

Synthesis of Low Viscosity, Fast UV Curing Solder Resist Based on Epoxy Resin for Ink-Jet Printing

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ABSTRACT: A novel photosensitive low viscosity epoxy resin was synthesized by polyethylene glycol (PEG)-modified bisphenol-A epoxy resin (E51). The resin was modified by ethylene glycol, diethylene glycol, and different molecule weights (200,300,400) PEGs to optimize the minimum viscosity. FTIR was used to determine molecule structure. Cationic photoinitiator (UVI-6976) mixed with modified resin (10 wt %), was utilized to boost the resin curing under UV light. The curing degree was beyond 90% within 40 s and the whole process was monitored by photo-DSC. The modified resin diluted with ethylene glycol diglycidyl ether, was screen printed onto polyimide and polyethylene terephthalate substrate, and the properties of solder mask were up to China printed circuit association standard. The solder resist also meet all requirements under ink-jet printing technology as the viscosity is under 60 mPa·s and the curing duration is <1 min. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 187–192, 2013

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INTRODUCTION

Traditional solder resist or solder mask is the usually green lacquer-like coating that covers the major part of most modern circuit boards. The solder resist consists of various kinds of polymers depending upon the demands of application and it plays a very significant role in the printed circuit board (PCB) manufacture such as preventing solder from bridging, protecting copper traces of PCB, adjusting the amount of solder attachment, reducing the contamination of weld, saving solder, increasing the degree of insulation, adjusting the high density of wiring, avoiding cold solder, and improving the inspection efficiency.^{1–5} With PCB industry growing, ink-jet printing technology emerged and attracted global attention on this new manufacture technology. According to research of association connecting electronics industries (IPC) in 2011, the market of printed and potentially printed electronics is beyond \$2.2 Billion. On the basis of IDTechEx Company's research, the new report "Brand Enhancement by Electronics in Packaging 2012–2022" forecasts that the global demand for electronic smart packaging devices is currently at a tipping point and will grow rapidly from \$0.03 billion in 2012 to \$1.7 billion in 2022. With the development of ink-jet printing technology, traditional solder resist ink cannot meet the requirements of the new technology, especially on viscosity and curing condition. In the meantime, traditional techniques not only waste large amount of raw

materials but also pollute our environment due to subtractive process and inevitable organic solvents.

Traditional solder mask can be divided into four types based on the manufacture procedure, dry film solder mask, thermosetting solder mask, UV curing solder mask, and photoimageable solder mask. The most widely used solder resist is epoxy liquid that is silkscreened through the pattern onto the PCB. Photoimageable solder masks both liquid ink and dry film, are also the main raw materials to fabricate PCB recently. The liquid solder mask can be silkscreened or sprayed on the PCB, exposed to the pattern and developed to provide openings in the pattern for parts to be soldered to the copper pads, while the dry film solder mask is vacuum laminated on the PCB then exposed and developed. The organic solvents mainly ethers and halohydrocarbon are used to reduce the viscosity of epoxy resin as well as achieve much more smooth coating film. However, these organic solvents can be harmful to workers' lung and also damage ozone layer as the halogen atoms decomposed from halohydrocarbon. All three processes go through a thermal cure of some type after the pattern is defined and lots of materials are wasted due to subtractive process. Besides, the screen printing technology as well as the photoimageable technology can only reach 100- μ m linewidth, which anchored the development of high density of PCB. To cope with this problem and achieve higher density interconnector, scientists began to study a brand new technique

