Measurement of Modulus Changes of a Phenolic Adhesive Using Nanoindentation for an Inkjet Printhead Nozzle Plate

James M. Mrvos, Girish S. Patil, Elizabeth C. Dickey, and Christopher T. Wonderly**
*Lexmark International, *University of Kentucky*
Lexington, Kentucky, USA

Abstract

Polyimide nozzle plates are bonded to inkjet printhead heater chips using a phenolic/polyvinylbutyral adhesive. A 25µm thick polyimide film is coated with a 12.5µm thick layer of a B-staged phenolic adhesive, which is cured after the nozzle plate is attached to the chip. B-staged phenolic materials undergo aging reactions at shipping and storage temperatures prior to being cured. This behavior makes it difficult to achieve consistent nozzle plate to chip adhesion. Understanding and quantifying the aging of the phenolic is necessary for predicting its adhesion performance before it is used in printhead production. In this study nanoindentation measurements of thermally aged phenolic adhesive samples were made in order to calculate the modulus of the material. Modulus measurements, XPS data, and nozzle plate adhesion results were then used as a basis for proposing a mechanism describing phenolic aging.

Introduction

The nozzle plate in an inkjet printhead is a very complex component. Beyond its most visible function of providing the means for directing drops of ink toward the media, the nozzle plate must also meet requirements for adhesion to the heater chip, ink compatibility and durability for the life of the printhead. Figure 1 is a representation of a polyimide nozzle plate attached to a heater chip for Lexmark's inkjet printheads. A detailed description of this material set has been previously presented.[1]

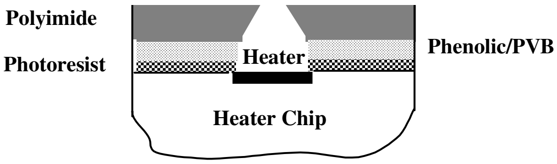

Figure 1. Nozzle Plate Mounted on Heater Chip

Briefly, the nozzle plate is composed of a 25µm polyimide base film coated with a 12.5µm layer of a phenolic/polyvinylbutyral (PVB) adhesive. The nozzles, ink chambers and flow features are formed in the material using an excimer laser ablation process. Prior to ablation, the phenolic side of the material is coated with polyvinyl alcohol (PVA).[2] The PVA acts as a sacrificial layer to prevent ablation debris from contaminating the adhesive material. After ablation, the PVA is removed with water. The nozzle plate is then aligned and bonded to the heater chip surface, which has been coated with a 2.5µm layer of a planarizing photoresist. The final step in the nozzle plate attachment process is a thermal cure of the phenolic adhesive. The focus of this study is to gain insight into the aging mechanism of the phenolic adhesive and the effect aging has on adhesion of the nozzle plate to the chip. Understanding adhesive aging is critical to maintaining high quality in production.

Phenolic/PVB Adhesive Chemistry

The adhesive is comprised of primarily a mixture of phenolic resin (Figure 2) and polyvinylbutyral (Figure 3). These two components are present in approximately equal amounts. Polyvinylbutyral is a thermoplastic material having a glass transition temperature (T_g) of approximately 70°C. Polyvinylbutyral imparts some flexibility to the fully cured phenolic resin, which is otherwise extremely brittle.

The cure of the phenolic resin can be divided into two main events. The first event consists of reactions between phenol and formaldehyde. This results in the formation of a partially crosslinked low molecular weight phenolic resin that is still soluble in several different solvents. The resin is now considered B-staged. The B-staged resin can continue to react at room temperature or above to gain molecular weight while still being soluble. Depending on the extent of reaction within the B-stage, the resin can have different physical and chemical properties. The second event during the phenolic cure occurs when the B-staged resin is subjected to a temperature excess of about 140°C. During this final cure, the resin rapidly crosslinks to form a 3-dimensional network. The crosslinked phenolic interacts with the photoresist to form a bond between the nozzle plate and chip that is essentially insoluble in ink.

