

Study on environment-friendly UV-led ceramic ink transfer film

Jingru Jia^{1,*}, Jinhai Zhang²

¹Beijing Institute Of Graphic Communication, 102600 Beijing, China

²Beijing Institute Of Graphic Communication, 102600 Beijing, China

Abstract. UV polyurethane acrylate (PUA-1) oligomer was synthesized and used to prepare the UV-LED ceramic ink transfer film. The effects of active thinner (or active monomer), photosensitizer type, photosensitizer percentage, photosensitizer consumption, etc. on the ceramic ink transfer film performance was studied. The results showed that the prepared PUA prepolymer, single functional group thinner, and the UV-LED curing system consisting of 2,4,6-Trimethyl Benzoyl Diphenyl Phosphine Oxide (TPO), 2,4-Diethyl-9H-Thioxanthen-9-one(DETX) and Reactive Amine (P115) could meet the technical requirements of transfer film.

1 Introduction

The ceramic ink transfer film traditionally contains solvent-type acrylic resin as bonding agent, and is thermally cured by infrared ray. Organic solvent volatilization during curing causes serious air pollution, so the use of ceramic ink transfer film is restricted. UV curing technique rapidly develops because of quick curing, no solvent, environment-friendliness, etc. However, traditional UV curing techniques generally have high energy consumption, high temperature, ozone release^[1], etc., due to use of high pressure mercury lamp or metal halide lamp, etc., and therefore their development is adversely affected. With technology progress, UV-LED curing technique can eliminate the defects of traditional UV curing technique, including high energy consumption, high heat and ozone release^[2,3], and therefore represents the photo curing development trend.

As an optoelectronic device for semiconductor, light emitting diode (LED) converts electric energy to luminous radiation. Compared with traditional light source, LED has the following features: (1) emission of monochromatic light, with very small spectral line width, 5~20 nm; (2) its light output of nearly 100%; (3) low energy consumption; (4) no ozone production; (5) low heat release; and (6) long service life. In the industrial production sector, the LED used for ultraviolet light curing is called UV-LED. UV-LED technique has good development prospect in the light-curing field because of its advancement, economy, environment-friendliness, etc.

UV-LED curing system mainly consists of prepolymer, active thinner, photoinitiator, and aids. Under UV-LED radiation, the photoinitiator in this system absorbs the ray at a wavelength to initiate polymerization of oligomer and active thinner before final crosslinking into a net structure resulting in curing.

Although UV curing technique is convenient, quick, energy-saving, and environment-friendly, the cured film has high hardness, and low flexibility and ductibility. Ceramic ink transfer film is different from ordinary films. During transfer, irregular ceramic surface requires bending, stretching, etc. Thus, the ceramic ink transfer film must have good hardness, flexibility and ductibility. Very flexible polyurethane acrylate (PUA) shall be selected from UV prepolymers. General polyurethane acrylate still fails to reach the requirement of ceramic ink transfer film for flexibility.

In this study, the flexibility and ductibility of ceramic ink transfer film were adjusted by (1) synthesizing the more flexible PUA prepolymer^[4]. According to the data, hydroxy terminated polybutadiene (HTPB) (relative molecular weight: 2000) and polydiol (relative molecular weight: 2000) were used as the skeleton to synthesize polyurethane acrylates. It was found during performance comparison that the PUA with HTPB as skeleton had good flexibility, ductibility and low temperature resistance; (2) selecting an appropriate active thinner to reduce the crosslinking density and enhance the flexibility and ductibility; and (3) selecting an appropriate photosensitizer composition and consumption to control the crosslinking density and curing rate.

2 Experiment

Equipment: UV-LED plane light source PT-75, wavelength of 395nm, made by IGEtec; DRK101B tensile testing machine, made by Shangdong Drick; IMT-NZ01 folding endreanc tester, made by Dongguan City International Material Tester Co., Ltd.

2.1 Flexible Polyurethane Acrylate Synthesis and Performance

* Corresponding author: hellojjajingru@163.com

2.1.1 Main Chemical Materials

Hydroxy terminated polybutadiene(HTPB) : technically pure, imported; Toluene diisocyanate (TDI): technically pure, made by Mitsubishi Group; Dibutyltin dilaurate (DBT): chemically pure, made by Beijing Chemical Factory 3; 2-Hydroxyethyl acrylate: chemically pure, made by Beijing Dongfang Chemical Factory of Beijing Chemical Industry Group Co., Ltd.; paradioxybenzene: chemically pure, made by Shanghai Chemical Reagent Factory 6; Commercial PUA prepolymer samples: SM6206 from Jiangsu Sanmu Group; CR3210 from Huizhou City Changchang Electronic Materials Co., Ltd.; DH316 from Shenzhen Dinghao PhotoChemical Technology Co., Ltd.; Leveling agent JZL-033: technically pure, home-made; Anti foamer: technically pure, home-made.

