Preparation of Color Filter Photo Resists for Generating Color Pixels in Liquid Crystal Displays by Synthesis and Applications of Polymeric Binders

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Color filter photo resist (CFPR) is a key material for manufacturing color filters of LCDs, which consist of additives such as pigments, binders, multi-functional monomers and surfactants.^{1,2,3,4,5} Among these additives, this study focused on binders that affect development time, pattern clarity, heat and chemical resistance.^{6,7,8} In addition, this study was carried out based on several purposes. First, introductions of new binders have been requested due to the recent trend of red pigments; that is, a dieketo-pyrrolo-pyrrole with a smaller particle size and less polarity for a high contrast ratio is desired. The pigments for a high contrast ratio usually have a particle size in the range of 40 -60 nm, while conventional pigments of anthraquinone have a particle size of approximately 90 nm. For this reason, less polar styrene was introduced to increase affinity by replacing or reducing benzyl methacrylate. Traditionally, a binder prepared from benzyl methacrylate and methacrylic acid has been widely used. Second, introductions of less expensive materials, such as styrene and methyl methacrylate, have been requested to contribute to the extreme competiveness of the LCD industry. For this study, styrene, methacrylic acid, methyl methacrylate and benzyl methaceylate were employed to synthesize the random copolymer into polymeric binders, as shown in Figure 1.



R = CH₂Ph, CH₃



Table 1. Characteristics of the synthesized polymeric binders

Finally, CFPRs were prepared from these binders to evaluate their properties.

The polymeric binders were synthesized by the usual method, using a IPA solvent and an AIBN (2.2'-Azobisisobutyronitrile) initiator under nitrogen purging at a concentration of approximately 30%.

The average molecular weights of the polymeric binders measured using GPC are listed in Table 1, with values ranging between 47,000 - 110,000 g/mol. The polymeric binder solutions were used without isolation for CFPR preparation, and concentrations of each polymer in the prepared solutions, measured by oven drying, showed a range of about 28%.

The CFPRs were prepared in the traditional manner, employing dispersed pigments, polymeric binders, multifunctional monomers, photo initiators, surfactants and solvents.⁹ The prepared CFPRs and their properties for the development processes are listed in Table 2.

First, the relationship between binders and the clarity of patterns was researched. The optimal properties for the development process should not give rise to remainder or exfoliation.

Table 2. Type, quantity and development time of binders for preparing CFPRs

CFPR No.	Binder	Binder solution content (%)	Developing time (start point/sec)
PR-1-1	BI-1	2	30
PR-1-2	BI-1	3	23
PR-1-3	BI-1	4	17
PR-2-1	BI-2	2	29
PR-2-2	BI-2	3	26
PR-2-3	BI-2	4	21
PR-3-1	BI-3	2	30
PR-3-2	BI-3	3	26
PR-3-3	BI-3	4	23

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Dindar	Component	Monomer ratio (w/w %)	Average molecular weight (g/mol)		
Dilidei			Mn	Mw	PDI
BI-1	Styrene/methacrylic acid	54.7/45.3	21,500	47,300	2.20
BI-2	Styrene/methacrylic acid/methyl methacrylate	33.3/45.3/21.4	31,600	106,100	3.36
BI-3	Styrene/methacrylic acid/benzyl methacrylate	33.3/45.3/21.4	21,000	94,100	4.48

Mn: number averaged molecular weight, Mw: weight/averaged molecular weight, PDI: polydispersity (Mw/Mn).

Notes



Figure 2. Micrographs of patterns generated on glass after the development process: (a) PR-1-1(BI-1 2%), (b) PR-1-2 (BI-1 3%), (c) PR-1-3 (**Bi-1** 4%), (d) PR-2-1 (**Bi-2** 2%), (e) PR-2-2 (**Bi-2** 3%), (f) PR-2-3 (**Bi-2** 4%), (g) PR-3-1 (**Bi-3** 2%), (h) PR-3-2 (**Bi-3** 3%), (i) PR-3-3 (**Bi-3** 4%).

Micrographs were taken and are shown in Figure 2. The size of the entire pattern was 2×2 mm, and the inner rectangular bars were typically $40 \times 400 \ \mu m$.

As shown in Figure 2, all CFPRs containing 3% binder solution showed excellent properties, with no remainder and no exfoliation. The CFPRs containing 2% binder solution had some remainder and exfoliation, regardless of the binders used, while the CFPRs containing 4% binder solution showed no remainder, but did show severe exfoliation.

