Different Systems of Epoxy Adhesives for Use with Ink-Jet Print Head

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Abstract

Epoxy adhesives are commonly used for bonding ink-jet cartridge and silicon base print head. A suitable adhesive provides good ink resistance and bonding strength. Its curing conditions, such as reaction time and temperature, are also limited by the requirement of manufacturing process. We compared the reactive mechanism of three epoxy systems, including epoxy-cationic initiator, epoxy-imidazole and epoxy-polyamine. The differences in reaction time, ink resistance, bonding strength and reaction temperature between these adhesives will also be discussed in this study.

Introduction

In an ink-jet cartridge, the epoxy adhesive is normally used for bonding pen bodies and silicone chips. Many ink-jet pens are made of Polycarbonate (PC) by injection molding. The heat resistance temperature (for continuous use) of PC is about 120°C. Other components, such as air bag in several types of black cartridge, can also be damaged by heat. Therefore, the curing conditions (temperature, time) needed for such adhesive are greatly limited.

Normally, the bonding surfaces of silicone chip and PC cartridge are very smooth, making it difficult for adhesive to have excellent physical bonding. Moreover, the PC material itself is also difficult for normal adhesive to bond with. The property of both bonding surface has to be considered while choosing suitable adhesive in order to reach good bonding strength.

The amount of adhesive applied will also strongly affect the bonding force. Normally, an automatic dispensing machine is used to control this factor. The rheological property is another important parameter for bonding adhesive. The adhesive that easily sags will block the ink slot which stops the ink running out the ink reservoir and then results in cartridge failure.

Another factor which will also cause cartridge failure is the residual air bubble within the adhesive. It will not only decrease the bonding force but, most important of all, cause the ink leakage or color mixing. The air bubble problem mainly results from two reasons: First, fail to perform well degas process during the package of adhesive. This will lead to unstable dispensing or intermittent dispensing. In this case, visible bubble can sometimes be seen within the adhesive. Second, if the air bubble only occurs after curing, this may result from the vaporization of some composition with low boil point. This can be improved by controlling the curing condition or changing the composition of the adhesive.

Another thing need to be considered is the mold release agent, which is used during the injection molding process. The residual mold release agent on cartridge will reduce the bonding force. Therefore, it is essential to clean the cartridge before bonding process.

One of the most important thing about adhesive design is ink compatibility. After filling ink into the cartridge, ink will contact the adhesive layer. The ink contains colorant, organic solvent, surfactant, etc. These chemicals can also interact with adhesive and damage it. In most cases of the adhesive failure, including leakage, color mixing, and chip detachment, poor ink resistance of the adhesive plays an important role.

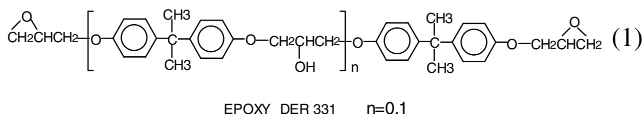
Most adhesives used in ink-jet cartridges are epoxy system. It not only fulfills the requirement of mass production at curing temperature and time (commercial product with 100°C curing temperature at 5 minutes is available) but shows good stability against ink and environment. The epoxy adhesive needs hardener to initiate the cross linking reaction to get required hardness. Therefore, choosing correct hardener system will also affect the hardness, bonding strength and ink resistance of the adhesive. This paper will focus on the performance of epoxy adhesive with different hardener systems.

Experiment

Materials

The epoxy resin used in this study was DER 331, a glycidyl ether of bisphenol A with an average MW of 380g/mol, supplied by Dow Chemical Company U.S.A. The latent epoxy hardeners were modified aryl-sulfonium salt, imidazole and polyamine, and were used as cationic

initiator, anionic initiator and amine hardener in this study respectively. The rheological additive used to thicken the epoxy resin was Aerosil R380, a fused silica produced by Degussa AG Germany. The PC used to produce the cartridge was Calibre 301-15 which is based on bisphenol A, with a melt index of 15, supplied by Dow Chemical Company U.S.A. The chemical structures of epoxy and PC were illustrated below:



(1)

(2)

Push Test

To evaluate the adhesive, we test the bonding force at the interfaces of adhesive, silicon chip, and PC cartridge. The bonding force is measured by a push/pull force gauge and a special design pin, which can go through the ink slot of cartridge to apply normal force on chip.