2.1.2 Experiment Procedure

HTPB was added to a three mouth bottle with a stirrer, thermometer and condenser, and then dibutyltin dilaurate (DBT) (consumption: 0.1%) was added. TDI was dropwise added. The mixture of reactants was heated under nitrogen supply until the reflux occurred. The reaction lasted for about 4 h. The system was cooled to 60°C, HEA was dropwise added, and paradioxybenzene polymerization inhibitor (400 ppm) was added. The reaction lasted for 3-4 h at 60-65°C. The free isocyanic acid group content was determined by di-n-butylamine method. The reaction was terminated when the free isocyanic acid group content is below 0.5%. The resulting product was PUA (PUA-1).

2.1.3 Photosensitizer Selection

Most of the photosensitizers in the market have strong absorbance at 300~370 nm, and poor absorbance above 370 nm. Hence, the emission spectrum of UV-LED curing system does not match with the absorption spectrum of traditional photosensitizers, resulting in a decrease in initiation efficiency of photosensitizers. This problem was solved by selecting many photosensitizers and mixing some of them in this study.

The spectral line of UV-LED had very narrow width, only 5~20 nm, and the light from UV-LED had a long wavelength, generally 395~405 nm. 395 nm was the common wavelength used for UV-LED curing^[5]. Thus, few commercial photosensitizers applied to UV-LED curing. The wavelength used by UV-LED curing machine in this study was 395 nm. The followings were the optional photosensitizers and their maxim absorption wavelength at 395 nm: Isopropyl Thioxanthone (ITX): 382 nm; phenyl bis(2,4,6-trimethylbenzoyl)-phosphine oxide (819): 370 nm; TP0:393 nm; Photoinitiator 651(DMPA): 390 nm; DETX: 384 nm.

According to the data analysis and experimental verification^[6], the cured DMPA film seriously yellowed, and DMPA photolysis products gave out odor, so DMPA was excluded. However, the absorption peak of 819 was far from 395 nm, and the light source at the wavelength of

395 nm had low initiation efficiency. The experiment also verified this presumption. Thus, 819 was excluded.

As a cracking (NorrishI) efficient photosensitizer, TPO especially applied to coloured system and thick-film curing system. However, the use of TPO alone would lead to bad surface curing because oxygen inhibited polymerization; as hydrogen abstracting (NorrishII) photosensitizers, ITX and DETX could avoid polymerization inhibition by oxygen, and were used along with amine potentiating agent, such as P115, etc., to greatly enhance the initiation efficiency. In addition, ITX always yellowed. According to various factors and experimental verification, TPO, DETX, and P115 finally were selected as the photosensitizer composition in this paper.

According to the following formulation, the transfer film was prepared: 15 g of PUA-1, 5 g of Tri(propylene glycol) diacrylate (Diluent TPGDA), 0.2 g of anti foamer + Leveling agent, and 2.2 g of photosensitizer. The reactants were printed on the transfer printing paper by the 100 mesh screen process press, and cured by the UV-LED curing machine. No sign after hand pressure represented complete curing. The curing times were recorded and listed in the table below:

Table 1. Effect of Photosensitizer Composition on the Curing Time.

No.	1	2	3	4	5	6	7
PUA-1, g	15.0	15.0	15.0	15.0	15.0	15.0	15.0
TPGDA, g	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Anti-foamer +Leveling agent, g	0.2	0.2	0.2	0.2	0.2	0.2	0.2
TPO, g	2.2	0.0	1.2	1.0	1.2	1.6	1.8
DETX, g	0.0	2.2	1.0	0.8	0.6	0.4	0.3
P115, g	0.0	0.0	0.0	0.4	0.4	0.2	0.1
Curing time, s	60	60	40	30	12	25	60

The experimental results review: No.1, Bad surface curing; No.2, Bad surface curing; No.3, Bad surface curing; No.4, Good curing; No.5, Good curing; No.6, Good curing; No.7, Bad surface curing.

According to the experimental results, No.6 is the best formula, the photosensitizer consisting of 55% TPO, 27% DETX and 18% P115 was finally selected.

According to the photosensitizer formulation, the effects of photosensitizer content on curing time were studied and shown in Figure 1:

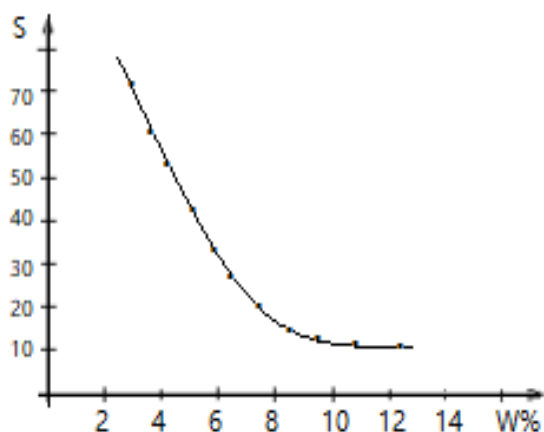


Figure 1. Photosensitizer Content (w%) Vs. Curing Time(s).