It is important to note that the adhesive is in the B-staged form when it is coated onto the polyimide film. In this form it can undergo additional reaction as it passes through the supply chain and into production. Prior to this study, the reaction of the B-staged phenolic was thought to be the major factor in causing inconsistent nozzle plate to chip adhesion.

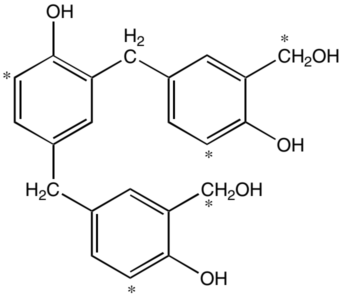

Figure 2 – Phenolic Resin Structure.
('s indicate sites available for crosslinking)*

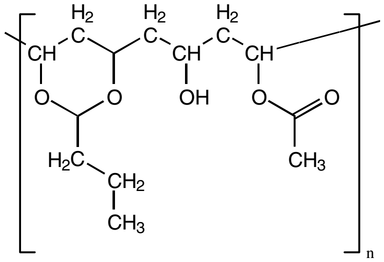

Figure 3 – Polyvinylbutyral Structure

In earlier work, several different analytical methods were used in attempts to quantify the extent of aging of the phenolic adhesive. As manufactured, the material has about 2% volatile components, approximately half of which is phenol (one of the raw materials of the phenolic adhesive). When the adhesive ages, the phenol reacts with B-staged phenolic chains. Therefore, an aged phenolic adhesive should have a lower amount of volatile compounds than a fresh sample. However, the differences measured in the percent volatile components between aged and non-aged samples were within experimental error and hence this method did not prove to be useful for understanding aging.

Attempts to quantify aging by determining percent extractables proved unsuccessful for the same reason discussed above. Here again, a more aged sample was expected to have less extractables.

Another technique that was explored was Gel Permeation Chromatography (GPC). The GPC data were expected to show that as the material ages, a reduction of low molecular weight fractions should occur. The GPC data however were inconclusive.

Use of Differential Scanning Calorimetry (DSC) to measure residual cure, as would be measured by the exotherm, did not show a sufficient difference between aged and non-aged samples to make a meaningful correlation.

A more aged sample would be expected to have a higher modulus. Dynamic Mechanical Analysis (DMA) was used to measure modulus differences between aged and non-aged samples. The fact that the phenolic adhesive was present on a polyimide backing complicated the analysis. The mechanical properties of the polyimide overwhelmed those of the phenolic adhesive. Thus, physical property changes in the phenolic due to aging could not be detected using this technique.

All of the above techniques characterize bulk properties of a material. However, adhesion is almost exclusively a surface phenomenon. To gain better insight into the surface of the adhesive, two techniques were employed: X-ray Photoelectron Spectroscopy (XPS) and nanoindentation. XPS was used to provide data on the chemical composition of the surface and nanoindentation was used for characterizing the physical properties of the surface.

Nanoindentation

Nanoindentation is a technique for measuring localized mechanical properties of materials. It is particularly useful when examining a film. While a traditional Vickers indentor must achieve a depth of several microns to provide useful data, a nanoindentor only needs to penetrate on the order of nanometers. The nanoindentor also produces an entire load displacement curve so that modulus and contact depth can be determined. The instrument used was the Hysitron Inc. Triboscope® nanomechanical testing system. The instrument was fitted onto a JEOL JSPM-4200 scanning probe microscope.

The nanoindentor's transducer measures both the force and the displacement of the nanoindentor tip. A current is applied to the top and bottom plates of the transducer (see Figure 3). The two currents are 180° out of phase. This causes the electric field to vary linearly towards each plate and be zero in the center. The tip is fastened to a third plate that is positioned between the top and bottom plates. The capacitance between the center plate and the outer plates is used to determine the vertical displacement of the tip. The magnitude of the current through the plates controls the strength of the electric field and indicates the force.

