Eco-friendly NMP Free Polyimide for AMOLED Display Substrate

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Abstract

NMP (N-Methyl-2-Pyrrolidone) is a liquid material at room temperature and is widely used in PI (Polyimide) solvent material, PR stripper, and mask cleaning required for OLED manufacturing process. However, the issue of reproductive toxicity disease has been raised in the field of ESG management and environmental safety, and it is necessary to develop materials and processes to replace NMP in the near future. In this study, we developed DMPA (N,N-Dimethylpropionamide) cosolvent as an eco-friendly solvent that does not contain NMP in the PI solution for OLED flexible substrate material. The properties of DMPA (N,N-Dimethylpropionamide) cosolvent PI have similar results of the conventional NMP PI. We applied this new PI to the OLED backplane panel and resulted in reliable low-temperature polysilicon (LTPS) TFT characteristics with robust OLED panel. It is very meaningful that we developed the world's first eco-friendly OLED flexible substrate material and panel.

Author Keywords

NMP free; Polyimide substrate; Cosolvent; Film characteristics; LTPS TFT; Panel reliability; Eco-friendly flexible OLED substrate

1. Introduction

During the OLED display manufacturing process, NMP solvent is used in various processes due to its excellent cleaning power, solubility, and reactivity. NMP is classified as a reproductive toxicant, and industrial accident claims by workers handling it. In addition, the customer disclosed the "Regulated Substances Specification" environmental report in 2023 as shown in Table 1, mentioning NMP as one of the seven major substances that can be regulated in the future. [1] Therefore, it is necessary to develop materials and processes to replace NMP in the near future.

Chemical	CAS No.	Future Restrictions
Ethylbenzen	100-41-4	Expect future restrictions
Formaldehyde	50-00-0	Expect future restrictions
Hydrogen Fluoride (HF)	7664-39-3	Expect future restrictions
Methanol	67-56-1	Expect future restrictions
N-Methylpyrrolidone (NMP)	872-50-4	Expect future restrictions
Tolune	108-88-3	Expect future restrictions
Xylene	1330-20-7	Expect future restrictions

Table 1 : Future Restrictions in Manufacturing Processes

In this study, we investigated several candidate materials without NMP and found that ketone (>=o) [2] is very crucial for the bonding between the PI monomer and the solvent. Figure 1 shows the chemical structure of solvent with ketone, and DMPA cosolvent composition has been proven to be the most suitable as an eco-friendly solvent for PI, when considering solvent solubility related to Hansen Solubility Parameter (HSP), and volatility related to boiling point. The following equations mean the formula and thermodynamic definition for HSP. Equation (1) means that dissolution between polymer and solvent progresses only when the Gibbs free energy of mixture (ΔGm) is negative, and that solubility can be improved only when mixing enthalpy (ΔHm) is small. Mixing enthalpy (ΔHm) in equation (2) is defined as a function of the solubility parameters (δ1, δ2) of the polymer and solvent. The closer the two values are, the lower the mixing enthalpy (ΔHm) can be. Therefore it improves the solubility between polymer and solvent. (Like dissolves like principle) [3] This is ultimately summarized in equation (3), where the dissolving power is expressed as the sum of the squares of dispersion force (δd), polar force (δp), and hydrogen bonding force (δH). Figure 2 is a graph theoretically analyzing the Hansen Solubility Parameter of BPDA (3,3',4,4'-biphenyltetracarboxylic dianhydride) - PDA (p-Phenylene diamine), which increases to level 21 as the number of polymer units increases. [4]

$$\Delta Gm = \Delta Hm - T\Delta Sm < 0 \quad (1)$$

Δ Gm : Gibbs free energy of mixture, Δ Hm : Mixing enthalpy,
T : Temperature, Δ Sm : Mixing entropy

$$\Delta Hm = \emptyset_1 \emptyset_2 [\delta 1 - \delta 2]^2 * Vm \quad (2)$$

$\emptyset_1$: Polymer volume fraction, $\emptyset_2$: Solvent volume fraction
δ_1 : Solubility parameter of polymer, δ_2 : Solubility parameter of solvent

$$\delta^2 = {\delta_d}^2 + {\delta_p}^2 + {\delta_H}^2 \quad (3)$$

δ_d : Dispersion force, δ_p : Polar force, δ_H : Hydrogen bonding force

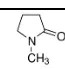
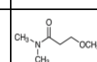
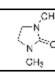
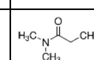
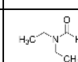
Solvent	NMP	MPA	DMI	DMPA	DMPA cosolvent	DEF
Structure					← + α	
Molecular Weight	99.13	131.18	114.15	105.15	-	101.15
Hansen Solubility	22.96	22.5	23	20.78	21.4	24.8
Boiling Point (℃)	202	215	222	176	187	177.5
Freezing Point (℃)	-24	-80	+8	-45	-38	-61

