FUEL AND MOISTURE RESISTANT ADHESIVES FOR AUTOMOTIVE ELECTRONICS & OTHER APPLICATIONS

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INTRODUCTION

Most of the polymer based adhesives will be affected by moisture, temperature and fuel and their combinations in various degrees, depending on the molecular and bulk structures of the adhesives. Most of the materials will normally be affected more by both water, fuel and moisture at higher temperatures than at the lower temperature. In fact, there are very few organic-based adhesives able to withstand a boiling fuel environment.

In this paper, we will discuss some of the developments and testing results of the adhesives that have been exposed to long term moisture and fuel exposure at elevated temperatures. An adhesive system capable of withstanding both of these extreme conditions has been successfully developed.

We have also examined the same family of materials with basically the same molecular structures but with varying degrees of flexibility. Some correlations between the glass transition temperature or its flexibility have been established.

FUEL RESISTANCE OF COMMON ADHESIVES

Most of the common adhesives such as silicone based, polyurethane-based, and acrylic-based adhesives are generally unsuitable for applications in a fuel exposure environment. This can be readily understood with the fact that fuel materials generally consist of both aliphatic and aromatic molecules which are generally good solvents, along with the fact that most of these materials have relatively low Tg, and thus large free-space within the polymer network for easy penetration by these types of solvents. Most of these adhesives will fail either in an adhesive or cohesive manner, depending on the type of adhesive, total duration, or temperature of exposures.

Thermoplastic materials are also unsuitable for these type of environments. In fact, some of the hot-melt adhesives can easily be de-bonded with simple water immersion when bonded to glass or smooth adherands.

Among the common class of adhesives, epoxy-based products generally performed satisfactorily under short term and low temperature exposures. However, all of the epoxy-based products that are commonly available on the market are unable to withstand fuel at high temperature(80C).

Table #1 is a compilation of some of the typical epoxy adhesives tested at various conditions of water and fuel exposures(1,2).

BOND STRENGTH AT ELEVATED TEMPERATURES

Bond strength of adhesives at high temperatures are generally dependent on the glass-transition temperatures of the materials. Most adhesives usually decrease in bond-strength when temperature is above the glass transition. Lower bond strengths are generally maintained at certain levels.

Figure #1 is an illustration of adhesives with glass transition temperatures of 135°C, 45°C, and 0°C with respect to the increase in temperatures.

The temperature dependence is correlated with the strength of the adhesives in general. The decrease in bond strength reflects in part the lowering of the modulus and the strength of materials under the stress/strain relationship.

The decrease in bond strength is sometimes beneficial for the purpose of reworkability in the case of electronic applications(3,4).

MOISTURE AND TEMPERATURE RESISTANCE

Humidity, along with temperature can be a substantial medium that affects the bond strength of a polymer-based adhesive. In the case of epoxy based adhesives, the effect is much more prominent in flexible materials than in higher strength versions.

There is also a substantial difference between epoxy adhesives that have been modified to achieve a more moisture and temperature resistant bond.

Figure #2 is a plot of bond strength as a function of humidity/temperature exposure over time. It is clear that for the same temperature, higher humidity produced a much faster decrease in bond strength, but the total decrease in bond strength depends on both temperature and relative humidity.

Adhesives with a glass transition of -25°C can only maintain bond strength of 15-20% of the original bond strength. With some minor modification of molecular structures, the decrease can be reduced to maintain 25-30% of the original bond strength. Many other approaches, such as second phase inclusion, coupling agents, etc. have been tried to improve the moisture resistance with out much success. Yet, efforts are being continued to achieve high moisture resistance, while maintaining good flexibility.

The two modified adhesives (epoxy #3 and #4) with glass transition temperatures of above 100°C were able to maintain at close to 100% of the bond strength rather than the typical decrease of 30-50% of bond strength that is commonly observed for typical epoxy adhesives(5,6,7).
However, it will be demonstrated that one of the modified epoxy adhesives showed much less high temperature gasoline resistance even though it showed outstanding moisture and high temperature resistance. Only one modified epoxy (#4) was able to withstand the "boiling" gasoline environment.

