The Effect of Extent of Cure of an Epoxy Adhesive in an Inkjet Printhead

James M. Mrvos, Jeanne M. Saldanha Singh, and Sean T. Weaver
Lexmark International
Lexington, Kentucky, USA

Abstract

Adhesives used in thermal inkjet printheads are frequently exposed to ink. Product life depends on the robustness of these adhesives. One area of application is the die attach adhesive that bonds the silicon heater chip to the printhead body. This adhesive is constantly in the presence of ink. The selection of the die attach adhesive is based not only on the performance of the adhesive in ink but also on the printhead manufacturing processes. This paper focuses on optimizing the selection of a die attach adhesive used in a water-based ink environment based on cure characteristics. Results are reported for an epoxy system, specifically, an anhydride cured diglycidyl ether of bisphenol A. Crosslink density, modulus, density and glass transition temperature are reported with respect to extent of cure. Extent of cure is then related to the ink absorption characteristics of the adhesive and its adhesion to the printhead body and to the heater chip.

Background & Theory

Ink chemists must be given as much freedom as possible to select the materials for their formulations to meet market demands for greater inkjet printing speed, improved image quality and durability as well as lower cost of printing,. Unfortunately, incompatibilities between ink components and the adhesives used in printheads can limit which ingredients can be included in inks. Incompatibilities between inks and adhesives can cause reductions in printhead reliability or changes in ink properties that can adversely affect print quality.

In an inkjet printhead, the die attach adhesive plays a critical role in meeting print quality and reliability requirements for the pen. This adhesive bonds the silicon heater chip to the thermoplastic body of the printhead. It is exposed to ink for the entire life of the printhead. If the die attach adhesive absorbs ink through solubility or diffusion kinetics and it loses adhesion to the chip or the body, then the pen can fail. The die attach adhesive therefore must have excellent compatibility with the ingredients in the ink. This study focuses on understanding the effect of crosslink density on ink resistance and adhesion to substrates. The crosslink density is dependent on several parameters including the adhesive cure conditions. Generally, a higher degree of crosslinking will increase the modulus of the adhesive and will provide better chemical resistance. However, increasing the modulus of the adhesive causes the polymer to lose its ductility making it more brittle and more susceptible to cracking.[1]

Determination of Crosslink Density

The crosslink density of a polymer is defined as the ratio of the number of backbone atoms in crosslinks to the total number of backbone atoms in the molecule.[2] Crosslink density can be determined using several techniques: [1]H nuclear magnetic resonance spectroscopy; dynamic mechanical measurements; equilibrium swelling measurements; rheological measurements; and mechanical stress-strain measurements.[3]

The Mooney-Rivlin equation, based on rubber elasticity, can be used to determine crosslink density based on equilibrium stress-strain measurements:[4,5]

$$\sigma = 2(\lambda - \lambda^{-2})(C_1 + \frac{C_2}{\lambda}) \tag{1}$$

where σ = engineering stress (force/unit original cross section), λ = extension ratio, C_1 and C_2 are empirical constants. Rewriting Equation (1),

$$\frac{\sigma}{2(\lambda - \lambda^{-2})} = C_1 + \frac{C_2}{\lambda} \tag{2}$$

Generally, for an unswollen vulcanized rubber network, plotting the reduced stress, $\sigma/[2(\lambda - \lambda^{-2})]$, as a function of $1/\lambda$, yields a straight line at low elongation. The value of C_1, in agreement with the theory of rubber elasticity, must increase with crosslink density. For an ideal network, C_2 approaches zero. It has been proposed that[4]:

$$C_1 = \frac{1}{2} NRT \tag{3}$$

where N = crosslink density, R = the gas constant and T = the absolute temperature. To assure near-equilibrium response, stress-strain measurements are done at very slow strain rates under swollen conditions or at elevated temperatures. The testing temperature should be at least 20°C above the glass transition temperature (T_g) of the cured polymer to ensure rubbery behavior.

By comparison, the crosslink density can also be calculated using network elasticity theory for Gaussian chains using the equation[5]:

$$G = NRT \tag{4}$$

where is G is the shear modulus. In this paper, the storage modulus G′ obtained from rheometer measurements was used to calculate crosslink density.

Durability of Crosslinked Networks in Inks

When a crosslinked polymer is placed in ink, several phenomena may occur: the exposure may cause extraction of soluble constituents from the adhesive by the ink; chemical reaction could occur between the liquid and the polymer; or the polymer may swell. The potential for a polymer to swell is dependent upon the interaction between the polymer and the solvent. The degree of crosslinking, which is a measure of the elastic potential, acts to resist swelling. Equilibrium is reached when these two potentials are equal.

