Printability Study of Electroluminescent Flexographic Inks

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Abstract. This paper uses Alq3 as the organic electroluminescent material in order to develop a high-performing electroluminescent flexo ink. The effects of single and mixed solvents, single and mixed resins on the viscosity, drying speed, surface tension, contact angle and other important printing parameters of the formulated EL inks were investigated. The results show that high printability can be achieved by using DMF and chlorobenzene as solvents and B-814 resin as link stuff.

Keywords: Formula experiments · Solvent · Resin · Electrofluorescence · Printability

1 Introduction

Organic materials are usually considered insulators. However, with the progress of science, scientists have not only invented organic materials that can conduct electricity, but also found that some organic semiconductor materials can be electroluminescent, which is electroluminescent materials [1]. After more than a decade of development, the performance indicators of electroluminescent materials continue to improve and enhance the market is usually used to produce OLED displays, but in addition, electroluminescent materials can be dispersed in organic solvents because of its characteristics, very suitable for the production of ink, so that the ink in the role of voltage to emit bright colour light, printed with electroluminescent ink, can be adjusted by adjusting the Luminous material and voltage to adjust the luminous colour and brightness, to the printed material to achieve a positive decorative effect. The flexographic printing technology, because it can be printed on large-format devices, printing materials, such as a wide range of advantages, you can print electroluminescent ink in conductive film, the production of electroluminescent printed materials. However, there is no available flexo luminescent ink on the market, therefore, the development of flexo luminescent ink is of critical importance.

Currently available electroluminescent materials can be divided into organic fluorescent materials and organic metal complex materials, with 8-hydroxyquinoline aluminum being a unique metal complex. Since it is able to do the light-emitting layer as well as

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electron transport layer, this material was chosen as the test material [2]. Printability directly affects the hue, saturation, gloss and reproduction effect of the printed material printed with the ink. In this paper, we aim to develop high quality flexo electroluminescent inks. The types and ratios of the key components of the inks - solvents and resins - are used in formulation experiments to carry out the corresponding research work in order to obtain good printability and to obtain electroluminescent inks suitable for flexo printing.

2 Experimental Section

2.1 Experimental Materials

Electroluminescent material: Tris-8-hydroxyquinoline Aluminum (Alq3).

Resin: B-814 resin, AZR resin, polyurethane resin.

Solvents: N-Methyl pyrrolidone (NMP), butyl acetate, o-xylene, N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), methanol, acetone, tetrahydrofuran, propylene glycol methyl ether (PMCAS), butyl acrylate (BA).

Auxiliaries: surfactant 410, surfactant 420, defoamer.

Printed material: ITO-PET film.

2.2 Experimental Equipment

Electronic analytical balance (FA2104N, Shanghai, Jing hai Instruments).

Flexographic proofing machine (FLEXIPROOF100, RK, UK).

Rheometer (AR2000ex, TA Instruments, USA).

Fully automatic surface tension meter (K100, KRUSS, Germany).

Multi-head magnetic heating stirrer (HJ-6, Jin tan, Jin nan Instruments).

Contact angle observer (DSA100, KRUSS, Germany).

2.3 Preparation of Inks

First, the resin needs to be pre-dispersed in a solvent. The resin is added to the organic solvent, placed on a magnetic stirrer and heated and stirred for 30 min to dissolve it completely. Various assistant agents are then added to obtain an electroluminescent ink.

2.4 Ink Performance Test Methods

Viscosity. Select the appropriate rotor for the rheometer according to the viscosity range of the ink to be measured. Take an appropriate amount of ink sample and add it dropwise to the centre of the rheometer measuring table. Adjust the height of the rotor with the software so that the rotor is just cling the ink sample. Then measure multiple viscosities of the ink sample to take an average value.

Surface tension. Mount the platinum plate on the surface tension meter test bench and place the measurement ink sample in the sample tray and then on the sample bench.

Adjust the height of the platinum plate above the sample liquid level and measure using the software's automatic measurement mode.

Angle of contact. Turn on the light source knob of the contact angle viewer and adjust the brightness of the light source according to the image displayed by the computer. Adjust the drip tip so that it appears in the middle of the image. Fill the glass syringe with the ink sample and mount it on the holder. Rotate the micrometer tip so that the liquid flows out and drips onto the glass on the table, measuring the contact angle between the ink sample and the glass. After waiting for 1 s, click on "Capture currently displayed image" to capture the image of the liquid on the solid surface and use the software to measure the contact angle of the liquid on the solid surface [3].