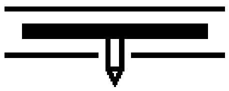

Figure 3 – Nanoindentation Schematic

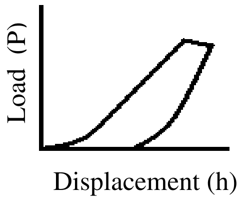

Figure 4 – Nanoindentation Load/Displacement curve

To make indents, a load function is first defined that controls the force applied to the tip with respect to time. As the indents are made the transducer senses the tip displacement and the load applied to the tip. The software then produces a graph. Figure 4 shows a typical load displacement curve. A power law relationship of the form shown in Equation 1 is fitted to the points of the unloading curve where P is the load, h is the displacement, A and m are constants and h_f is the displacement after unloading

$$P=A(h-h_f)^m \tag{1}$$

The derivative of the power law at the first unloading point with respect to displacement is equal to the stiffness, S. Contact depth, h_c, can then be determined from Equation 2 where P_{max} is the maximum load and h_{max} is the displacement at the maximum load. The modulus, E_r can be estimated for the material from Equation 3. The area function A(h) is calibrated from the area of an indent of a standard with a known modulus at a given contact depth. The area function is different for each tip. The 0.75 prefactor is an appropriate constant for a Berkovich indentor.[3]

$$h_c = h_{max} - 0.75P_{max} / S \tag{2}$$

$$E_r = \frac{\sqrt{\pi}}{2\sqrt{A(h_c)}} S \tag{3}$$

Experimental

Two experiments were designed to determine the effects processing and aging of the phenolic adhesive have on modulus and adhesion to the heater chip. Experiment #1 was focused on the effects of PVA coating, washing with water, and phenolic curing. Preliminary work had shown that coating the phenolic/PVB with PVA and subsequently removing it by washing with water tended to reduce adhesion to the chip. The design of Experiment #1 incorporated combinations of PVA coating, washing, and curing in an effort to understand the effects of these processes on the modulus and adhesion of the material.

In Experiment #2, aging effects on modulus and adhesion were investigated. Samples were aged for 3 days at 50°C, 60°C or 70°C. In addition, because the chemical interaction between PVA and the adhesive was not known, the stage of the film manufacturing process in which aging occurred was investigated (either aging before the PVA was coated or after it was coated). As in Experiment #1, cure was also a variable in Experiment #2. The samples for Experiment #2 were all washed to remove PVA and all underwent additional thermal processing that is similar to the thermal conditions the material experiences during the laser ablation process.

The designs of the experiments and the averages for modulus and 90° peel for each trial are shown in Tables 1 and 2. Note that in both Experiments #1 and #2, peel strength could only be measured on specimens that were not cured. This is because to test adhesion, the phenolic had to be cured with the nozzle plate film in place on a chip.

Adhesion & XPS Measurements

Adhesion of the phenolic to the chip was measured by performing a 90° peel on an Instron™ tensile tester.[4]

XPS measurements were performed after the washing step for each of the trials of both experiments using a VG Scientific SigmaProbe X-ray photoelectron spectrometer.[5] Photoelectrons were produced by monochromated AlKα x-rays focused to an oval spot approximately 400 x 800μm^2 and a flood gun was used to reduce the effects of electrical charging. The materials were adhered to carbon tape prior to outgasing to <10^{-8} mbar at ambient temperature. Survey scans (0-1200 eV, 1.0 eV increments, pass energy 160) were made for each specimen, followed by high-resolution scans (0.1 eV increments, pass energy 40) in the regions of the major peak of each element identified in the survey scan.

The maximum C1s peak heights for C-O and C-C were measured from the XPS plots of rate of emitted electrons vs. binding energy (Figure 5). Changes in the peak height ratio indicate that chemical reactions have occurred leading to differences in the relative amount of residual PVA on the phenolic surface.