FUEL RESISTANCE AT LOW AND HIGH TEMPERATURE

The effort to improve the fuel resistance of epoxy adhesives was initiated by a project to bond an electronic fuel sensor to nickel plated metal. Many different materials have been tried with very little success when exposed at 80°C in pressurized conditions. This includes both the rigid, high strength and flexible adhesives.

Table #2 is the results of some of the materials that have been tested by ourselves and our customer.

It is clear that most epoxy adhesives, even with good strength, will fail in extended exposure of fuel and temperature. This renders them not usable for long term reliable use.

Epoxy adhesive #4 however, demonstrated close to 100% retention of bond strength and has been deemed suitable for fuel sensing application for automotive applications.

THERMAL CONDUCTIVITY OF DIFFERENT ADHESIVES

All of the adhesives being tested in the above applications have been filled, with more than 45% by volume, of alumina powders to impart high thermal conductivity. Thermal conductivity is extremely useful in the case of an electronic device assembly if the device generates some heat. The bond strength without fillers will be increased substantially (up to 6000 psi in lap-shear).

Thermal conductivity depends on the amount of filler and adhesive quality for any particular material. However, for the same epoxy adhesive, the thermal conductivity can be increased with the use of different fillers.

Figure #3 is an illustration of thermal conductivity that was achieved by AI Technology with the use of different types of materials, at 45-55% by volume of fillers.

FILM VS PASTE FORMAT

The fuel, moisture, and temperature resistant epoxy adhesive #4 can be made into both a film and paste format. The material that was used for this testing is a film adhesive.
The film adhesive in this case is self-supporting and can be stored at room temperature for more than 3 months, which is substantially more convenient than traditional film adhesives being used in the composite or electronic industries. The thickness is available from 1 mil to as thick as required.

The paste adhesives are available in both single component or two component formats, with very similar performances.

FUEL RESISTANT COATINGS

While the fuel resistant epoxy adhesive is useful for most applications, it is high strength and has a high modulus. Thus, when the adhesive is used in bonding adherands or components with drastically different thermal expansion coefficients than it's own, the induced stress can be quite substantial.

Figure #4 is an illustration on how the stress is induced on bonding silicon to silicon. The internal stress can be as high as 10,000 psi to 50,000 psi depending on the modulus of the adhesive being used.

In order to reduce the stress being stored between the adhesive and the adherands, the use of a low modulus adhesive is preferred. Figure #5 is an illustration of the use of a flexible, low stress adhesive for bonding the same silicon to silicon. The internal stress has been reduced to less than 300 psi.

While the use of a low stress adhesive is preferred for long term reliability application, these adhesives have been proven inadequate in withstanding fuel exposure at elevated temperatures. The moisture resistance is also insufficient. The used of the more resistant materials to cover the edges of the adhesive bondlines will be effective in constructing an assembly with both low stress and high moisture and fuel resistance.

Besides bonding components which are constantly exposed to fuel, it is also anticipated that for electronic devices used in under-hood conditions, a humidity and fuel resistant "conformal coating" can be an effective protective method.

CONCLUSIONS AND APPLICATIONS

Modified epoxies with both fuel and moisture resistance have been developed. They are able to withstand boiling gasoline and 100% humidity at 85°C without degredation in bond strength in both paste and film formats. These modified epoxies are typically high strength and thus closely matched thermal expansion adherands should be maintained. The epoxy system can be modified to have TCE of 15-60 ppm/^{O}C depending on lamination and fillers. It has been demonstrated that such adhesives are very effective at sealing against moisture to protect microelectronics in commercial use.