Environmental Test

Using high temperature and humidity to speed up the test can shorten the time needed to evaluate the adhesive failure caused by ink. Bonded samples are submerged into test ink and put in an environmental test chamber. Take the sample out off the chamber for observing on daily basis to see if there is any leakage, adhesive swollen or chip detachment.

Blending Procedure

The hardener and rheological additive were dispersed in epoxy by roller, and degassed under vacuum for 1hr. These blends were cured for 10min at 100°C.

Results and Discussion

Miscibility of PC in epoxy

The miscibility of PC in epoxy was studied.[1] When PC was dissolved in epoxy resin by the hot-melt method at 200°C for 3hrs, a clear, homogeneous and viscous solution was found. By calculating the solubility parameter components from group contributions which were developed by Hansen,[2] the difference of solubility parameters (δ) of epoxy and PC is very small, explained in Table 1. These phenomena indicated the miscibility of PC in epoxy is good enough to achieve adherence.

Table 1. Solubility parameters of epoxy and PC

	δd	δp	δv	δh	δ
Epoxy	21.48	3.39	21.74	7.63	23.04
PC	22.22	5.66	22.93	6.84	23.93

δd : contribution of dispersion forces
δp : contribution of polar forces
δv : $(\delta d^2+\delta p^2)^{1/2}$
δh : contribution of hydrogen bonding
δ : $(\delta d^2+\delta p^2+\delta h^2)^{1/2}$

Wetting Velocity (Viscosity of Epoxy Adhesive)

The wetting ability of epoxy adhesive on the PC substrate is governed by two parameters: the relative surface tensions of the epoxy and the PC, and the wetting velocity of the epoxy adhesive on the PC substrate.[3] The surface tension of the epoxy is equal to or lower than the surface tension of the PC since they are compatible. Therefore, epoxy and PC could be wettable with each other. Besides, the wetting velocity of epoxy on the PC is influenced by the viscosity of epoxy adhesive. Table 2 reveals the bonding strength of epoxy adhesives with different viscosities. The formulations of these epoxy adhesives are similar. The epoxy with higher viscosity was thickened by fused silica, which will not change the properties of epoxy adhesive. However, The epoxy with higher viscosity has lower bonding strength. This result indicates that the viscosity of epoxy adhesive is an important factor that should be considered.

Table 2. The bonding strength of epoxy adhesives with different viscosities.

	Viscosity (c.P.s)	Bonding Strength (Kg)	Environmental test (day)
Ex-B387	500,000	7.73	7
Ex-B461	100,000	12.40	11

*Color ink was used in environmental test

Specific Physical Interactions

Epoxy resin has specific affinities for PC substrate and can swell and attack it. An interpenetrating of both PC substrates and cured epoxy networks is obtained, the semi-interpenetrating polymer network(semi-IPN)[4] is formed at the interface. This kind of interaction leads to excellent adhesion (Figure 1).

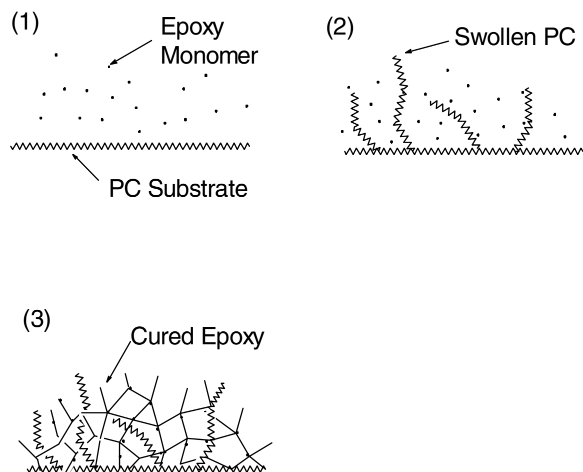
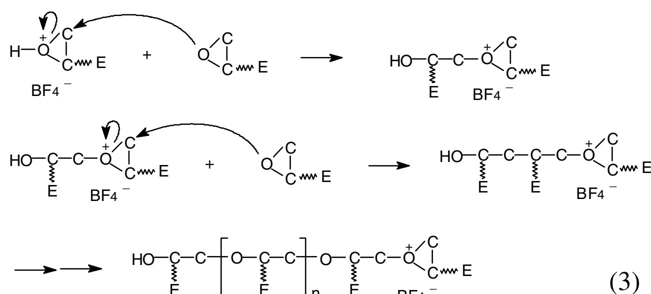


Figure 1. The procedures of forming the semi-IPN structure. (1) The epoxy monomer applied on the PC substrate. (2) The PC substrate swollen by epoxy monomer. (3) The semi-IPN structure obtained during the epoxy curing.