The ability of a cured adhesive to swell by absorbing a large amount of a low viscosity liquid depends on thermodynamic considerations. A polymer will absorb a liquid if there is a negative Gibbs free energy change, ΔG, that takes place during mixing. The free energy change is given by[6]:

$$\Delta G = \Delta H - T\Delta S \tag{5}$$

where ΔH is the change in enthalpy, ΔS is the change in entropy and T is temperature. Thus the requirement for mixing is that $T\Delta S$ be greater than ΔH. The enthalpy change is largely influenced by the value of the solubility parameters, (δ) of liquid and of the polymer. The physical significance of the solubility parameter is that δ^2 is the material's cohesive energy density. Essentially it is a measure of the energy of attraction between like molecules. The solubility parameter can be calculated using the equation[7]:

$$\delta = \sqrt{\frac{\Delta H_v - RT}{V_m}} \tag{6}$$

where ΔH_v is the heat of vaporization, V_m is the liquid molar volume calculated from density data. Referring to Equation 5, ΔH will be less than $T\Delta S$ only when certain conditions for δ are met. For instance, if δ values for a polymer and a solvent are within about $2(MPa)^{1/2}$ of each other, then ΔG will be negative and considerable absorption of the solvent will occur.[7]

Experimental

Materials

The adhesive investigated in this work was a commercially available one-part epoxy system, specifically, an anhydride cured diglycidyl ether of bisphenol A. It is similar to Shell Epon 828 (see Figure 1). The adhesive also contained an acrylonitrile butadiene rubber component.
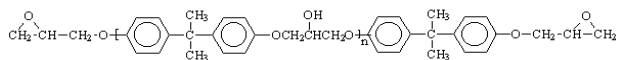

Figure 1. Adhesive Structure

Test Methods and Equipment

A TA model 2920 modulated Differential Scanning Calorimeter (DSC) was used to measure the T_g of the cured samples. The samples were heated from –50°C to 200°C at a scanning rate of 3°C/minute. The T_g's from the DSC scans were defined as the temperatures at the inflection points of the scans.

Stress-strain measurements were done on a Model 1123 Instron at a low extension rate of 1.25mm/minute. The samples were tested at 120°C, which is above T_g of the material.

A Haake Model TC500 Controlled Stress Rheometer was used to measure the storage modulus, G′ of the adhesive in the shear oscillation mode. The modulus measurements in this study were made at 1Hz and a strain of 1% at a gap distance of 1mm. The temperature was ramped from ambient to the different cure temperatures of 100°C, 110°C, 130°C and 150°C in 15 minutes and then held at that temperature for 45 minutes while the adhesive cured *in situ.* The temperature was then ramped down to ambient within an additional 15 minutes.

Hardness was measured using a Shore D hardness gauge as per ASTM D2240. Specific gravity measurements were made using ASTM D792. Ink absorption data were obtained by immersing the cured adhesive specimens in ink at 60°C for four weeks. The weights of the specimens were measured each week the adhesive was in contact with the ink.

Chloroform extraction was used to determine amount of solvent absorbed in a specimen. Quantitative analysis of extracted solvents was done using a gas chromatograph/ mass spectrometer.

Heat of vaporization was measured using the isoteniscopic method. With this technique, vapor pressure is measured as a liquid is heated in a closed system. Using the Clapeyron equation and assuming ideal gas behavior, the heat of vaporization is given by[6] :

$$\Delta H_v = -R\frac{d(\ell n P^v)}{d(1/T)} \tag{7}$$

where P^v is the vapor pressure and R is the gas constant. A plot of ln P^v vs. 1/T has a slope equal to $-H_v/R$.

A wedge test (ASTM D3762) was used to test bond durability. In this test, a wedge was inserted at ambient conditions into the bondline of a flat-bonded aluminum specimen. This created a tensile stress in the region of the tip of the resultant crack. The length of fracture was measured after the initial crack came to equilibrium. The samples were then submerged in ink and placed in a 60°C oven. The purpose of creating the crack was to increase the diffusion rate of the ink into the adhesive. The crack length was measured as a function of time and the failure mode was evaluated. This test is primarily qualitative, but can be used in determining the effects of various adherend surface preparation processes and adhesive durability when exposed to ink.

Lastly, die shear testing was performed to assess the adhesion of the heater chip to the printhead body material.