The results showed that different photosensitizer contents led to different curing times of ceramic ink transfer film. With increasing photosensitizer content below 9%, the curing time gradually decreased; with increasing photosensitizer content, the curing time did not change significantly. Thus, the photosensitizer content of 8%~9% was selected.

2.1.4 PUA Performance Comparison

The transfer film formulation: 67% PUA; 24% TPGDA; 8.8% photosensitizer; 0.1% leveling agent; and 0.1% anti foamer. The reactants were printed on the transfer printing paper by the 100 mesh screen process press, and cured by the UV-LED curing machine. No sign after hand pressure represented complete curing.

The dried transfer film was tested on its pencil hardness, elongation at break, and folding endurance. The results were listed in the table below. The self-prepared PUA-1 had higher flexibility than the control sample.

Table 2 Effect of Prepolymer Type on Transfer Film Performance.

Sample	PUA -1	SM -6206	CR -3210	DH -316
Transfer film thickness, μm	35	35	35	35
Curing time, s	12	8	10	8
Hardness	H	3H	2H	2H
Folding endurance (at 25°C), times	180	60	80	50
Elongation at break, %	20	5	10	10

2.2 Effect of Thinner Type on Ceramic Ink Transfer Film Performance

At the constant consumption of main resin, PUA, active monomers with varying functionality are generally used to adjust the flexibility of transfer film. The active monomer with higher functionality will provide higher cross linking density, smaller distance between molecular chains, higher hardness and lower flexibility of transfer film, and higher curing rate because of its more functional groups, whereas the active monomer with mono functional group will provide lower cross linking density,

bigger intermolecular distance, higher flexibility and lower strength of transfer film, lower curing rate because of few functional groups, and lower industrial production efficiency. Active monomers with two functional groups are used to enhance the curing rate and strength and those with mono functional group is used to adjust flexibility in order to try to reach both specified flexibility and curing rate considering all the factors, including strength, flexibility, curing rate, etc.

2.2.1 Main chemical materials

PUA-1; bifunctional group thinner (technically pure): TPGDA, 1,6-Hexanediol diacrylate (HDDA); single functional group thinner (technically pure): isodecyl acrylate (IDA), and 2-ethylhexyl acrylate (2-EHA), Isobornyl acrylate (IBOA).

2.2.2 Preparation and Test

Ceramic ink transfer film formulation: 67% PUA-1; 24% thinner; 8.8% photosensitizer; 0.1% leveling agent; and 0.1% anti foamer. HDDA, TPGDA, IDA, 2-EHA and IDOA, were used to prepare five samples.

According to the formulation, five different diluents were used to prepare five ceramic ink transfer films, which were cured, respectively. The curing times were recorded and the ceramic ink transfer films were tested on their pencil hardness, elongation at break, and folding endurance.

Table 3. Effect of Thinner Type on Transfer Film Performance.

Thinner	Curing time	Hardness	Folding endurance, times	Elongation At break, %
HDDA	8	H	130	20
TPGDA	12	H	180	18
IDA	23	2B	600	45
2-EHA	25	2B	500	42
IBOA	16	H	300	30

It could be seen from the above table that bifunctional group thinner had higher curing rate, but low ductibility and flexibility, while single functional group thinner had the best ductibility and flexibility, but lower curing rate. It was recommended that the single functional group, especially IDA, should be selected in practice considering the special requirements of ceramic transfer printing ink for ductibility and flexibility.

3 Ceramic printing decoration process

3.1 Water transfer printing paper

The water transfer printing is a decoration process in which a pattern is printed on a piece of special paper to which watersoluble adhesive is applied, and the paper is soaked and wetted in water before the pattern is transferred to the surface of an article. Water transfer printing paper is mainly used for decoration of irregular surfaces of ceramic, glass, metal, etc. Water transfer printing paper consists of base paper as the lower layer, watersolu-

ble adhesive as medium layer, pattern as the upper layer, and transfer film ink on surface.

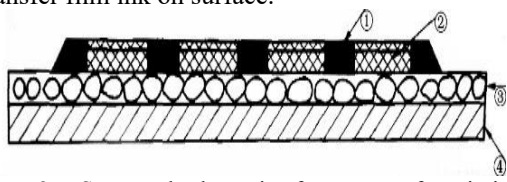


Figure 2. Structural schematic of water transfer printing paper.