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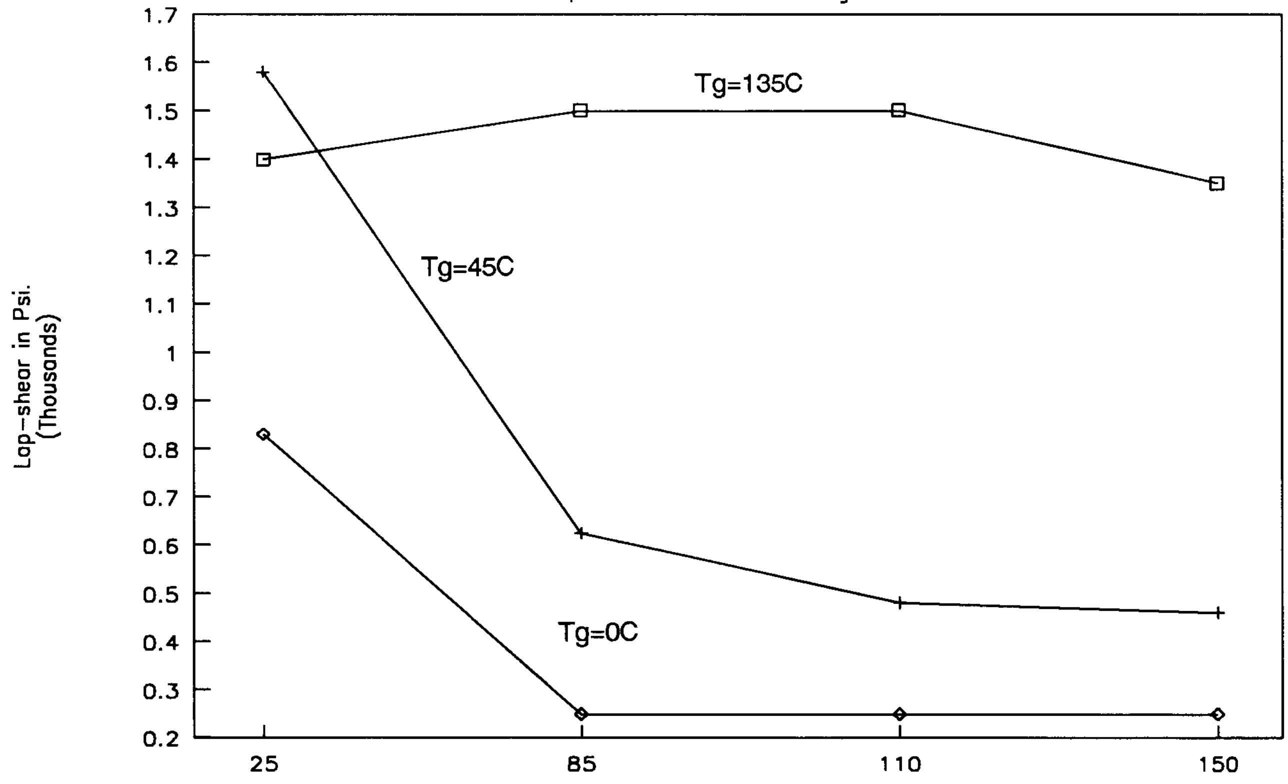

FIGURE #1: Bond Strength vs. Temp.
of Epoxies With Different Tg.