Figure 1 : The properties of NMP free solvent candidates

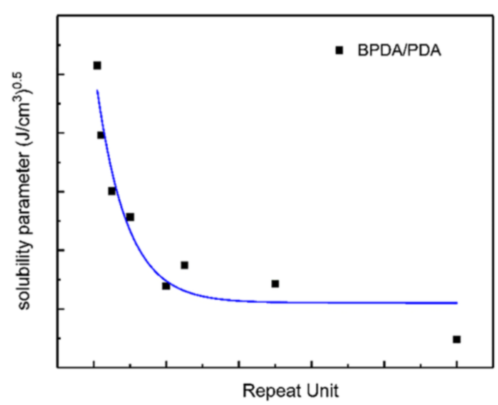


Figure 2 : PI BPDA-PDA Monomer solubility parameter

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2. PI solubility and film characteristics

PI experiments with DMPA cosolvent were implemented in laboratory scale. Figure 3 shows the results of a reactivity experiment between the solidified residues inside the PI coater and various solvents. As explained in Figure 1, the HSP of DMPA alone is 20.78, and this value is similar to PI residue 21 composed of BPDA-PDA in Figure 2. Therefore, theoretically we predict that DMPA alone will be able to dissolve and remove PI residues (BPDA-PDA) better, and lab experiments also show that DMPA alone conditions are more likely to dissolve and remove PI residues in Figure 3. At the same time, DMPA cosolvent has an HSP value of 21.4, which is relatively larger than the HSP of PI residue 20.78 and close to the HSP of NMP which is 22. As considering HSP value, DMPA cosolvent shows similar dissolving and separation (swelling) abilities to NMP in Figure 3.

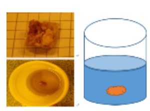
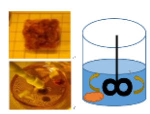
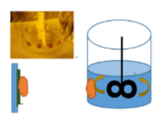
	Dipping (3hr)	**Stirring (30rpm)**	**Swelling (0.2g, 10ea, 30rpm)**
NMP	1.33 → 0.26g	Dissolved @4hr	10 → 0 @4hr
DMPA	1.33 → 0.03g	Dissolved @2hr	10 → 0 @2hr
DMPA cosolvent	1.33 → 0.19g	Dissolved @4hr	10 → 0 @4hr
Experiment			

Figure 3 : PI solubility experiments with various solvents

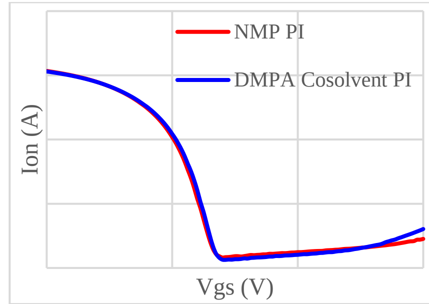
DMPA cosolvent PI with a thickness of 10μm was produced by Gen2-sized slit coater, HVCD, and 470℃ furnace, and then film properties were compared with mass-produced NMP PI. Figure 4 shows the relative comparison values between two samples. It can be confirmed that the transmittance, thermal resistance, CTE (coefficient of thermal expansion), absorption/moisture permeability, and mechanical properties are almost similar.

Relatively Comparison	**NMP PI (Reference)**	**DMPA cosolvent PI**
PI Imidization	100 %	97 %
Transmittance (450 / 550nm)	100 % / 100 %	97% / 103%
Thermal Resistance	100 %	100 %
Absorption / moisture permeability	100 % / 100%	75% (Better) / 100%
CTE	100%	9.8% (Best)
Adhesion	100%	105% (Better)
Modulus / Elongation	100% / 100%	115% (Better) / 100%

Figure 4 : PI film properties with NMP and DMPA cosolvent PI

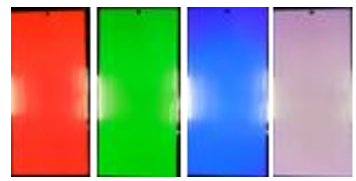
3. LTPS TFT Characteristics and Panel Reliability

OLED panel with DMPA cosolvent PI was optimally processed to get the reliable I (load)-V (output) curve as shown in Figure 5. Then, RGB luminance was analyzed to be relatively reliable in case of DMPA cosolvent PI. After manufacturing OLED module with DMPA cosolvent PI, A harsh environmental reliability test was conducted under 85°C, 85% RH (Room Humidity) conditions to 500hr, and finally RGB luminance also performed equivalent to that of NMP PI.



(a)

PI	Red	Green	Blue
NMP PI	100 %	100%	100%
DMPA cosolvent PI	95 %	92%	103%



(b)

Figure 5 : (a) I-V curve with NMP PI and DMPA cosolvent PI, (b) OLED RGB luminance with DMPA cosolvent PI

4. Conclusions

DMPA cosolvent material, an eco-friendly new solvent that replaces NMP solvent, was developed considering solvation and volatilization characteristics. Especially, PI coating process was optimized to achieve PI properties equivalent to mass-produced colored NMP PI. Afterwards, backplane, evaporation, encapsulation, cell, and module processes were carried out normally using the research line model to fabricate OLED panel. R, G, B, W, and DC device characteristics were confirmed to be equivalent to mass-produced colored NMP PI. Device and environmental reliability test resulted in same level as mass production. By applying DMPA cosolvent material that is NMP free to flexible OLED substrate, we developed the industry's first OLED panel using eco-friendly PI substrate.

5. Acknowledgments

The author gives heartfelt to thanks to SDC engineers in A-advanced research and process research teams for their technical support and helpful discussion for this work.

6. References

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