Novel Silicone Sycar® Hybrid Adhesives for Harsh Fluid Resistance

Susan Krawiec, Elizabeth Walker, Robert Palmer, Chih-Min Cheng, and Kate Pearce, Emerson & Cuming, Billerica, MA, USA

Abstract
Sycar®-silicone hybrid materials are explored for applications where resistance to harsh environments, immersion in or contact with printing inks and other harsh fluids, is required. The primary application for such products is circuit assembly and protection materials for microelectronic devices such as ink jet printheads. The Sycar®-silicone hybrid technology has been proven effective for circuit protection in MEMS devices where increased reliability in harsh operating environments is required. Platform work showed that Sycar® can be crosslinked with vinyl polydimethylsiloxane through platinum catalyzed hydrosilylation chemistry. The resulting materials are flexible, in a wide range of moduli and adhere well to silicon, metals and engineering substrates. Furthermore, properties are retained when the materials are immersed in corrosive fluids such as inks. These hybrids have an advantage over conventionally crosslinked silicones, which have limited chemical resistance. It has been demonstrated that silicones can be used in small quantities to toughen fully crosslinked Sycar®, which is otherwise brittle. These hybrids are approaching epoxies for mechanical properties but maintain many desirable properties of silicones. From this platform work, three product types have been identified, based on Sycar®-polysiloxane. They are: hybrid gels, tough rigid elastomers, and high hardness, abrasion resistant materials which are unique to the silicone product family.

Introduction
The manufacture of jettable fluid delivery devices requires the precise assembly of various components. The structural integrity and reliability of the assembled components can be achieved through the use of molding materials, mechanical fasteners, and structural adhesives. Structural polymeric adhesives are most often the ideal choice because they mate the substrates to form a continuous surface. The bonding surfaces often consist of multi-layer silicon die, thin and thick wall engineered plastics, noble metals, and flexible substrates. Adhesives then become the barrier holding fluids within the device and also prevent the outside environmental contaminates from entering the device.

There are inherent disadvantages with polymeric adhesives. However, the use of a novel material called Sycar® is providing a solution to the challenges of harsh environment applications. Sycar®, an organosilicone, is a patented technology owned by National Starch & Chemical Company. Figure 1 shows the chemical structure of Sycar®. The organosilicone resin is self cross-linkable and, when used alone, forms a hard, rigid material that demonstrates desirable properties including low moisture uptake, good electrical properties and adhesion. A number of Sycar®-silicone hybrid materials have been developed by Emerson & Cuming for use in harsh environment applications requiring chemical resistance and reliable joint assembly over the life of the device. Data, gathered from recent experiments, indicates that Sycar®-silicone hybrid materials offer performance improvements in these environments and can be customized through a range of hardness (gels to rigid materials) and moduli, without compromising performance of chemical resistance and adhesion.

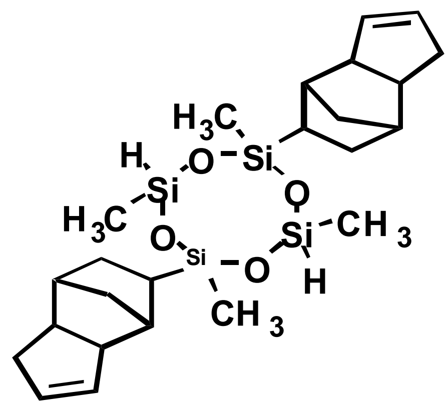

Figure 1. The chemical structure of Sycar®, an organosilicone.

Compatibility with Fluids
The Sycar®-silicone hybrid materials demonstrate good stability at high temperatures and excellent adhesive properties to a range of substrates, which they are able to retain after immersion in harsh fluids. These properties make them suitable for use as adhesives, sealants and encapsulants for circuit assembly protection where packages must operate in harsh environments.

Chemistry
Silicone resins are frequently used in electronic packages since they combine temperature stability with the flexibility needed to encapsulate electronic devices for their protection from high mechanical and thermal stresses. Silicones do not generally have good chemical resistance, thus fluorosilicones have been offered as an alternative. This paper focuses on the combinations of silicone resins in conjunction with Sycar® and presents possible products to yield tough hybrid materials with a range of hardness, moduli, chemical resistance, and adhesion. Figure 2 shows the range of hardness obtained by varying the loading of Sycar® with various silicone resins.

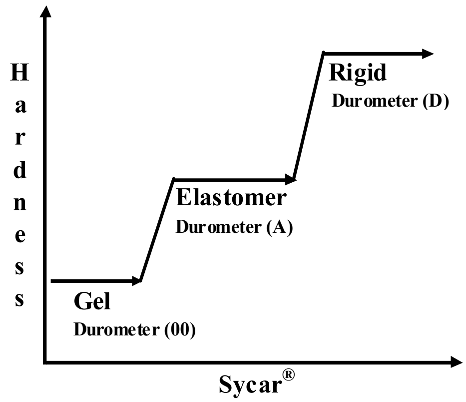

Figure 2. Sycar® level effect on hardness.

Chemical Resistance: Effect of Inks

Adhesion

In this section, a semi-rigid, non-fluorosilicone Sycar® hybrid adhesive is compared to traditional silicone and epoxy adhesive chemistries. Various substrates are examined by two different adhesion testing methods. The adhesives are denoted as follows:

Adhesive	E1	S1	S2
Chemistry	Epoxy	Silicone	Silicone hybrid
Flexible	Yes	Yes	No

The substrates are aluminum (Al), polycarbonate (PC), polyetherimide (PEI), polybutylene terephthalate (PBT). The chemical environments are none or dry, water and commercial dye and pigment aqueous inks. Adhesion tests often must be developed for a specific part design. Some standard tests can be used for screening various adhesives. One such test is a tensile lap shear test, which can be developed for a specific grade of plastic or metal. The overlapped part can be tested at various temperatures or before and after exposure to the harsh chemical environment. Figure 3 demonstrates that adhesive strength will vary with both the substrate and with the adhesive selected. Dry lap shear strength is compared on Al, PBT and PC substrates. Dry adhesive strength on aluminum is much greater than on the plastics for the epoxy and silicone adhesives tested.