Drying rate. A small amount of ink will be placed in the scraper instrument slot of 100 µm, quickly scrape down, immediately open the stopwatch, after 30 s with a sheet, the lower end aligned with the zero scale, flat against the groove, with the palm of your hand quickly pressed, remove the paper, measure the length of the unsticky ink, expressed in millimetres, that is, the initial drying [4].

3 Results and Analysis

3.1 Influence of Solvents on the Printability of Inks and Their Determination

Prescreening of solvents. The production of electroluminescent inks, of which the electroluminescent material is one of the key components, requires additional considerations. The most basic premise of the solution method of film formation is that the solvent dissolves the solute as fully as possible [5]. The Alq3 electroluminescent material used here is a luminescent material that is insoluble in most organic solvents. Therefore, the solubility of Alq3 needs to be tested first to ensure that the solubility of Alq3 in the chosen solvent can be greater than 5 mg/ml.

Commonly used laboratory organic solvents with different polarities and boiling points were chosen to test the solubility of Alq3 and the final test results are shown in Table 1.

Table 1. Solubility of Alq3 in different solvents

Solvent	Methanol	Ethanol	DMSO	DMF	Chlorobenzene
Solubility	×	×	√	√	√
Solvent	Acetone	NMP	PMCAS	BA	Tetrahydrofuran
Solubility	×	√	×	×	×

As can be seen from Table 1, the solubility of Alq3 in DMF, DMSO, NMP and chlorobenzene meets the requirements and these four solvents can be selected for the preparation of the ink.

Effect of solvents on the printability of inks. Solvents play a role in solvent-based ink systems by dissolving solutes, resins and additives. The type of solvent directly affects the drying speed, surface tension and viscosity of the ink. And, in electroluminescent ink systems, the solvent evaporation process directly affects the thickness uniformity of the film and thus the luminescent properties of the printed electroluminescent ink [6]. According to the above screened solvents, the corresponding samples of electroluminescent inks were prepared. Their viscosity, surface tension, contact angle drying speed and other printability were measured, as shown in Table 2.

Table 2. Properties of electroluminescent ink samples prepared with different solvents

Solvent	Viscosity (Pa s)	Surface tension (mN/m)	Angle of contact	Drying rate (min)
DMF	0.79	22.41	15	3
DMSO	1.98	23.78	20	3
NMP	1.65	22.96	24	5
Chlorobenzene	0.36	20.43	23	1

As can be seen from Table 2, different solvents contribute differently to the various printing indicators of electroluminescent inks. DMF has the smallest contact angle, which facilitates the spreading of the ink on the substrate; chlorobenzene has the lowest boiling point, so the fastest drying speed and good film formation; the most suitable viscosity range for flexographic inks is 0.1–2 Pa s, and NMP has a moderate viscosity, which is conducive to ink transfer.

Determination of solvents. In order to obtain the best overall performance of the electroluminescent ink, the formulation test was used to design a mixed solution formulation. The number of solvents selected was m = 4. DMF was designed as x1, DMSO as x2, NMP as x3, chlorobenzene as x4. 15 solvent ratios were designed according to the simple gravity method. The designed experimental sequences and solvent ratios are shown in Table 3.

Since m = 4, the regression equation is as follows:

$$\begin{aligned} y = {} & \mathrm{b1x1} + \mathrm{b2x2} + \mathrm{b3x3} + \mathrm{b4x4} + \mathrm{b12x1x2} + \mathrm{b13x1x3} \\ & + \mathrm{b14x1x4} + \mathrm{b23x2x3} + \mathrm{b24x2x4} + \mathrm{b34x3x4} \\ & + \mathrm{b123x1x2x3} + \mathrm{b124x1x2x4} + \mathrm{b134x1x3x4} \\ & + \mathrm{b234x2x3x4} + \mathrm{b1234x1x2x3x4} \end{aligned} \tag{1}$$

According to Table 3, prepare the electroluminescent ink and test the printing properties as shown in Table 4. According to the comprehensive analysis of the needs of electroluminescent inks, the viscosity of the ink, surface tension, contact angle, and drying speed of four important parameters are set at 0.3, 0.2, 0.1, and 0.4. The best viscosity is not a specific value, but from the range in which it is determined. Therefore the viscosity indicators are first rated and then, together with the other indicators, the

Table 3. Ratio of solvents

Experimental serial number	X1	X2	X3	X4
1	1	0	0	0
2	0	1	0	0
3	0	0	1	0
4	0	0	0	1
5	0.5	0.5	0	0
6	0.5	0	0.5	0
7	0.5	0	0	0.5
8	0	0.5	0.5	0
9	0	0.5	0	0.5
10	0	0	0.5	0.5
11	0.33	0.33	0.33	0
12	0.33	0.33	0	0.33
13	0.33	0	0.33	0.33
14	0	0.33	0.33	0.33
15	0.25	0.25	0.25	0.25

data are processed. This is doneate the index affiliation of each performance indicator and the overall score for each formulation.

