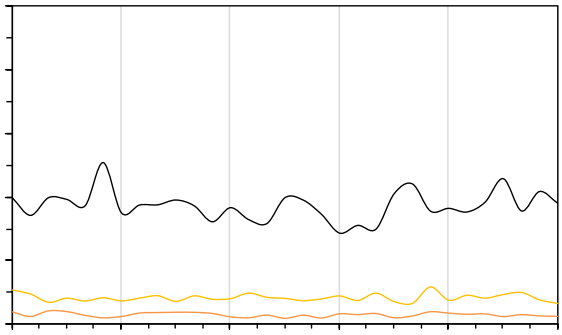

Fig. 4. AES depth profile of the base material surface. Inset: SEM micrograph of the analyzed surface.

Fig. 5. AES depth profile of the glue surface. Inset: SEM micrograph of the analyzed surface.

Elemental mapping (Fig. 3) generated using SEM-EDS are consistent with the material composition. Interestingly, the proprietary component of the glue contains fluoroalkyl substituents, making it a distinctive feature of the glue material. Hence, the presence of F is an indication of the presence of the glue material. In contrast, Ca is the only component that selectively identifies the presence of the cap material.

To better understand the failure mechanism, AES analysis was performed on the fractured surface, both in the glue surface and the base material surface. AES was chosen because of the surface sensitivity where about 1 nm penetration depth can be accessed during analysis. Depth profiling was achieved via progressive surface etching, wherein a 50 nm depth was accessed for the base material and a 25 nm depth was evaluated for the glue surface.

Results from the base material at the fracture plane suggest homogeneous composition within the 50 nm surface slab (Fig. 4). More importantly, these results indicate that the fracture plane is within the base material layer.

AES results from the glue surface (Fig. 5) indicate remnants of the base material. Elemental depth profile indicate that the fracture plane is mainly organic (5 nm) with Wollastonite ($CaSiO_3$)-rich layer (7 nm) present near the intercalation zone. A 5 nm intercalation zone exists 12 nm from the surface. This intercalation zone is responsible for the

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adhesion strength between the polymer of the base material and the glue. It is apparent from the results that the filler material is densified near the fracture plane, suggesting that this densification reduces the resistance of the interface to thermomechanical stress [6]. The softening of the cap surface during thermal treatment and/or the mutual solubility with the glue material causes the localization of $CaSiO_3$ at the interface. The higher filler content means that the epoxy content is lower, and hence less material that acts as dispersing medium. In addition, the filler-to-filler contact is higher resulting in weaker resistance to mechanical stress [7-8].

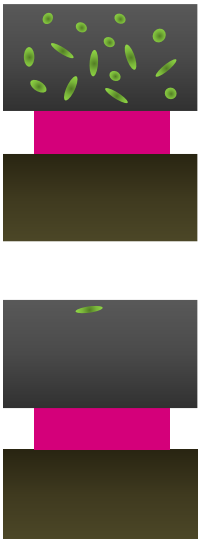

Fig. 6. Proposed mechanism of the filler-densification induced fracture.

The failure mechanism deduced from the results is shown in Fig. 6. In good assemblies, the filler is well dispersed in the epoxy matrix; hence, we speculate that PPC has higher resistance to thermomechanical stresses. The epoxy matrix acts as a cushion to prevent the fracture. However, in the case of the failing units, the densified filler creates a brittle layer sandwiched between the intercalation zone and the epoxy-rich glue matrix. The intercalation zone is expected to be strong because of the polymer (base material)-to-polymer (glue) compatible interaction. However, the interface of the brittle layer and the epoxy matrix (soft) is expected to be weak due to □ □ □ □ □ □ □ □ □ □ - environment. This weakness translated to fracture, and by extension component failure.

IV. Conclusion

Component failure due to the fracture along the base material and glue interface was systematically analyzed using SEM-EDS and AES analytical techniques. Results show a 7 nm filler-densified layer sandwiched between a 5 nm intercalation zone located 12 nm from the surface, and the 5 nm epoxy-rich layer within the glue material layer. The $CaSiO_3$-densified layer offered weaker resistance to thermomechanical stress resulting in the fracture, and eventual component failure.

Acknowledgment

The authors acknowledge the support of the failure analysis group and the DOST-ADMATEL in performing the material characterization.

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