It can be concluded from our research that 3% binder solution is optimal for the desired results. In addition, we can conclude that less binder solution (2%) results in a remainder due to the lack of carboxylic acid, which is washable via an alkali developer, and simultaneously results in exfoliation owing to the lack of adhesion caused by the decrease in quantity. Larger quantities of binder solution, about 4%, result in severe exfoliation of patterns, as shown in Figure 2. It was thus determined that the role of the binder is crucial for generating pixel patterns through control of both washability and adhesion forces. Second, binders can also affect development time; latent pattern images usually appear after about 20 seconds when treated with alkali-developer, while the entire process of development should finish within a minute. The start point in Table 2 refers to the time it takes a pattern image to appear, and the development times of each CFPR are listed in Table 2. All CFPRs showed variable starting points depending on the quantity, but not the type of, binder. The CFPRs containing 2% binder usually started at about 30 seconds, while the CFPRs containing 3% binder started ideally at approximately 20 seconds and those containing 4% binder solution started at less than 20 seconds, but produced severe exfoliation, as discussed previously. It was found that the addition of 3% binder solution provided the best results in

35 33 -BI-2 31 🛨 BI-3 29

Relationship between binder quantity and developing time



Figure 3. Relationship between binder quantity and development time.

both pattern clarity and development time.

As expected, pattern images appeared quickly depending on the quantity of binder used. Figure 3 clearly shows the relationship between binder quantity and development time, as discussed above.

In addition, the binding force of binders can also affect color properties, as this force plays an important role in preventing color changes of pigments via sublimation or decomposition. If sublimation or decomposition takes place, color change will occur. However, good binders minimize this color change, which is evaluated by a ΔE value of CIE xy color coordination. This property is heat resistant and was tested by treating the test materials at 250 °C for 1 hour. In addition, chemical resistance to isopropyl alcohol (IPA) and N-methylpyrrolidone (NMP) was tested by dipping the test materials in the above chemicals at 25 °C for 30 minutes. Color differences were recorded in the same manner as heat resistance results; the results of the heat and chemical resistance tests are represented in

Table 3. CFPRs' resistance to heat and chemicals

CFPR	Heat resistance $(\Delta E, 250 \text{ °C/1 hr})$ –	Chemical resistance (ΔE, 25 °C/30 min)		
		NMP	IPA	
PR-1-1	4.9	3.6	2.7	
PR-1-2	4.4	3.2	2.1	
PR-1-3	3.5	2.7	1.6	
PR-2-1	3.6	3.5	2.0	
PR-2-2	3.0	2.9	1.6	
PR-2-3	2.6	2.4	1.1	
PR-3-1	3.8	3.4	1.9	
PR-3-2	3.3	3.1	1.6	
PR-3-3	2.9	2.9	1.3	





Figure 4. Relationship between binder quantity and resistance properties.

Table 3.

Table 3 shows that an increase in binder quantity improved heat and chemical resistance. PR-1-2 with 3% **BI-1** binder solution gave a ΔE value of 4.4 for heat resistance, while PR-2-2 and PR-3-2 containing 3% binder solution gave improved ΔE values of 3.0 and 3.3, respectively. Tests of chemical resistance to NMP showed similar performances depending on the quantity of binder utilized. For example, PR-1-2 was 3.2, PR-2-2 was 2.9 and PR-3-2 was 3.1 ΔE . In addition, resistance property to IPA also showed a similar trend, commensurate with the quantity of binder used. PR-3-2 showed the best result, with 1.6 ΔE . Figure 4 clearly indicates that resistance improves with an increase in binder quantity, but for pattern clarity, a 3% binder solution is optimal. All binders showed similar performance in chemical resistance and heat resistance except binder **BI-1**, which had poor heat resistance.

It was determined that the newly designed binders in this study were very useful for preparing CFPRs in terms of pattern clarity, development time and heat and chemical resistance. As expected, the binders containing styrene were quite suitable for the red pigment, a less polar diketo-pyrrolo-pyrrole with a smaller particle size for a high contrast ratio. Additionally, if these polymeric binders were applied commercially, they would provide improved price competitiveness due to their use of inexpensive materials such as styrene. All binders containing styrene showed acceptable performance; in particular, **BI-2** had the best heat and chemical resistance properties. It was speculated that a molecular weight of above 100,000 g/mol gave rise to the better resistance properties. We can draw the conclusions that the polymeric binders newly designed are suitable for the diketo-pyrrolo-pyrrole pigment with fine particle shape. The polymeric binders containing styrene and methyl methacrylate showed good performances as expected in terms of development time, pattern clarity, heat and chemical resistance for the use of LCD color filters.

Experimental Section

Equipments. Data of color difference (ΔE) and CIE xy value were measured using an MCPD 3700 (spectrophotometer specially designed for LCD colour filter, Otsuka electronics, Japan). A spin-coater (Sungwon electronics, Korea) was used for coating of CFPR on glass substrates. Thickness of coated materials on glass was measured using a profiler (alpha-step IQ, KLA-tencor, USA). A photo mask aligner (MDE-400, Midas system Co., ltd., Korea) was used for UV-curing of CFPR. GPC (ACME 9000, Young Lin instrument Co., ltd., Korea) was used for measuring average molecular weight. The pigments selected were specially designed for LCD colour filters by their manufacturers.