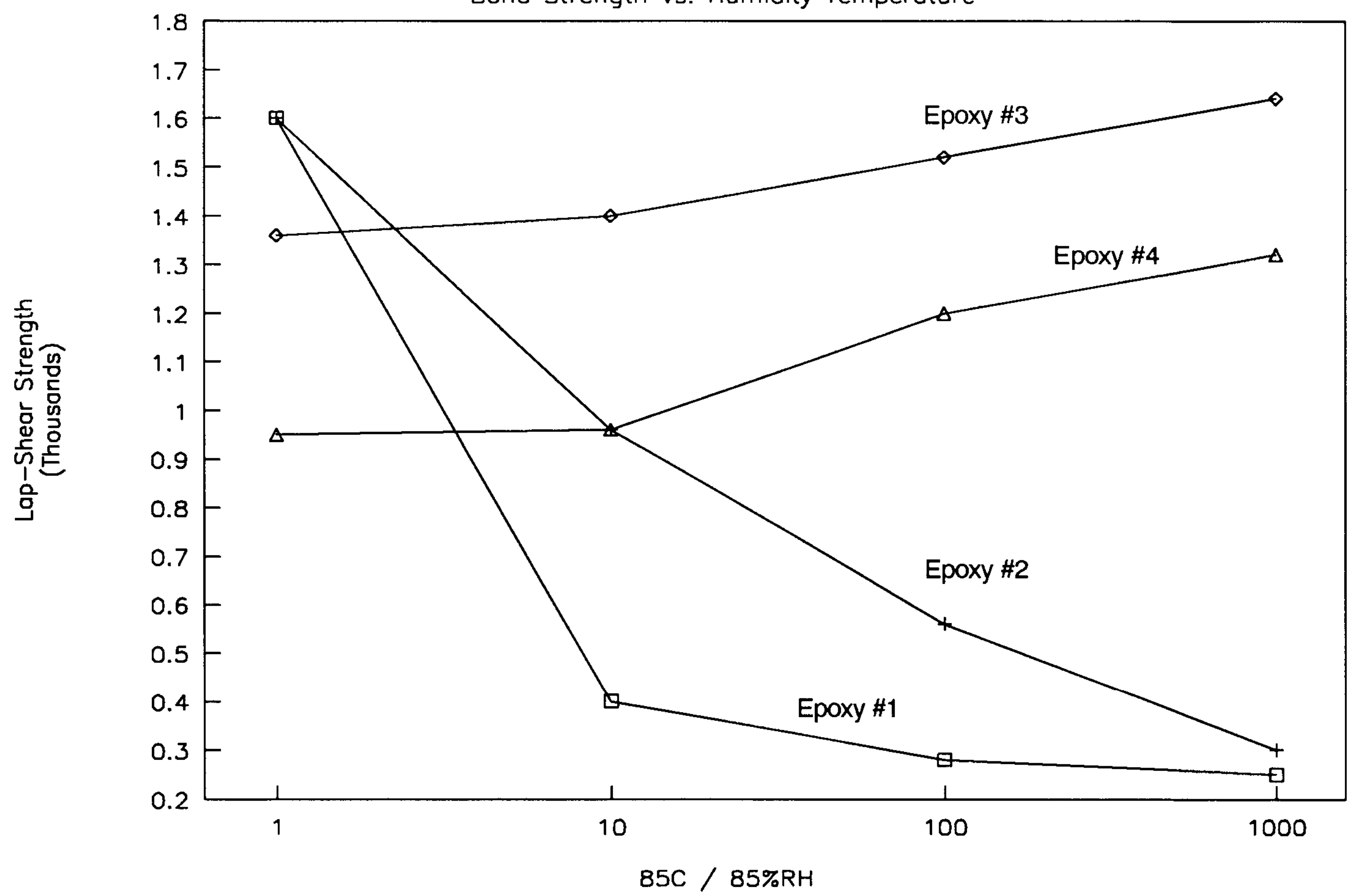
FIGURE #2
Bond Strength vs. Humidity Temperature
Lap–Shear Strength
(Thousands)
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
1
10
100
1000
85C / 85%RH
Epoxy #3
Epoxy #4
Epoxy #2
Epoxy #1

Table #1: Effect of Moisture & Fuel on Bond Strength Retention

Medium	Exposure Condition	Bond Strength Retention (%)	
		DGEBA / DICY	DGEBA / Polymamide
Gasoline	30 days / 25°C	70	55
	30 days / 80°C	0	0
Ethanol / Gasoline (30/70 Mixture)	30 days / 25°C	65	50
	30 days / 80°C	0	0
85°C / 85% RH	1000 hours	30	10

Table #2: Effect of Moisture & Temperature on Bond Strength

Medium	Exposed Condition	Bond Strength Retention (%)			
		Epoxy #1, Tg=-25°C	Epoxy #2, Tg=-25°C	Epoxy #3, Tg=150°C	Epoxy #4, Tg=160°
Gasoline	30 days / 25°C	300 psi/20%	450 psi/30%	880psi/70%	1200 psi/ 100%
	80°C/Pressurized	0% after 24 hrs.	0% after 24 hrs.	20% after 7 days	90-100% after 30 days
Ethanol/ Gasoline (30/70 Mixture)	30 days / 25°C	300psi/20%	440psi/30%	900psi/70%	1200 psi/ 100%
	80°C/Pressurized	0% after 24 hrs.	0% after 24 hrs.	10% after 7 days	90-100% after 30 days