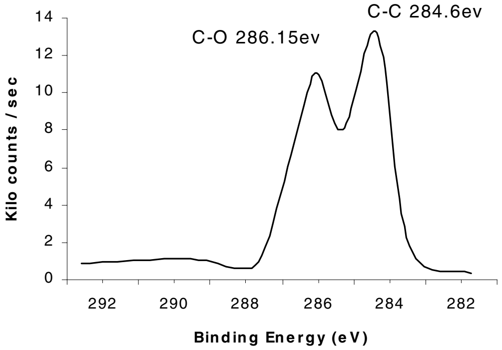

Figure 5. High Resolution C1s XPS Spectrum Representation

Nanoindentation Measurements

The maximum load for the nanoindentation measurements was between 250μN and 400μN. When results varied widely between indents, larger loads were used to help reduce the standard deviation. The larger load caused an indent that covered more area and as a result was less influenced by small anomalies. During each indent, the load was increased linearly from 0 to the maximum over a period of 5 seconds. It was then held the maximum load for 5 seconds. Finally, it returned to zero linearly over 5 seconds. The contact depth of the indents was always less than 600nm, 1.6% of the film thickness, to minimize the influence of the substrate on the measured hardness and modulus. The unloading curve was analyzed removing the first 5% and the last 20% to ensure only the true unloading curve was being analyzed and not the effects of the initial movement or the tip leaving the surface.

Sample Preparation

A freshly coated sample sheet of B-staged phenolic on polyimide was obtained. PVA coated test specimens were prepared by spin coating using process conditions similar to those used in production. All samples were stored at 4°C while awaiting processing or measurements. Ten to 12 samples were prepared for each cell in the experiments. Five nanoindentation measurements were made over a 25µm x 25µm area of each sample. Specimens for peel measurements were bonded to chips and cured using the same processes as are used for production.

Table 1. Experiment #1 Design & Results

Trial	PVA	Wash	Cure	Average Modulus (Gpa)	Avgerage Peel (g)
1	No	No	No	4.21	293
2	No	No	Yes	3.26	
3	No	Yes	No	4.58	185
4	No	Yes	Yes	4.16	
5	Yes	Yes	No	4.85	175
6	Yes	Yes	Yes	4.30	

Table 2. Experiment #2 Design & Results

Trial	Aging Stage	Aging Temp.	Cure	Avg, Modulus (Gpa)	Avg. Peel (g)
1	Before PVA	50°C	No	4.05	142
2	Before PVA	50°C	Yes	3.18	
3	Before PVA	60°C	No	4.85	92
4	Before PVA	60°C	Yes	2.43	
5	Before PVA	70°C	No	4.97	61
6	Before PVA	70°C	Yes	4.20	
7	After PVA	50°C	No	4.77	139
8	After PVA	50°C	Yes	1.73	
9	After PVA	60°C	No	4.18	61
10	After PVA	60°C	Yes	2.65	
11	After PVA	70°C	No	4.75	25
12	After PVA	70°C	Yes	4.17	

Results & Discussion

XPS Results

Figure 6 shows data from XPS analysis of residual PVA after the wash step for Experiment #2. These data show that the amount of residual PVA decreases as the aging temperature increases if the aging is carried out before applying PVA. The amount of residual PVA increases when the aging is done after PVA application.

The lower amount of residual PVA with increased temperature of aging before PVA application suggests that higher temperatures make the phenolic adhesive surface less reactive toward PVA. This could be a result of the phenolic further progressing in its B-stage and thus losing some of its reactivity. Another possibility is that the phenolic surface becomes increasingly PVB rich as the temperature increases.

Since PVB is the less reactive of the two components in the adhesive, a PVB rich surface should have lower levels of PVA residue. When the thermal aging is done after the PVA is applied to the phenolic surface, its reaction with phenolic competes with both the B-stage advancement and with PVB migration to the surface. This could explain the increase in residual PVA when the material is aged at a higher temperature in presence of PVA.