Heater chips bonded to polyphenylene oxide plaques were immersed in ink for 4 weeks at 60°C. The samples were then mounted on the Instron and a force parallel to the long axis of the silicon chip was applied at a speed of 20mm/min. The failure mode was recorded for each sample.

Test Specimen Preparation

Tensile specimens were prepared and cured for 1 hour at cure temperatures of 100°C, 110°C, 120°C, 130°C and 150°C. No post curing was done. The 12mm x 20mm x 3.5mm specimens for density measurements were prepared using the same curing conditions as above.

Die shear samples were prepared by bonding silicon chips onto 30mm x 30mm x 3mm polyphenylene oxide plaques with a bondline thickness of 0.03mm to 0.04mm.

Wedge test samples were prepared by degreasing two type 2024T-3 aluminum substrates with ethanol followed by a 1 minute O_2 plasma etch. The adhesive was then dispensed to a 0.0075-inch bondline thickness onto the cleaned aluminum substrates. The bondline was maintained by placing a 0.0075 inch diameter gauge wire between the two substrates. After the adhesive was dispensed, the adherends were bonded under pressure for the specific cure cycles.

Results and Discussion

Figure 2 is a plot of reduced stress vs. $1/\lambda$ of tensile specimens tested at 120°C. The plot yields straight lines for all the cure conditions studied. From Equation 2, the lines have slopes equal to C_2. The values of C_1 are found from the intercepts when the curves are extrapolated to $1/\lambda = 0$. It was realized that for this system, the data followed the Mooney-Rivlin behavior.

Table I lists the intercepts C_1 and slopes C_2 for tensile samples cured for 1 hour at various temperatures. The corresponding crosslink densities, N_{mr}, were calculated using the Mooney-Rivlin equation (Equation 3). A comparison of the crosslink density calculated from Equation 4 using the rheometer, N_{rheo}, is also presented in the Table I. The 130°C and 150°C cured samples produced the highest crosslink densities. It is seen that both methods represent similar trends in crosslink density. Because of its simpler test procedure and the ease of sample preparation, the rheometer method was chosen as the preferred technique for determining crosslink density for subsequent measurements.

Table I – Comparison of Crosslink Densities

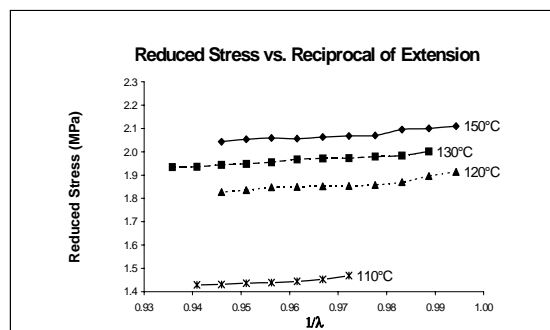| Cure Temp.	Mooney-Rivlin Equation Testing at 120°C			Rheometer	
	C_1 (MPa)	C_2 (MPa)	N_{mr} (mol/cm³)	G'_{rheo} (MPa)	N_{rheo} (mol/cm³)
100°C	0.31	.846	1.88E-4	.275	8.86E-5
110°C	.0.32	1.17	1.96E-4	1.41	4.42E-4
120°C	0.38	1.52	2.35E-4		
130°C	0.81	1.20	4.97E-4	2.66	7.95E-4
150°C	0.81	1.31	4.93E-4	2.65	7.53E-4

Figure 2 – Mooney plots of the adhesive under different cure conditions in simple extension
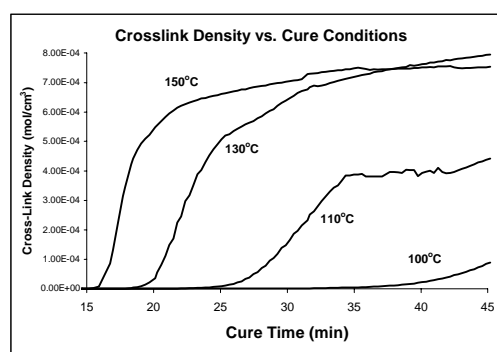

Figure 3. Crosslink Density vs. Cure Time Using the Rheometer

Figure 3 presents the increase in crosslink density over time for each cure temperature calculated using Equation 4. Not surprisingly, the rate of crosslinking increased as the temperature increased. By the end of the 45 minute cure however, the crosslink densities of the 130°C and 150°C samples were very similar. It is possible that the faster rate of cure for the 150°C sample could cause its network structure to be different from the 130°C sample.