Preparation of CI Pigment Red 254 paste. 15 g CI Pigment Red 254 (Ciba Specialty Chemicals) was stirred into 15 g dispersant (Disperbyk 163, active ingredient 45%) and 70 g PGMEA (propylene glycol methyl ether acetate, Aldrich Chemicals, USA) for about 1 hour in the wetting process. The mixture was ground with 300 g zirconia beads (diameter: 0.5 mm) in a plastic vessel (diameter: 7.5 cm; height: 15 m) for 5 hours. A gearshaped agitator (diameter: 5 cm) was employed at a rotation speed of about 2500 rpm. The pigment paste was cooled to 15 - 20 °C using an ice-water bath during grinding. The beads were filtered off using a sieve to collect the pigment paste.

Poly(methacrylic acid-co-styrene) binder solution (BI-1). Methacrylic acid (13.6 g, 0.158 mol) and styrene (16.4 g, 0.157 mol) were stirred into 69.1 g IPA under nitrogen purging to expel oxygen. The polymerization was carried out at 80 °C for 10 hours using 0.9 g of 2,2'-azobisisobutyronitrile (Junsei Chemicals, Japan) as a radical initiator. Polymer content was calculated by drying a small amount of the mixture in an oven at 200 °C, and the polymer content was about 28.2%.

Poly(methacrylic acid-co-methyl methacrylate-co-styrene) binder solution (BI-2). Methacrylic acid (13.6 g, 0.158 mol), styrene (10.0 g, 0.096 mol) and methyl methacrylate (6.4 g, 0.064 mol) were stirred into 69.1 g IPA. Polymerization and preparation of the binder solution were carried out using the same method described for **BI-1**. The polymer mixture gave about 28.6% (w/w) polymer content.

Poly(benzyl methacrylate-co-methacrylic acid-co-styrene) binder solution (BI-3). Methacrylic acid (13.6 g, 0.158 mol), styrene (10.0 g, 0.096 mol) and benzyl methacrylate (6.4 g, 0.036 mol) were stirred into 69.1 g IPA. Polymerization and preparation of the binder solution were carried out using the method described for **BI-1**. The polymer mixture gave about 28.8%

(w/w) polymer content.

Preparation of CFPRs. 40.0 g of the above pigment paste in appropriate amounts (2, 3, and 4 g) of each binder solution, 5.0 g dipentaerythritol penta-/hexa-acrylate, 1.0 g Irgacure-369 and 0.1 g FC-4432 were mixed, and PGMEA solvent added to make up 100 g total weight. The mixture was stirred for 1 hour in a dark room. The resulting solution was filtered using a membrane PTFE (porosity 1.0 μ m) filter and exposure to light was avoided.

Preparation of test glass sheets. A small glass sheet (5×5 cm) was coated with the CFPRs by a spin coater at adequate rpm to achieve target color value, x = 0.64, y = 0.33 in CIE xy coordination. The coated glass was pre-baked to evaporate the solvent at 80 °C for 90 seconds. UV exposure was carried out with a patterned photomask of 200 mJ/cm² strength at 360 nm. The development process for generating pixels was carried out by spraying an alkali-developer (0.5% potassium carbonate aqueous solution with 0.01% Surfynol 465 surfactant), followed by a post-bake process for 15 minutes at 220 °C.

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References

- Kubo, M.; Fujioka, S.; Ochi, T.; Narutaki, Y.; Shinomiya, T.; Ishii, Y.; Funada, F. *Technical Digest of IDW'99*; SID: Okata, 1999; p 183.
- 2. Ichimura, K. *Advanced Technologies for LCD Color Filters*; CMC Publishing: Tokyo, 2006; p 8.
- 3. Takahashi, T. J. Imag. Soc. Japan 2002, 41, 68.
- 4. Sugiura, T. J. Print. Sci. Tech. Japan 1996, 356.
- 5. Jung, I. B.; Ahn, S. H.; Nam, S. Y. Clean Tech. 2008, 14, 21.
- 6. Baba, K.; Mori, T.; Nakatsuka, K. USP 6,653,031; 2003.
- Tajima, Y.; Bessho, N.; Takinishi, F.; Yokoyama, Y.; Masuko, H. USP 5,368,976; 1994.
- Sano, K.; Endo, M.; Shimada, A.; Yokoyama, Y.; Bessho, N. USP 5,530,036; 1996.
- 9. Yoon, C.; Choi, J. H. Bull. Korean Chem. Soc. 2009, 30(8), 1821.