The PVB enrichment mechanism was also suggested by the XPS data from the non-aged phenolic surfaces of Experiment #1. However, it was not possible to resolve the peaks sufficiently to permit quantification of the enrichment.

The XPS data alone could only provide an insight into PVB migration as a possible aging mechanism. Nanoindentation and adhesion measurements were used to validate the hypothesis.

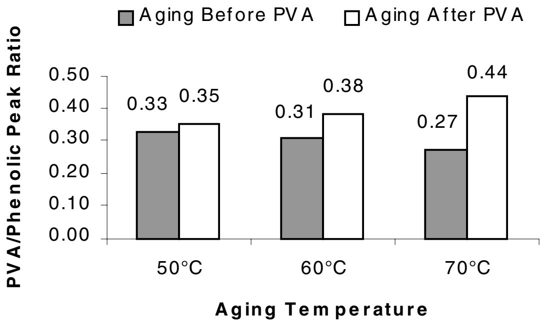

Figure 6 – XPS C1s Peak Ratios for PVA and Phenolic for Samples Aged Before and After PVA

Nanoindentation & Adhesion Results

Figures 7-10 are plots of the effects of the variables studied on modulus of the adhesive surface and 90° peel for the two experiments. The graphs show the mean responses for the variables. The data were analyzed using a T-test for comparison of means and an F-test for analysis of variance. Tables 3 and 4 summarize the results. The data in the tables show the statistical confidence levels for the effect of each variable on modulus and peel. The tables also show the R^2 value for the F-Test. The R^2 indicates how much of the total variation of the data can be accounted for by the variable. The closer R^2 is to 1, the stronger the variable's effect on the experimental responses. It is important to recognize that a variable can have an R^2 considerably less than 1 and still be significant, indicating that other variables in the experiment also had significant effects.

The most surprising result from the experiments was that the modulus of the adhesive decreased when it was cured (see Figures 7 and 9). Curing was the only factor that lowered modulus in either of the experiments. Tables 3 and

4 show that the effect is statistically significant and accounts for 25% - 50% of the variation in the experimental results. The expectation had been that curing would increase the modulus because of the crosslinking of the phenolic that occurs during cure.

This unexpected result was verified through repeat samples. In addition, to verify that the reduction of the adhesive modulus was not the result of changes to the polyimide film, the modulus of polyimide without the adhesive was measured by nanoindentation before and after being exposed to the thermal curing process. These measurements showed that there was no change to the polyimide. This validated the conclusion that curing lowered the adhesive modulus.

To further understand the reduction of adhesive modulus after cure, samples of polyimide film were coated with PVB only. The modulus of the as-coated PVB was 3.05 Gpa. The modulus dropped to 1.10 GPA after the film underwent the normal adhesive curing process. The reduction in modulus after the PVB was exposed to the curing temperature is likely due to diffusion of lower molecular weight fractions of the polymer to the surface of the film. When the PVB modulus measurements are compared to those of a phenolic/PVB adhesive sample that never was coated with PVA (see Table 1, Trials 1 & 2), it can be seen that PVB is a lower modulus material than phenolic. Because PVB's modulus drops after the cure process, the proposed mechanism of PVB migration during the phenolic/PVB adhesive cure is further supported.

Figures 7 and 8 and Table 3 show that PVA and washing have the same effects. Both increase modulus and decrease peel. Closer examination of the data however calls into question whether PVA actually reduces peel. In order to isolate the effect of PVA on peel, Trials 3 and 5 of Experiment #1 were analyzed separately from the rest of the data. The only difference between these trials was whether the adhesive was coated with PVA. This analysis showed that PVA coating did not have a statistically significant effect on peel. The strong effect washing had on reducing peel (Trials 3 and 4) and the unbalanced design of the experiment caused the statistical analysis of data from all the Experiment #1 trials to generate an incorrect assessment of the significance of PVA's effect on peel.