The glass transition temperature, T_g, of a polymer can be interpreted as its increase in free volume as it changes from a glassy state to a rubbery state during heating. It is theoretically a measure of overall molecular mobility of a polymer network. The glass transition temperature of a polymer tends to increase with cure.[8] Table II presents T_g data obtained through modulated DSC. The data suggest an increase in T_g with cure temperature. However, the T_g's do not correlate well with the calculated crosslink densities for samples cured at 130°C and 150°C. Only the T_g of the 100°C cure sample was significantly different from the other T_g's. This lack of correlation between T_g and crosslink density demonstrates the point that a simple glass transition temperature measurement does not fully characterize a thermosetting polymer's extent of cure.

Table II also shows that the techniques used to measure density and hardness were not sensitive enough to differentiate the extent of cure.

Table II – Effect of Cure on Epoxy Material Properties

Cure Temp.	T_g	Density (g/cm³)	Hardness (Shore D)
100°C	77°C	1.25	78
110°C	85°C	1.25	79
120°C	87°C	1.24	79
130°C	88°C	1.25	80
150°C	91°C	1.25	80

The effect of cure conditions on ink absorption is depicted in Figure 4. The samples were immersed in a water-based ink at 60°C over a four week period. The amount of ink uptake was monitored through weight change. It was apparent that the higher the crosslink density, the less the weight change. Samples cured at 130°C absorbed less ink than those cured at 150°C, 110°C and 100°C. The slightly lower ink absorption of the 130°C cured sample compared to the 150°C cured sample is an interesting result. Although the two samples had similar crosslink densities, it is possible that the faster rate of the 150°C cure created a slightly greater free volume inside the polymer network that allowed more solvent absorption to occur.
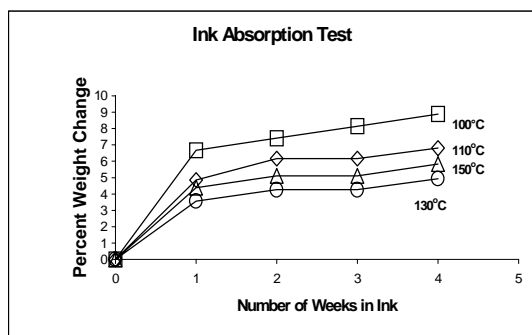

Figure 4. Ink Absorption vs. Cure Conditions

The samples that had been immersed in ink were subjected to chloroform extractions. Figure 5 presents the amount of the two co-solvents extracted from the samples. At all cure temperatures less 2,2-thiodiethanol was absorbed compared to 1,2-hexanediol. The remainder of the weight gain of the is due to water absorption. The solubility parameters for the two co-solvents calculated using Equation 6 at 25°C are shown in Table III. They are fairly close to each other and also to the literature value for Epon 828.[7] The difference in δ's between 2,2-thiodiethanol and Epon 828 is 1.1(MPa)^(1/2) and the difference between 1,2-hexanediol and Epson 828 is 0.3(MPa)^(1/2). It is therefore not surprising that a significant amount of both solvents was absorbed into the adhesive. Also, the preferential absorption of the 1,2-hexandiol can be understood by the difference between its solubility parameter and Epon 828 being smaller than the difference between 2,2-thiodiethanol and

Epon 828. For this adhesive/solvent set, solubility parameters appear to be a useful guide to help predict which solvents are likely to be absorbed into the adhesive. This knowledge can be applied by ink formulators to either limit the concentrations of ink ingredients likely to be absorbed by the adhesive or to formulate using solvents with solubility parameters that are significantly different from that of the adhesive.
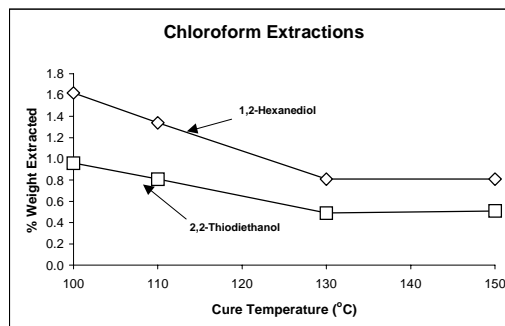

Figure 5. Extractions of Solvents from Adhesives after 4 Weeks of Immersion in ink