- ①transfer film②printed pattern ③watersoluble adhesive layer
- ④absorbent wood paper

A layer of watersoluble adhesive is applied to the surface of 120-180 g/m² very absorbent raw paper. Then a pattern is printed on the watersoluble adhesive layer. Finally, a layer of cover ink is applied to it by screen printing, and dried to form a transfer film, which is called water transfer printing paper.

Water transfer printing paper manufacturing process:
 Base paper → Pattern printing → UV-LED drying → printing by transfer film ink → UV-LED drying → finished product.

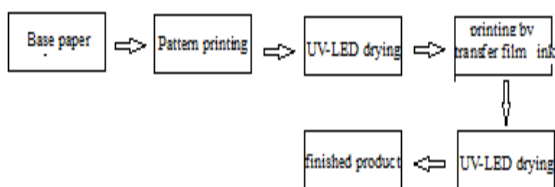


Figure 3. Water transfer paper production process

Water transfer printing paper use method: The water transfer printing paper is cut along the edges of the pattern, and soaked in water until the adhesive is dissolved in water and it is separated from the base paper. It is applied to green ceramic, biscuit or ceramic glaze, flattened by a rubber scraper, naturally aired, and fired at 800~1350°C until the transfer film decomposes and volatilizes at high temperature. Finally, the ceramic ink develops into a color pattern.

Water transfer printing paper quality criteria: (1) During transfer, the cover film has ideal ductibility, high strength and ideal firing effect;(2) The water transfer printing paper has short release time, good gliding property, and no residue after release;(3) No pop and film trace during firing at high temperature. (Pop refers to crack or pinhole in the pattern after firing; film trace refers to residual cover film.)

3.2 Testing of transfer film property

The transfer film ink is made according to the following formulation: PUA-1 67%; HDDA 6%; IDA 18%; photosensitizer 8.8%; leveling agent 0.1%; anti foamer 0.1%.

The release performance and ductibility of the cover film (80 mesh screen printing, 20 μm thick):

Table 4. Release time and elongation at break.

NO	Temperature, °C	Release time, s	Elongation at break (at 25°C), %
1	20	0	
2	25	3	

3	30	42	28
4	35	83	
5	40	90	

The base paper with pattern is printed by cover ink in the 80 mesh screen printing machine, cured by UV, released with water, transferred to ceramic plate surface, naturally aired, kept at constant temperature in a tubular furnace at varying temperature for 40 min, tested on the weight loss percentage at varying temperature, and observed under a magnifier for printing to check crack or pinhole. For the results, see the table below.

Table 5. Volatility of cover film at varying temperature.

Temperature, °C	350	400	450	500	550	600
Volatility, %	3	42	83	90	100	100
Pop	No	No	No	No	No	No

The resulting transfer film has outstanding ductibility, ease to release and aging resistance, and completely volatilizes below 600°C.

4 Conclusion

The self-prepared PUA-I, i.e. polyurethane acrylate oligomer, was used to prepare the ceramic transfer printing ink for UV-LED curing in order to study the photosensitizer composition and consumption and the effects of active thinner type on the cured film ductibility and flexibility. The followings were concluded from the results:

(1) The optimal photosensitizer composition for UV-LED curing at the wavelength of 395 nm consisted of 55% TPO, 27% DETX and 18% P115;

(2) The optimal photosensitizer consumption was 8~9% of total ink mass. With increasing photosensitizer content above 8~9%, the curing rate did not significantly increase;

(3) Among the thinners, multi-functional group thinners had high curing rate, but low ductibility and flexibility. Among single functional group thinners, IDA had the best flexibility and ductibility, but lower curing rate. Therefore, the combination of IDA and HDDA should be used, and the effect is better.

(4) The resulting transfer film has outstanding ductibility, ease to release and aging resistance.

References

- R.W. Stowe, Key Factors in the UV Curing Process-the Relationship of Exposure Conditions and Measurement in UV Process Design and Process Control partII: Lamp Systems.J. Metal Finishing, 4,50(2006)
- S.F. Zhang, Y.S. Ma, W.W Huang, Application of UV-led Technology in number Ink.J. Label Technology, 5,30(2015)
- D.L. Ji , The application and development direction of led in uv printing.J. Printing Field, 5,56(2010)

4. Wu S, Deng J R, Study on high flexibility polyurethane acrylate synthesis and application. *J. Exploration and Research*, 6,1(2004)
5. L. Zhang, Development Trend of UV-led Curing Techniques. *J. Electronic Components and Materials*, 6,99 (2015)
6. K. Jian, D.B. Li, C.Q. Hu, J.L. Yang, Research Progress in Photoinitiator for LED-Curable System. *J. Paint & Coatings Industry*, 10,75 (2016)