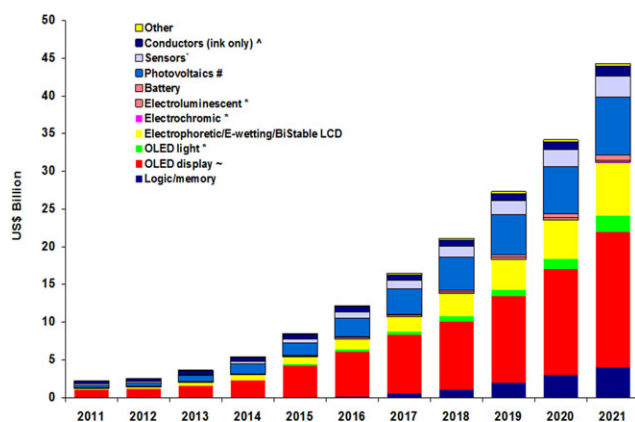


Figure 1. Printed Electronics' market Forecast 2011–2021 from IDTechEx. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

named printed electronics technology in 2003.^{6,7} Organic Electronics Association (OEA) held an organic electronics conference while IDTechEx Company conducted printed electronics conference at the same time in 2003, which stimulated PCB industry giants' interest. Hence, more and more resources and fundings were invested in scientific research institutions and potential market was extremely promising as the international authorities predicted. Figure 1 shows the Printed Electronics' market forecast conducted by IDTechEx Company.

While Printed Electronics' manufactures are totally different from traditional procedures, more requirements on raw materials came out. To ensure the ink can be jetted continually and nonclogging, the viscosity of the ink must be <80 mPa·s and for the sake of controlling the smallest linewidth, the curing of solder mask must be cured before the ink spread on the substrate, so the duration of curing should be <60 s.⁸ Besides, excellent flexibility, adhesivity, and chemical resistance are also obliged.

In this article, we used different molecule weight polyethylene glycol (PEG), such as ethylene glycol, diethylene glycol, PEG200, PEG300, PEG400 to modify the universal epoxy resin E51 to achieve low-viscosity epoxy resin. FT-IR was employed to ensure the modified resin's structure. Various amounts of active dilute were also tested to make sure the viscosity of the solder resist reach the ink-jet printing standard. To reduce shrinkage rate, traditional epoxy acrylate system was aborted and cationic photoinitiator was utilized to activate the curing process. The whole

curing process was monitored by photo-DSC so as to determine the curing duration.

EXPERIMENTAL

Materials

E51 epoxy resin was obtained from Shanghai Xinhua Resin Manufacturing. Diglycol, and different molecule weigh (mw) PEG (mw: 200, 300, 400) were purchased by Sinopharm Chemical Reagent Beijing. Ethylene glycol diglycidyl ether (EGDGE), neopentyl glycol diglycidyl ether (NGDGE), and 1,4-butanediol diglycidyl ether (BGDGE) were provided by Changshu Jiafa Chem, while cationic photoinitiator (UVI-6976) was received by Dow Chemistry. Catalyst boron trifluoride etherate and triethylamine were obtained from Aladdin Reagent (Shanghai, China).

Synthesis

The synthesis scheme of the low viscosity epoxy resin is shown in Figure 2, respectively. First, the E51 epoxy resin and PEG were prepared by vacuum drying for 12 h.⁹ The epoxy resin and PEG were mixed in a four-necked reaction flask equipped with a mechanical stirrer, a cooler, a nitrogen inlet, and a thermometer. Catalyst boron trifluoride etherate was added dropwise into the flask and the amount of catalyst was 1% of the PEG weight. The four-necked flask was put into an oil bath at 80°C . The product was colorless, transparent and good flowability liquid.

In the first experiment, different molecules of PEG (200, 300, and 400) were used to optimize the viscosity. Besides, we also tested ethylene glycol and diethylene glycol to compare the characteristics with the PEG. The epoxy group: hydroxyl group was 2 : 1.

In the second experiment, we tried different molar ratio of E51 : PEG200, measured by epoxy group : hydroxyl group, to achieve not only lower viscosity but also faster curing speed under UV. The molar ratio of epoxy group : hydroxyl group were shown in Table I.

