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Thank you for the opportunity to talk to you about sealing packages with polymer adhesives. The data contained in this report were mostly measured by an outside testing lab (ORS) although most of the pre-conditioning was performed in our laboratory. This is a continuous program and much more information will be published in the future.

Sincerely,

Richard J. Ross
President
RJR Polymers

AUTHOR
Richard J. Ross

The author is founder and President of R.J.R. Polymers, Inc. located in San Francisco, California. He is a graduate of Oberlin College in Ohio and holds an MBA in Marketing from Northwestern University, in Illinois.

Mr. Ross began his career as a polymer chemist in the Bonding Division of Union Carbide Corporation in 1955. In product development, his activities were mainly in epoxy and polyester formulations for filled and reinforced structures. He is the author of patents covering fiberglass reinforced structures and curing agent formulations.

In 1958 he joined Amoco Chemical Corporation as a Group Leader responsible for testing and evaluating polyamide, polystyrene and polyolefin formulations and products. After two years he was promoted to Section Leader with responsibilities for both product development and product evaluation. Patents covering Polyolefin Catalysts and Process Stabilizers were authored by Mr. Ross.

In 1962 Mr. Ross joined Kaiser Aluminum and Chemical Corporation in Oakland, California as a Manager of Commercial Development for Polymers and Plastics. In his 20 year tenure with the Chemicals Division, he held several positions in both development and manufacturing and rose to the level of Division Manager for Polymer and Plastic Products. Several patents were authored in this 20 year tenure involving both isocyanate manufacturing process and composite polyurethane products and manufacturing processes.

The R.J.R. Polymers product line originated in 1982. In 1987, new product lines were added, including package assembly, package sealing process equipment and application of B-staged die attach adhesives. The company has grown to over 60 full time employees and now occupies a 30,000 square foot building in Oakland, California, in addition to our San Francisco facility.

HERMETIC POLYMER PACKAGE SEALS

R. J. Ross

INTRODUCTION

Electronic packages of a variety of types and descriptions, including single chip carriers, microwave headers and hybrids have been sealed with epoxy adhesives using ceramic, glass, plastic and metal lids for more than ten years. Service experience has been excellent. In addition, epoxy glob to compounds are being used successfully in a great variety of commercial ICs.

Actually, epoxies have been used in electronic applications for a lot more than ten years in many applications. Most of the transfer molded parts used in electronics employ the same polymer chemistry as the adhesives and sealants discussed in this paper. There are a couple of important differences. The transfer molding compounds are generally based on standard commercial grade resins which may have as much as 150 ppm ionizable halogens and contain internal mold releases to keep them from sticking to the mold. These mold releases also keep them from sticking to lead frames and is a major influence in making transfer molded parts difficult to mark with inks.

A majority of the PC board used in electronics contain from 22% to 40% general purpose epoxy resin. The fire retardant grades usually achieve the fire retardance by the addition of halogen bearing compounds (chlorine or bromine). Again, the chemistry is the same.

The chemistry may be the same, but the compounding and purity of materials are quite different. Most B staged package adhesives have very low levels of contaminants, usually less than 10 ppm., regardless of the supplier. The same is generally true of epoxy based die attach adhesives. The binder resin compounds providing the adhesion and strength for these die attach products also employ the same basic epoxy chemistry as package seals.

Epoxies work in a variety of electronic applications. There are tens of millions of parts which have functioned successively in electronic and aerospace applications dating back to the late 1950's when the author's career was just beginning. Now there are sealing compounds and process technologies available which provide an economical and new level of performance in hermetic package sealing.

THE SEALING PROCESS

The remainder of this paper will be addressed principally to B-staged epoxy compounds which are directly applied to either the lid or package surface. Some of the information would also apply to pre-forms or liquid one or two package sealants, but there are some additional variables involved, so care must be exercised in drawing conclusions.

Typical sealing practice used throughout the electronics industry involves the use of a clamping device and an oven. Sometimes this clamping device is a simple spring clap or two and alignment is by eyeball. At the other end of the spectrum is a sophisticated alignment tool or jig with built-in spring clamps. However, they almost always employ an oven process wherein the clamped parts are heated to a sealing and/or curing temperature for a fixed time interval.

What happens when a lid and package are clamped together and put through a process cycle for sealing and curing? Nothing much happens to the lid and the package, especially if they are ceramic. However, the chemical and thermomechanical processes taking place with B-staged adhesive and the atmosphere contained under the lid must be controlled to achieve high yields and maximum seal performance.