As mentioned above, washing increased modulus and decreased peel in Experiment #1. This was another unexpected result from the experiment. It was anticipated that because the phenolic resin is hygroscopic, the modulus of the adhesive would drop after washing. The increase in modulus could possibly be due to the water extracting lower molecular weight fractions of the phenolic or the PVB. The reduction in peel caused by washing seems to support this hypothesis. Further work is needed to prove this.

Figures 9 and 10 show the effects of aging stage on modulus and peel from Experiment #2. Table 4 shows the statistical analysis of the data. Modulus was higher and peel was lower when the adhesive was aged after the PVA was coated, however these effects were not statistically significant. When combined with the XPS results described above, these data tend to support the hypothesis that PVA reacts with the phenolic. The weakness of the response indicates that PVA is not as important of a factor in bonding of the film to the chip as had been thought when the experiment was designed.

Figures 9 and 10 also show that peel decreased and modulus of the adhesive increased at higher aging temperatures. As shown in Table 4, the difference in peel was statistically significant for all 3 temperatures, but only the 70°C temperature was significantly different for modulus. This set of results demonstrates the competing mechanisms of reaction of the phenolic and migration of the PVB. When the aging temperature is 60°C or less, the modulus and peel are lower than non-aged samples (see Trials 5 and 6, Experiment #1), indicating PVB migration is occurring. As the aging temperature is increased to 70°C, the modulus increases because the crosslinking reaction of the phenolic resin begins to occur and higher molecular weight fractions of the PVB are reaching the surface. Both of these factors will reduce the peel strength. Crosslinking the phenolic before it is attached to the chip reduces the interaction between the adhesive and the photoresist on the heater chip.

When PVB is at the interface between the adhesive and photoresist, a weak boundary layer is formed that is incapable of bonding strongly to the chip. Evidence for this can be found by examination of the failure interface of specimens with high and low peel strength. The failure interface for samples with low peel strength is exclusively between the adhesive and the photoresist. For specimens with high peel strength the locus of failure is very different. The adhesive pulls some of the photoresist off of the chip and some of the adhesive is left on the photoresist surface after delaminating from the polyimide.