Characterization

The modified resin was dropped onto a potassium bromide tablet and its FTIR was carried out using a Thermo Scientific Nicolet iS10 spectrometer. The NDJ-5s rotational viscometer made by Shanghai Sendi Scientific Instruments was employed to compare viscosities of different modified resin. Because the resins were non-Newtonian fluid, the values of the viscosity varied under different measure conditions, especially at different rotate speed.¹⁰ The parameters of the viscometer must be set exactly the same so we can still prove the variation trend of viscosity

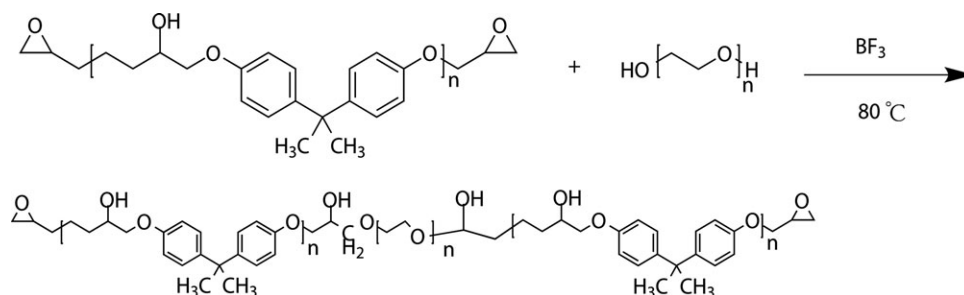


Figure 2. The synthesis scheme of the low viscosity epoxy resin.

Table I. The Molar Ratio of Epoxy Group : Hydroxyl Group

Sample name	Epoxy group : hydroxyl group
1	5 : 1
2	4 : 1
3	3 : 1
4	2 : 1
5	1 : 1
6	4 : 5
7	3 : 5

while different modify agents were used during synthesis. No. 2 rotor, whose rotate speed was set as 12 r min^{-1} was chosen, and all the experiments were conducted at constant room temperature 25°C . The curing process was monitored by Photo-DSC 204 F1 made by NETZSCH-Gerätebau GmbH. The cationic photoinitiator (UVI-6976) was added to the modified resin as the weight ratio of 10%, and then the mixture was dropped into an alumina crucible. The illuminance of the UV optical source was 1 w cm^{-2} and the wavelength was 350 nm. The crucible was exposed under UV light every 3 min at steady temperature 35°C and exposure duration was 10 s. The solder mask was screen printed on the PI and PET films to test its performance under CPCA standard (CPCA/JPCA 4306-2011).

RESULTS AND DISCUSSION

FT-IR Spectrums of E51 and Modified Resin

The FT-IR spectrums of E51 epoxy resin and PEG200 modified E51 resin (epoxy group : hydroxyl group = 2 : 1) were shown in Figure 3. The absorption peak at 1100 cm^{-1} indicates that the PEG was successfully grafted on epoxy resin while the absorption peak at 910 cm^{-1} still remains strong, which indicates that the epoxy group still maintains a relatively high concentration level.¹¹ In fact, hydrochloric acid-acetone method was carried out to determine the epoxy value of modified resin. The epoxy value can still be beyond 0.35, while the epoxy group : hydroxyl group was 2 : 1. The density of epoxy group essentially determined the curing speed and the mask quality, which will be discussed in the

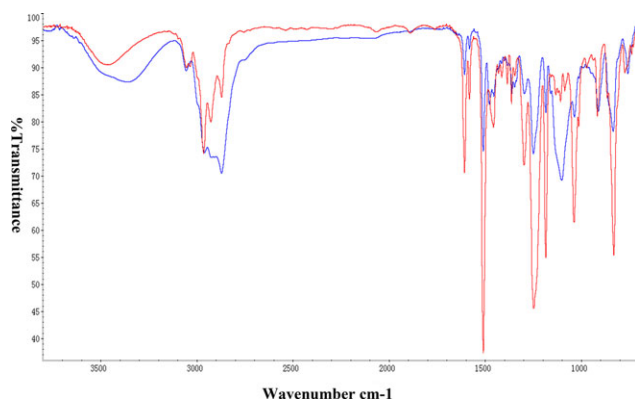


Figure 3. FT-IR spectrums of E51 (red) and PEG modified resin (blue). [Color figure can be viewed in the online issue, which is available at www.onlinelibrary.com.]