In this research, the first type of epoxy reaction systems, Epoxy-cationic initiator, was used to cure the epoxy adhesive. The curing mechanism of cationic polymerization that initiated by HBF4 is presented as follows (Eq. 3).[5]



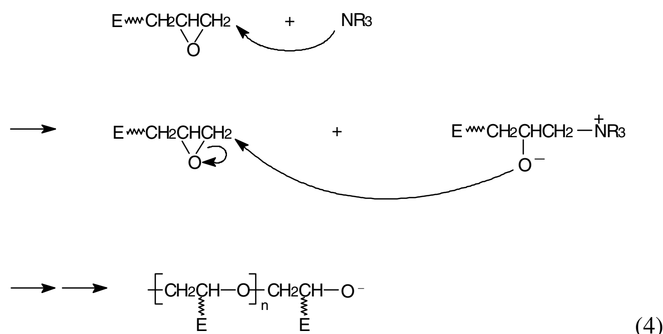
(3)

Our other research demonstrates the PC molecular chain would not participate in the cationic polymerization of epoxy.[6] Thus, the cured epoxy proceeds with cationic polymeriztion and the semi-IPN structure with the PC substrate can be observed.

Specific Chemical Reactions

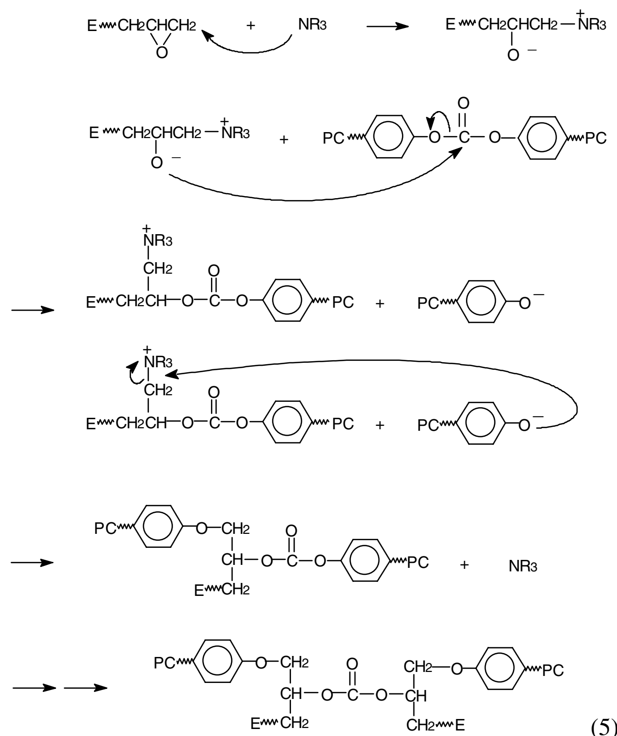
Basically, two major parameters contribute to the thermodynamic work of adhesion: Wetting of the epoxy on the PC and the specific physical interactions between the adhesive and the substrate. This research also investigated other specific chemical reactions appearing in some different epoxy curing systems and PC substrates.

Epoxy-Imidazole is the second type of epoxy reaction systems. Epoxy could be cured by a tertiary amine through the process of anionic polymerization. The mechanism of the curing reaction is illustrated as follows (Eq. 4).



(4)

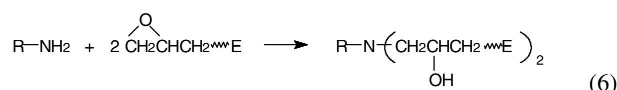
In our previous study,[7] PC-epoxy blends cured by a tertiary amine will appear in a transesterification reaction between epoxy and PC. The transesterification reaction will convert the original carbonate group of PC, between two aromatic nuclei Ar-O-CO-O-Ar, into either one aromatic and one alkyl group Ar-O-C-O-R, or two alkyl groups R-O-CO-O-R. The mechanism of the transesterification is illustrated as follows (Eq. 5).