If dissimilar substrates are to be bonded and a lap shear test is not practical an alternative test needs to be developed. For example, a plastic and glass substrate bond may always fail with the glass fracturing. In this /situation, the adhesive bond strength is not tested so an alternative test such as a shear strength push test could be developed. In this test, a shear force is applied to an edge of a substrate bond, such as a die bonded to plastic.

Changing to the die shear test from the lap shear test will change the failure mode of pull to peel force. This test may be better suited to studying the adhesive bond failure when the bonding assembly substrates are dissimilar. Figure 4 is a chart of silicon die adhesive strength to 3 plastics –PBT, PEI and PC before and after immersion in ink at 40°C for 7 days. Each bar is the die shear strength on one of the 3 substrates tested for each adhesive and environmental exposure. Adhesive strength most often decreases after chemical exposure. The exception is with silicone products. The adhesive strength varies very little with the environments which may be due to the hydrophobic properties of silicones.

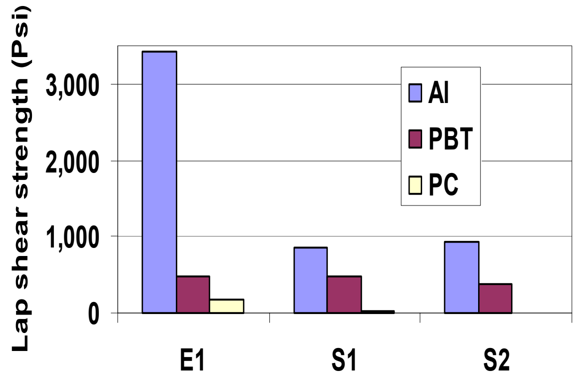

Figure 3. Adhesive tensile lap shear lap shear on aluminum and plastic substrates before harsh environment exposure.

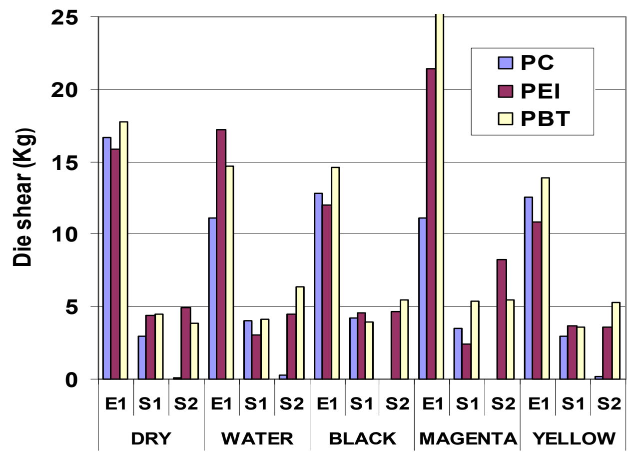

Figure 4. Die shear strength of 100 mm x 100 mm silicon die to plastic before and after exposure to chemical environments.

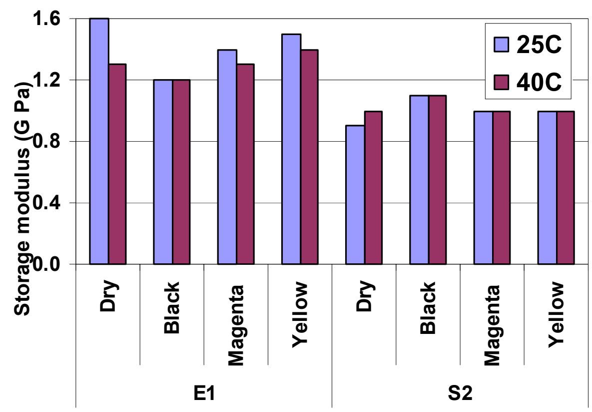

Figure 5. DMA storage modulus of adhesives before and after 1 week exposure to chemical environments at 25°C and 40°C fluids.

Bulk Properties

Dynamic mechanical analysis (DMA) is used to study the chemical resistance effect on physical properties with time and temperature for the epoxy and the silicone hybrid. Figure 5 shows that there is a greater change in storage modulus (E') after both 25°C and 40°C chemical exposure for the epoxy adhesive. However, the E' for the silicone hybrid is lower than the epoxy and it exhibits less change at both temperatures.

Conclusion

Often times the best test is to actually assemble a "real" part and observe performance over the anticipated useful life, while exposing the part to expected environmental hazards. The adhesive may fail or it may not adhere to one or both of the assembly substrates. In addition, the failure mode may be related to the chemical environment, mechanical or thermal stress, incomplete cure, or improper surface preparation. Most often a combination of tests is required to match the adhesive with the application and the ideal test is to build a complete part and monitor its performance over time.

In the water and ink environments the traditional silicone and the hybrid varied less than the epoxy adhesive studied. Yet the epoxy had higher strength on all substrates.

Future work in this area will focus on decreasing the cure time and temperature of these materials as well as improving overall adhesion performance.

Author Biography

Susan Krawiec is a Business Scientist in New Product Development of Emerson & Cuming Inc. Billerica MA. Currently, Susan supports the development of adhesives for the ink jet printer market. Susan holds BS in Chemistry from Merrimack College