Table II. The Epoxy Values of Different Molar Ratio of Epoxy Group : Hydroxyl Group

Sample name	Epoxy group : hydroxyl group	Epoxy value/mol/100 g
1	5 : 1	0.42
2	4 : 1	0.39
3	3 : 1	0.37
4	2 : 1	0.35
5	1 : 1	0.21
6	4 : 5	0.16
7	3 : 5	0.14

later section. The epoxy values of different molar ratios of epoxy group : hydroxyl group was shown in Table II.

The Viscosity Trends with Different Modifying Agents and Various Amount of Dilute

The viscosity of original E51 epoxy resin is more than 10,000 mPa.s. We tried different molecule of PEG as well as ethylene

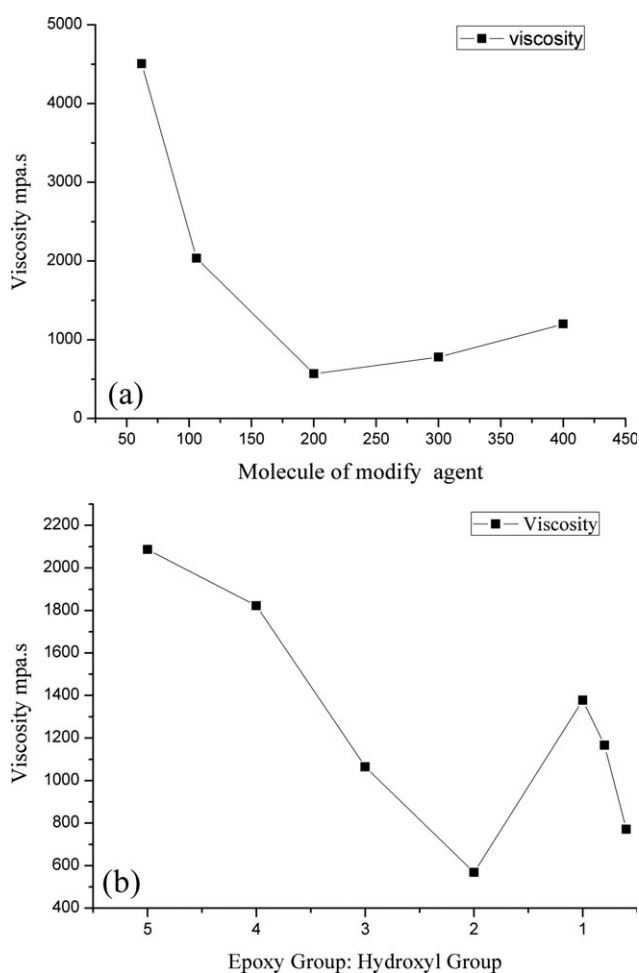


Figure 4. (a) Viscosity of modified resin grafted with different molecule PEG. (b) Viscosity of modified resin grafted to PEG 200 with different molar ratio of epoxy group: hydroxyl group.

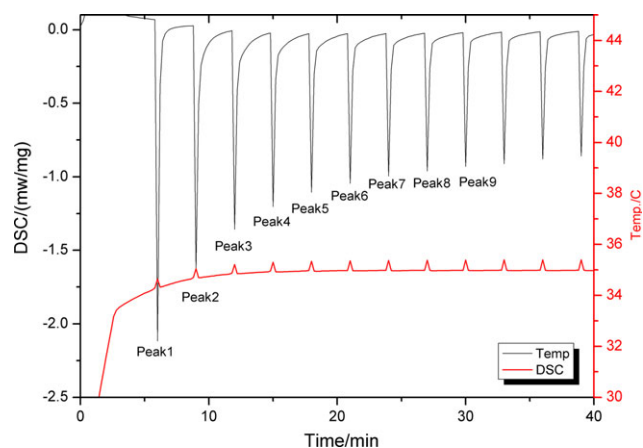
Table III. The Viscosity of Different Molar Ratio of Epoxy Group : Hydroxyl Group Using PEG-200