Take the example of a one step seal/cure cycle using a temperature of 165° C as the cure temperature. Assume also that the parts are sealed in a dry nitrogen atmosphere after being clamped at room temperature (25° C). As the temperature starts to rise, the fixed volume of nitrogen under the lid will want to expand or increase in pressure according to Boyle's and Charles' gas laws. The gas will freely escape before the adhesive has softened enough to make a gas tight seal due to the clamping pressure. Typically this will occur in the temperature range of 60° to 80° C.

At the same time the contained gas volume wants to increase in pressure as the temperature increases, viscosity of the adhesive is decreasing. The adhesive starts as a tack free solid at room temperature and goes through a minimum viscosity, something like a 10 weight motor oil before the chemical reaction takes the adhesive to a thermoset solid condition. The melted, low viscosity adhesive won't hold much gas pressure (probably less than 0.4 psi.), so a gas bubble will blow through the adhesive cross-section. If the adhesive viscosity is still low, it will re-flow into the hole made by the bubble so perfectly that in most cases, even sophisticated detection equipment cannot find where the bubble occurred.

If the initial seal temperature is 65° C and the cure temperature is 165° C, temperature rise would result in a pressure rise of approximately 5 psi. This means that 4 to 8 bubbles will penetrate the adhesive before a stable temperature of 165° C is reached. This was actually observed and video taped through a glass oven door, using a ceramic lid clamped to a glass microscope slide. Now, if the adhesive reactivity is such that its viscosity rises rapidly before a stable cure temperature is achieved, a bubble may penetrate the adhesive, but the resultant hole will not "heal" because the adhesive viscosity is too high. This is the main cause of blow holes, blow outs or "leakers" in package sealing.

AVOIDING LEAKERS

Outgassing is a buzzword used around the industry as a cause of blow holes. With most commercial sealants supplied as B-staged semi-solids in lids or packages, outgassing of products from the adhesive is almost zero. For example, a sample of adhesive applied to an opaque ceramic lid was submitted for TGA/IR analysis using a temperature increase to complete pyrolysis. This was not a laboratory sample, but a standard QA sample taken during production. The curve shows essentially zero outgassing until 300° C was reached. The curve is shown in Figures 1 and 2.

Unless there is some other source of moisture or other gas products, a main cause of leakers in sealing packages with epoxy adhesive is a change in temperature of more than 3° C when the adhesive is gelling. The answer is to heat the clamped package to the sealing temperature as fast as possible, usually less than 10 minutes, and hold the assembly within + or - 3° C until the adhesive gels (sets). Massive fixtures can be a real problem if provisions are not made to heat them to a stable temperature fast enough in the seal cycle.

Sometimes a supplier of B-staged adhesives will suggest a two step sealing cycle of large packages or parts which are difficult to seal. A typical cycle is 1 hour at 125° C followed by an additional heat soak to give the adhesive its final cure. This reduces blow holes because the gel time will be lengthened several fold at the lower temperature, thus allowing more time to achieve temperature stability before the adhesive gels.

HERMETICITY

Assume for the moment that a package is sealed in a one step cycle at 165° C. When that sealed package is cooled to 25° C, the nitrogen pressure inside will be close to 2/3 atmosphere (a partial vacuum of nearly -5 psi.) At 85° C the vacuum would be around -2.5 psi. and at 121° C it would be 1.5 psi. If the same package were sealed at 165° C under a nitrogen pressure of approximately 5 psi., the internal pressure would be nearly 1 atmosphere at 25° C and the pressures at 85° and 121° C would be positive instead of negative with the values being the same as mentioned above.

Why are 85° and 121° C important to this discussion? Because they are the temperatures selected for accelerated humidity testing. Gross and fine leak testing are relatively easy to satisfy using an epoxy seal. In a series of tests using RJ-4B as the standard adhesive, fine leak results less than 3×10^{-8} were obtained after PCT, 1,000 hours 85/85, temp shock, temp cycling and 1,000 hours heat soak at 125° C. RGA testing after 96 hours PCT and 1,000 hours 85/85 showed organic outgassing of less than 2500 ppm in every case. There are probably other materials which will test similarly after the above conditioning. If fine leak is the criterion for Hermeticity, then hermetic polymer seals have been available for 10 years or more. Table 1 shows some of these data.

Testing for moisture vapor transmission is another matter. After 96 hours PCT testing or 1,000 hours at 85° C and 85% RH, those same packages mentioned above showed moisture levels ranging from 100,000 to 350,000 ppm, depending upon how the packages were sealed and cured.