(5)

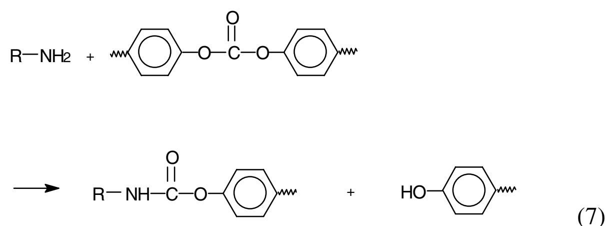
The transesterification occurring between the surface of the epoxy and the PC would insert epoxy structure into PC. In other words, the semi-IPN structure initiated by epoxy monomer will be converted to a cross-linking structure during the curing reaction.

Epoxy-Polyamine, which is usually aliphatic amine, is the third type of epoxy reaction systems. The mechanism of the curing reaction is illustrated as follows (Eq. 6).



(6)

However, various PC-epoxy blends cured by aliphatic amines were studied.[8-10] The aliphatic amine reacts with carbonate of PC to yield carbamates with a much higher rate. The residual amine proceeds the normal curing reaction with epoxy. The mechanism between carbonates and aliphatic amines is illustrated as follows (Eq. 7).



(7)

The transamidation occurring between the PC and aliphatic amine hardener of epoxy during the curing reaction would cause a PC chain scission. In other words, the semi-IPN structure existing in the interface will be destroyed during the curing reaction.

Figure 2 shows the reaction rate of three types epoxy adhesives. Among them, cationic initiator has the shortest reaction time.

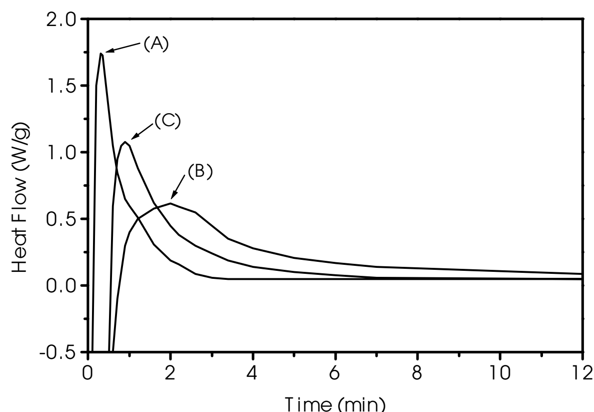


Figure 2. Isothermal runs of DSC at 110°C, Curve A, B and C are cationic, Imidazole and polyamine curing system respectively.

Different types of epoxy adhesives show the different results in bonding strength and environmental test. Table 3 shows that epoxy-cationic initiator system has the strongest bonding strength and high ink resistance.

Table 3. The bonding strength and environmental test results of different types epoxy adhesives.

	Bonding Strength (Kg)	Environmental test (day)
Epoxy-cationic initiator	16.37	44
Epoxy-Imidazole	7.85	5
Epoxy-Polyamine	15.35	27

∗ Color ink was used in environmental test

Conclusion

In this research, different types of epoxy adhesive systems show different bonding performances. According to the experiment results, epoxy-cationic initiator system has the fastest reaction rate and the best ink resistance. This kind of epoxy adhesive system has proved to be the most suitable system for ink-jet print head among three.

In the future, the ink-jet technology will be applied in different industries broadly and different kinds of inks will also be used. Thus, the request for adhesives will be more critical. The better ink resistance for different solution systems is our future goal.

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Biographies

Huen-Ling Chen jointed the Printing Component Department of OES/ITRI in 2001. She received her M.S. from Institute of Chemistry of National Cheng Kung University, Taiwan. Her interest lies in analysis and evaluation of ink and adhesives for ink jet printing.

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Wei-Chum Chao jointed the R&D Department of Everwide Chemical Company in 2002. She received her B.S. in food engineering from Da Yeh University, Taiwan. Her work mainly focuses on the formulations of epoxy used in opto-electronic devices.