Sample name	Epoxy group : hydroxyl group	Viscosity/mPa·s
1	5 : 1	2087
2	4 : 1	1822
3	3 : 1	1065
4	2 : 1	568
5	1 : 1	1378
6	4 : 5	1166
7	3 : 5	771

glycol and diethylene glycol, to optimize the viscosity. Figure 4(a) shows viscosity trend of modified resin grafted with different molecule PEG and all the reactions were conducted with the molar ratio of epoxy group : hydroxyl group as 2 : 1. Theoretically, the viscosity of modified resin decreased due to the increasing percentage of flexible chain and the main chain of PEG was flexible aliphatic chain that consisted of numerous C—O and C—C structures. Hence, the viscosity of ethylene glycol, diethylene glycol, and PEG200 modified resin decline because of increasing percentage of flexible chain, while PEG300 and PEG 400 modified resin increased owing to the molecules of resins increase, which will cause chain entanglement. Obviously the lowest viscosity we achieve was the resin grafted with PEG200 from Figure 4(a). Various amounts of reagents measured by molar ratio of epoxy group : hydroxyl group were reacted and another trend of viscosity variation was shown in Figure 4(b) and Table III. With the amount of PEG200 increasing, the percentage of flexible chain increased, which caused the remarkable decline of resin's viscosity from thousands to 560 mPa·s. However, the increasing percentage of flexible chain will increase the molecule of the modified resin and it would cause chain entanglement. Therefore, the viscosity rose reversely as the epoxy group : hydroxyl group reached 1 : 1 (Sample 5). As the flexible chain increased, the major part of the modified resin were PEG not the epoxy resin, whose epoxy group : hydroxyl group was between 3 : 5 and 4 : 5. The viscosity began to decline as the ratio of flexible chain increased, while the molecule weight became a minor factor.^{12,13} Although the viscosity

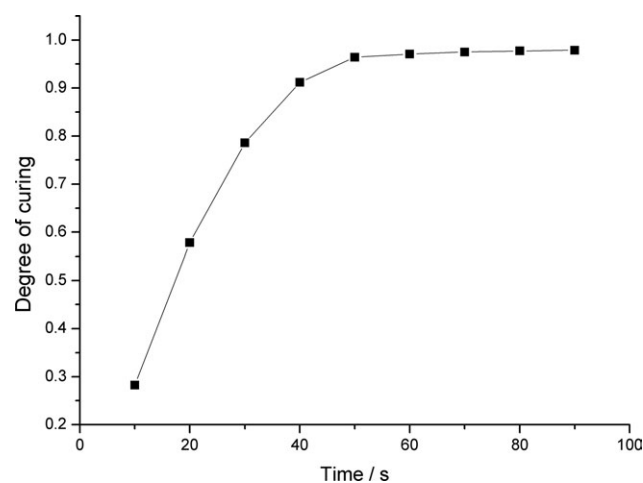
Table IV. The Viscosity of Different Weight Ratio of Dilute with Sample-4

Weight ratio of dilute	Viscosity/mPa·s
0%	568
10%	230
20%	135
25%	80
30%	60
35%	56
40%	54
50%	52
60%	50

**Figure 5.** DSC result of Sample 4 under UV sources. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]**Table V.** The Heat Differential of Each Peak (the Peak Number was Agreed with Figure 5)