Yes, the sealing process does play a major role in the results obtained in accelerated humid aging. It should be pointed out that properly sealed packages aged for 1,000 hours at 45° C and 95% RH showed moisture levels less than 10,000 ppm. The initial moisture levels were less than 5,000 ppm.

Actually, the easiest way to get "good" results in either of the above mentioned accelerated humid aging tests is to test a material which has very high moisture vapor transmission. This is because the test calls for a "drying" heat soak before the moisture level is tested. If the moisture can get out as well as in, the package could be full of water after the moisture conditioning and the test results after the drying would be excellent. For this reason, fine leak results were obtained in every test set, and the "pass" condition was considered to be results less than 5 x 10^{-8} helium leak.

SOME CHARACTERISTICS OF EPOXY SEALANTS

Cured Epoxy adhesive compounds of the type discussed in this report are thermosetting, amorphous organic compounds. They will all have a moisture vapor transmission rate, but some will be a lot lower than others. None of them will behave Hooke's law, so any strength values reported will be rate sensitive, and the moduli will be the slope of a tangent point to a curve since there will be no straight line portion of a stress/strain curve. They will all have thermal expansion coefficients ranging from around 25 to 35 ppm. per °C.

In addition to the above, strength values will be temperature sensitive. For example, RJ-4B final cured for 2 hours at 165° C has a room temperature shear strength at a testing rate of 0.05 in/min., averaging 6,500 psi when the bond line is between 0.001 and 0.002 inch and 96% alumina ceramic is the parent bonding material. At 100° C this value drops to 4,000 psi. On the newer version of the same material, RJ-10MVR, the 25° C value is 7,200 psi and at 100° C the shear strength is 4,000 psi. The moisture content curves are shown in Figure 3 and some physical properties in Figure 2. Both of these materials have Tg values of approximately 165° C when cured on this cycle.

Using seal conditions in dry nitrogen, both RJ-4B and RJ-10MVR show initial moisture levels less than 5,000 ppm. Both materials also have He leak rates less than 3 x 10^{-8} when sealed under 3 psi. nitrogen pressure. Using the IsothermSeal process, RJ-4B-MVR displayed moisture levels less than half of the standard RJ-4B sealed under the same conditions.

Accelerated aging tests are very useful for making comparisons of materials, but they can also be misleading. If, for example, one is comparing two compounds with very different glass transition points, pressure pot results could be both misleading and meaningless. If one of the products had excellent moisture resistance but its glass transition point was around 120°C, it would probably look bad in the pressure pot test at 121°C. Another material with a higher glass transition point might look a lot better in a pressure pot and not perform nearly as well at or near room temperature.

A series of long term humid aging tests are underway using RJ-4B RJ-10MVR and another competitive material used extensively in package sealing applications. The conditions we have chosen are 35, 45, 55, and 65°C and a moisture level at 95% RH. It is too early to report any meaningful data since we intend to measure gross and fine leak, moisture levels by RGA and shear strength at RT and 100°C. There are enough samples in the program to obtain results out to about 5,000 hours. This testing will continue and be reported late in 1992.

INFLUENCE OF PROCESS CONDITIONS

Throughout this report we have mentioned either directly or by implication that the sealing process has a major impact on the efficiency of the seal. One may obtain a good looking seal simply by placing it in an oven for a prescribed cure time. We have found that large differences in moisture resistance can be found using the same adhesive and package configuration. One assembly was clamped together with two 1 pound spring clamps at the quarter points and the second was sealed in an IsoThermSeal tool under dry nitrogen. Initial moisture levels were 26,000 ppm. Both samples had similar visual appearance and they both had helium leak rates less than 3×10^{-8}.

There are still many package seal production operations which are based on manual clip/oven cycle methods. However, there are several customers using automated systems based upon seal cycles of nine seconds to twelve minutes, and pilot units are in place which operate at seal rates of three to five seconds. Perhaps more important is the 99%+ yield performance which has been sustained for more than a year. In one case, operating levels are over 100K units per month. Yes, process control and mechanization pays off.

CONCLUSION

Epoxy package sealants can perform very well as "Hermetic" package seals. Both the adhesive formulation and the sealing process have a major influence on moisture resistance. Gross and fine leak results can be met rather easily without much regard to preconditioning. However, a simple pass/fail conclusion after humid aging tests is sufficient. The "pass and "fail" terms should be defined, and gross leak, fine leak and shear strength need to be reported before and after conditioning.