Table III – Comparison of Solubility Parameters

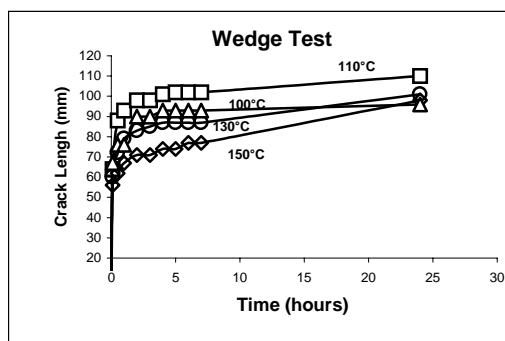| Material	Density[9] (g/cm³)	V_m (cm³/mol)	ΔH_v (cal/mol)	δ (MPa)^(1/2)
1,2-Hexandediol	0.951	124.3	14600	21.9
2,2-Thiodiethanol	1.221	100.1	12800	22.7
Epon 828				21.6

Figure 6. Wedge Test Results

The effect of cure conditions on adhesive-bonded structures using the wedge test is presented in Figure 6. The samples cured at 110°C appeared to have a higher rate of crack propagation than the ones cured at 130°C and 150°C. These results correlate well with the crosslink density calculations. The 100°C cured sample had a smaller crack length than the others. This was probably due to the low

level of crosslinking in the sample. It is likely that the stress created by the insertion of the wedge into the specimen was dissipated by the undercured material.[10]

Die shear tests done on the 110°C, 130°C and 150°C cured samples after immersion in ink for 4 weeks at 60°C showed that the heater chip shattered before the adhesive bond failed. This indicates the bond strength was higher than the strength of the chip. On the 100°C cured samples however, the adhesive experienced a cohesive failure. This is not surprising since the crosslink density was lowest of all the cure conditions. The low level of cure and the high (8%) ink uptake of this sample probably caused the cohesive strength of the adhesive to be poor. This led to failure of the bond.

Conclusion

Crosslink density has been shown to be an important metric for assessing the performance of a die attach adhesive in an inkjet printhead. Wedge testing and the use of solubility parameters were also shown to be useful in predicting adhesive performance when exposed to ink.

In order to attain robustness of the adhesive for the application, it appears that a curing cycle at 130°C for 45 minutes is optimal, based on crosslink density and resistance to the ink used for this study.

Curing at 150°C could allow a shorter cure time to be used in manufacturing to the printhead without reducing crosslink density. The ink resistance of the adhesive however, may be reduced.

Curing this adhesive at 110°C does not produce a high crosslink density and does not provide the best ink resistance compared to higher temperature cures. However, it does allow the use of a lower cost thermoplastic substrate with a low heat deflection temperature for the printhead body. While this does provide sufficient reliability for disposable printheads, it may not meet the reliability requirements for longer life printheads. It will be preferable to have a higher level of cure while still maintaining good adhesion as with the 130°C cure. This may call for a higher temperature resistant material or perhaps a longer cure cycle.

Further work is planned to investigate the relationship between the rate of solvent diffusion into a polymer network and the network's crosslink density.

Acknowledgments

References

1. J. S. Sayre, et. al., *Rubber-Modified Thermoset Resins*, American Chemical Society, Washington, DC (1984).
2. L. A. Errede, *J. Appl. Polym. Sci.*, **31**, 1749 (1986).
3. A. Y. Coran, S. Lee and H. Pawlowski, *Rubber Chemistry Technology*, **67,** 845 (1994).
4. A. N. Gent, Ed. *Engineering with Rubber – How to Design Rubber Components*, Oxford University Press, NY (1992).
5. L. R. G. Treloar, *The Physics of Rubber Elasticity*, Oxford University Press (Claredon), London (1975).
6. J. M. Smith and H. C. Van Ness, *Introduction to Chemical Engineering Thermodynamics*, McGraw-Hill, NY (1975).
7. J. Brandrup and E. H. Immergut, Eds., *Polymer Handbook*, John Wiley and Sons, NY (1989).
8. W. Yu and E. D. von Meerwall, *Macromolecules*, **23**, 882 (1990).
9. Sigma-Aldrich, Milwaukee, WI.
10. E. H. Andrews and A. J. Kinloch, *J. Polym. Sci.,* **11**, 269 (1973).

Biography

Jim Mrvos received a BS in chemical engineering from Carnegie Mellon University in 1981 and an MS in chemical engineering from the University of Kentucky in 1991. He has eighteen years of experience with Lexmark International and IBM in the manufacture and development of imaging supplies. Since 1990, he has worked on inkjet ink and printhead development. He is currently manager of inkjet process and materials development for Lexmark. Mr. Mrvos is the co-author of eight patents and is a licensed professional engineer.