Peak	Heat differential/J/g	Reaction heat/J/g	Degree of curing
1	37.30	19.20	28.28%
2	38.17	20.07	57.84%
3	32.19	14.09	78.59%
4	26.66	8.56	91.19%
5	21.65	3.55	96.42%
6	18.53	0.43	97.05%
7	18.40	0.30	97.49%
8	18.28	0.18	97.76%
9	18.19	0.09	97.89%

of Samples 6 and 7 decreased, the end of polymer chain was mainly hydroxyl group and it cannot be completely cured under UV light no matter how much photoinitiator was mixed while other modified resin's curing performance will be discussed in

**Figure 6.** The curing degree of Sample 4.

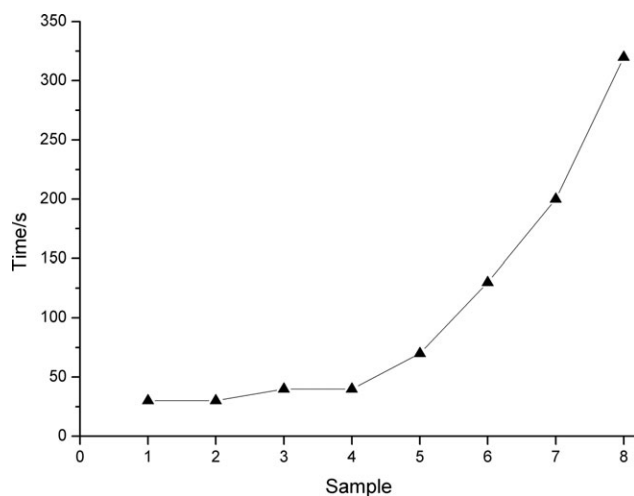


Figure 7. The curing times of different samples.

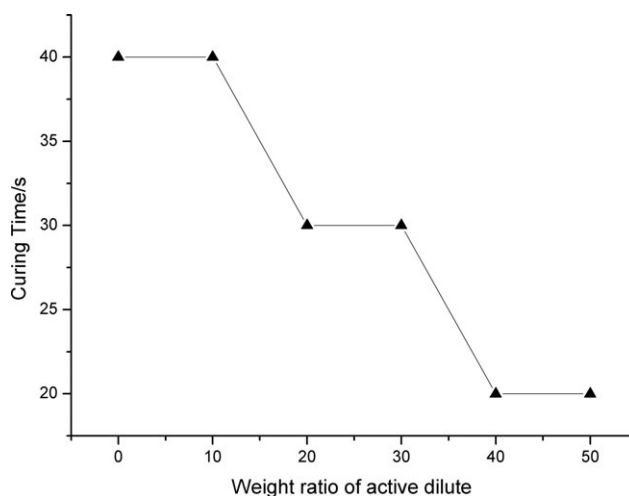


Figure 8. The curing times of Sample 4 with various amount of active dilute.

the later part. Considering viscous requirement, Sample 4 seems the best choice. Hence, EGDGE was used as active solution to dilute the Sample 4. The viscosity was decreased remarkably and the exhaustive results were shown in Table IV. The viscosity can be reduced to about 50 mPa·s while the range of the changing decline gradually. The weight ratio of dilute beyond 30% can fully meet the requirement of ink-jet printing technology.

The Curing Process Monitored by Photo-DSC

Photo-DSC 204 F1 made by NETZSCH-Gerätebau GmbH was employed to monitor the curing process. Figure 5 shows that the DSC curve during the curing process. Because the crucible was under the UV radiation which will cause the heat change, the experiment was not halted until each exothermic peak was almost the same. Each of these accordant peaks (peak 8, 9 etc.) indicates the energy UV radiation generated. And the difference of peak area between the previous peak and accordant peak gives us the heat produced during the exothermic curing reaction.¹⁴ From Figure 5 we can learn that the curing process was completed within 5 pulse of UV radiation, which means that it took only 50 s to cure entirely. All peaks marked in Figure 5 were integrated so that we could calculate the exact heat change during the curing process and the results were shown in Table V.¹⁵ The total release of heat was $\sim 63.5 \text{ J g}^{-1}$. An early study on heat curing process of Bisphenol-A epoxy resin with Diamine proved that the release heat is 110 J g^{-1} ^{16,17} approxi-