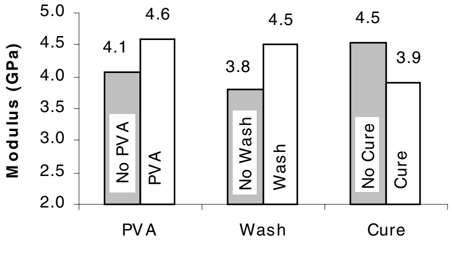

Figure 7 – Experiment #1 Average Modulus

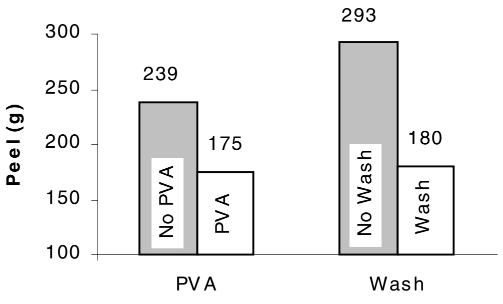

Figure 8 – Experiment #1 Average 90° Peel

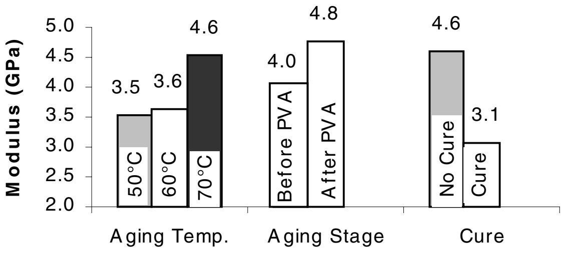

Figure 9 – Experiment #2 Average Modulus

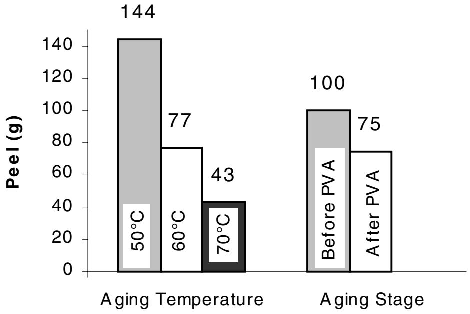

Figure 10 – Experiment #2 Average 90° Peel

Table 3. Experiment #1 Responses

Factor	Effect	T Test Conf.	F Test Conf.	R^2
PVA	PVA ↑ modulus	≥ 95%	≥ 99%	0.14
	PVA ↓ peel (all trials)	≥ 95%	95%	0.27
	No difference comparing Trials 3 & 5 only			
Wash	Washing ↑ modulus	≥ 95%	≥ 99%	0.28
	Washing ↓ peel	≥ 95%	≥ 99%	0.83
Cure	Curing ↓ modulus	≥ 95%	≥ 99%	0.25

Table 4. Experiment #2 Responses

Factor	Effect	T Test Conf.	F Test Conf.	R^2
Aging Temp.	70°C ↑ modulus (50° & 60° not different)	≥ 95%	≥ 99%	0.19
	Higher temp. ↓ peel	≥ 95%	≥ 99%	0.74
Aging Stage	Weak modulus effect	< 90%	98%	0.01
	No effect on peel			
Cure	Curing ↓ modulus	≥ 95%	≥ 99%	0.52

Figure 11 is a graph of nozzle plate peel strength vs. modulus. The data from Experiments #1 and #2 are plotted separately. The ultimate goal of this work was to be able to use adhesive modulus to predict nozzle plate bond strength. There is a good correlation for the data from Experiment #1 (R^2 = 0.88). The correlation for Experiment #2 data however is much weaker (R^2 = 0.12). It is not known why there is such a difference between the two sets of data. Further work is needed to understand these results.

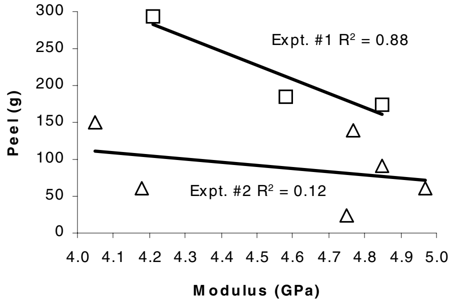

Figure 11 – Peel Strength vs. Modulus

Conclusions

Nanoindentation was used as a way to characterize the effects of aging, curing, PVA coating and washing on the modulus of a phenolic/PVB adhesive that is used to bond a nozzle plate to a heater chip for an inkjet printhead. When combined with XPS data, an aging mechanism of PVB migration to the surface has been demonstrated. The presence of PVB on the surface was associated with low adhesion to the chip. In addition, water extraction of low molecular weight fractions of phenolic resin has been postulated to cause reduction in adhesion. Future work is planned to better determine if modulus as measured by nanoindentation can be useful for predicting nozzle plate adhesion. In addition, more study into the extraction of phenolic resin by water is planned.

References

1. J.M. Mrvos, A. Murthy Proc. NIP14, IS&T, Springfield, VA, 1998, pg. 85.
2. A. Murthy, S.R. Komplin, G.R. Williams, T.H. Jackson, U.S. Patent 6,120,131.
3. G.M. Pharr, “Measurement of Mechanical Properties by Ultra-Low Load Indentation”, Materials Science and Engineering A 253 (1998) pg. 151-159.
4. A. Pocius, *Adhesion and Adhesives Technology – An Introduction*, Hanser, New York, NY, 1997, pg. 226.
5. D. Briggs, M.P. Seah eds., *Practical Surface Analysis, Vol. 1*, John Wiley & Sons, New York, NY (1990).

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 twenty 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 printhead process and materials research for Lexmark. Mr. Mrvos is the co-author of eight issued and eight pending U.S. patents. He is a licensed professional engineer.