According to the weights given for calculating the composite score y obtained by the ink, and putting y, x1, x2, x3, x4 into the formula (1), to get 15 fourth-order regression equation. The regression equation can be solved by combining the regression equation of the overall performance of the electro-luminescent ink.

$$\begin{aligned} y = {} & 0.77\text{x1} + 0.64\text{x2} + 0.59\text{x3} + 0.78\text{x4} + 0.005\text{x1x2} - 0.008\text{x1x3} \\ & + 0.03\text{x1x4} - 0.016\text{x2x3} + 0.065\text{x2x4} - 0.095\text{x3x4} + 0.208\text{x1x2x3} \\ & - 0.536\text{x1x2x4} - 0.345\text{x1x3x4} - 0.445\text{x2x3x4} - 3.15\text{x1x2x3x4} \end{aligned} \tag{2}$$

Through the programming solver can be obtained, when x1:x2:x3:x4 = 0.48:0:0:0.52, with DMF and chlorobenzene in the ratio of 0.48:0.52 resulting in the best performance of electroluminescent ink.

3.2 Effect of Resin on Ink Performance

The resin, as the linking material of the ink, plays a major role in connecting and allowing the ink to flow evenly during the transfer process, which can have a large impact on the viscosity and drying time of the ink. Three resins, B-814 resin, AZR resin and polyurethane resin, were selected to prepare samples of electroluminescent inks. The viscosity, surface tension and drying speed of the ink samples were tested and the results are shown in Table 5.

Table 4. Properties of electroluminescent ink samples prepared with different samples

Experimental serial number	Viscosity (Pa s)	Surface tension (mN/m)	Angle of contact	Drying rate (min)
1	0.79	22.41	15	3
2	1.98	23.78	20	3
3	1.65	22.96	24	5
4	0.36	20.43	23	1
5	1.41	22.47	15	3
6	1.26	22.45	18	4
7	0.52	20.89	18	2
8	1.86	23.14	22	4
9	1.03	21.19	21	2
10	0.85	21.07	24	4
11	1.27	23.09	21	4
12	0.84	23.05	20	3
13	0.73	21.88	22	4
14	1.13	22.86	23	4
15	1.09	22.39	22	4

Table 5. Properties of ink samples made of different resins

Experimental serial number	X1	X2	X3	Viscosity (Pa s)	Surface tension (mN/m)	Drying rate (min)
1	1	0	0	0.57	21.14	2
2	0	1	0	0.63	21.49	6
3	0	0	1	0.84	22.94	8

As can be seen from Table 5, there is little difference in surface tension and viscosity between the samples prepared from the three resins. The content of the resin in the ink system is much lower than that of the solvent and the surface tension and viscosity are more influenced by the solvent. The resin is not the decisive factor for surface tension and viscosity in the ink system. Of the three different types of resin, B-814 is the fastest drying, AZR is moderate and polyurethane is the slowest. This is because the B-814 resin is more soluble in the solvent and therefore the solvent evaporates more easily and dries faster.

It was concluded that the most effective performance of the electro-luminescent ink was obtained by using only B-814. Consequently, it is preferable to use only B-814 resin in the experiments.

3.3 Printability of the Developed Electroluminescent Flexographic Ink

Through the above experiments, the main properties of the inks were tested by making the corresponding ink samples according to the best solvent-based ink formulations obtained. The data are presented in Table 6.

Table 6. Performance of Ink sample after formulation optimization

Solvent	Resin	Viscosity (Pa s)	Surface tension (mN/m)	Angle of contact	Drying rate (min)
DMF:chlorobenzene = 0.48:0.52	B-814 resin	0.51	20.84	18	2

According to the data in Table 6, it can be seen that after the formulation test to study the suitability of electroluminescent ink printing is optimal.

4 Conclusion

In the solvent-based electroluminescent ink system, the solubility of different solvents for electroluminescent materials varies greatly, and the solvents have an effect on the viscosity, surface tension, drying speed and contact angle of the ink, and the prepared electroluminescent ink samples have optimal performance when the ratio of DMF and chlorobenzene is 0.48:0.52.

The resin in the solvent-based electroluminescent ink system mainly affects the drying speed of the ink, and has little effect on the surface tension and viscosity of the ink. The ink samples formulated with B-814 resin have better drying speed than those formulated with AZR resin and polyurethane resin, and the overall performance of the prepared ink samples is good.

The developed electroluminescent flexographic ink has good printability.

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