mately, whose epoxy value was 0.51. The epoxy value of Sample 4 was 0.35 and the resin weight ratio of solder resist was 90%; so theoretically, the release heat should be $110 \times 0.35/0.51 \times 0.9 = 67.9 \text{ J g}^{-1}$. As Figure 6 shows, the curing degree of Sample 4 was over 90% after 40 s, which will avoid the spread of solder resist ink even the viscosity decline. We believe that with proper jet, the linewidth can reach $20 \mu\text{m}$ in laboratory.¹⁸

We used this method to determine different samples' curing speed and the results in Figure 7 was as we expected that the lower of modified resin epoxy value, the longer time it takes to cure. We also the test Sample 4 with different amount of active dilute and its results was shown in Figure 8, the more dilute was added, the shorter time it takes to cure. From the results mentioned above, the conclusion was when the epoxy value was beyond 0.3, the difference between each samples' curing duration is so subtle that we can use the active dilute to compensate for the curing speed. So, for the sake of curing requirement, the amount of active dilute should be more than 30% and the epoxy value of modified resin should be over 0.3. However, the more active dilute was added to the solder resist, the more brittle curing mask was. This was because the active dilute (EGDGE, etc.) was bifunctional aliphatic alcohol ether-type epoxy molecule whose main chain was short. Thus, the curing film will exhibited brittleness not flexibility. So the best formulation of solder resist should involve 30% active dilute.

Table VI. The Performance of the Solder Masks

Sample	Pencil hardness	Adhesion with flexible PCB	Chemical resistance	Soldering resistance	Insulation resistance (MΩ)
1	2H	Qualified	Qualified	Qualified	530
2	2H	Qualified	Qualified	Qualified	475
3	2H	Qualified	Qualified	Qualified	412
4	3H	Qualified	Qualified	Qualified	380
5	3H	Disqualified	Qualified	Disqualified	292
6	3H	Disqualified	Disqualified	Disqualified	192
7	4H	Disqualified	Disqualified	Disqualified	82

The Performance of Solder Mask

Considering not only the curing request but also the viscosity requirement, the PEG-200 modified resins were chosen as the mask's matrix resin. About 30 wt % active dilute (EGDGE) was mixed with the matrix resin and 10% of UVI-6976 was added as photoinitiator. Then the UV curing solder resist was successfully prepared. The solder resist screen printed on both PI and PET, was exposed under UV optical source with illuminance 1 W cm^{-2} and wavelength 350 nm. All the test experiments were conducted under the CPCA/JPCA 4306-2011 Standard and the results were shown as Table VI. The formula of Samples 1, 2, and 3 may meet the standard but their viscosities could not match the requirement of ink-jet printing. Hence, the formula of Sample 4 was the ideal one for a practical solder resist for ink-jet printing, which exhibited good hardness, flexibility, chemical resistance, soldering resistance, insulation as well as low viscosity and fast curing.

CONCLUSIONS

Low viscosity, fast UV curing solder resist based on epoxy resin for Ink-jet Printing was synthesized and the curing mask has shown great performances under CPCA 4306-2011 Standard. With proper active dilute, the solder resist can meet the requirements of ink jet printing, on both viscosity (lower than $60 \text{ mPa}\cdot\text{s}$) and curing speed (40 s). The UV curing solder resist consist of 60% PEG200 modified epoxy resin (molar ratio of epoxy group: hydroxyl group was 2 : 1), 30% active dilute (EGDGE) and 10% photoinitiator (UVI-6976). Low-cost, materials saving, environment friendly, fast manufacturing and good linewidth of the novel solder resist will drive the printed electronics to higher level to produce more practical devices and the additive process can lead another leap for the PCB industry.

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