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Fluorene 단위 구조를 함유한 감광성 고분자의 합성 및 LCD 컬러필터용 카본블랙 포토레지스트로의 응용

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Synthesis of Fluorene-containing Photosensitive Polymer and Its Application to the Carbon Black-based Photoresist for LCD Color-Filter

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초록: 본 연구에서는 LCD 컬러필터 레지스트용 fluorene 단위 구조를 가지는 다기능 바인더 고분자를 개발하여 카본블랙 기반 감광성 레지스트(CBR)를 제조하고 블랙 매트릭스(BM)에 적용하였다. 다기능 바인더 고분자를 얻기 위해 bisphenol fluorene epoxy acrylate를 함유한 불포화 폴리에스터(BFEA−polyester)를 합성하였으며 이는 ^{1}H NMR, GPC 및 FTIR을 이용하여 분석하였다. 합성된 BFEA−polyester 바인더 고분자를 상업용 아크릴 바인더와 비교 평가하기 위하여 각각 CBR 제조 후 BM 리소그래피 테스트를 수행하였다. 그 결과, 본 연구에서 합성된 BFEA−polyester 바인더 고분자는 적합한 광경화 반응성과 알칼리 용해성을 가질 뿐만 아니라 기존 아크릴 바인더보다 더 우수한 공정 마진, 패턴 특성 및 유리 기판에 대한 접착력을 나타내었다.

Abstract: We developed a fluorene−containing multifunctional binder polymer for LCD color filter resist, and employing the binder polymer, carbon black based black photoresist (CBR) was prepared in order to apply it to the black matrix (BM). To obtain the multifunction of the binder polymer, we synthesized bisphenol fluorene epoxy acrylate−containing unsaturated polyester (BFEA−polyester) and identified the binder polymer structure with ^{1}H NMR, GPC and FTIR. The corresponding BFEA−polyester binder polymer was compared with the commercially available acryl binder toward the application to the CBR. From the BM lithography test, we found that the synthesized BFEA−polyester binder had better photo−crosslinking capability and alkali solubility. In addition, the newly developed binder gave a good process margin, good resolution and adhesion property on a glass substrate.

Keywords: multifunctional binder, carbon black photoresist, black matrix, color filter.

Introduction

In TFT−LCD, color filter is one of the most important parts which reproduces color signals. Typically, the color filter is prepared by forming red, green and blue picture elements and a black matrix (BM) on a glass substrate. To date, various processes have been engaged in the preparation of color filter for TFT−LCD. For example, dye process, printing process, pigment dispersion process, electro−deposition process and inorganic multilayer thin film process (including chemical deposition method) have been introduced so far.[1,2] Currently, color filters are generally manufactured by the pigment dispersion method. Color filters manufactured by such process have better light resistance and heat resistance. In the color filter process, the color pattern is made by negative photoresist process using color pigment−containing formulations.

Photoresists are used for transfer of images to a substrate. A coating layer of photoresist is formed on a substrate, and the photoresist layer is then exposed through a photo−mask to a source of activating radiation. The photomask has areas that are opaque to activating radiation and other areas that are transparent to activating radiation. Exposure to activating radiation provides a photoinduced che−

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mical transformation of the photoresist coating to thereby transfer the photo-mask to the photoresist-coated substrate. Following exposure, the photoresist is developed to provide a relief image that permits selective processing of a substrate. For negative photoresists, those coating layer portions that are exposed to activating radiation polymerize or crosslink in a reaction between a photoactive compound and polymerizable reagents of the photoresist composition. Consequently, the exposed coating portions are rendered less soluble in a developer solution than unexposed portions.

In general, color pigment or carbon black based black resist (CBR) compositions include photo-initiator, binder resin, color pigment (or carbon black) and multifunctional monomer. Photoinitiator and multifunctional monomer affect on the photosensitivity, color and crosslink density. On the other hand, binder resin affect on resolution and adhesion of photoresist. In the CBR BM, the carbon black almost cuts the UV light transmittance of the photoresist. In addition, according to the improvement of TFT-LCD color coordinate, the high optical density (OD) BM is necessary to obtain the high contrast and good color coordinate. For the higher OD CBR BM, the quantity of carbon black increases more and more. However, the larger amount of carbon black would decrease the UV light transmittance of the photoresist. In other words photo-crosslink density goes from bad to worse. To overcome the limit of crosslink density, researchers have developed new raw materials such as photo-initiator or monomer.[3,4] Unfortunately, those methods, to get the high sensitivity with new photo-initiator or monomer, have limits in the advanced high OD CBR BM since only a little part of photo-initiators can be used up in exposure process, resulting in a large amount of photo-initiator residues, which leads to decrease in thermal, mechanical and electrical properties of photoresist.[5,6] Therefore, it is necessary to improve crosslink density without mechanical and electrical quality deterioration. On the other hands, the low photo crosslink density makes the poor pattern property of CBR BM resulting in poor contrast ratio, back light leakage and so on.

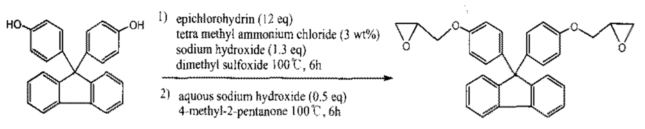
In this research, in order to improve crosslink density without mechanical quality deterioration and obtain the good pattern property of CBR BM, we developed the new multifunctional fluorene-containing binder polymer and the corresponding CBR formulations. Original binder roles are alkali soluble and mechanical binding function on developing process. However, the multifunctional binder should also have photo crosslink ability on UV exposure process. To get this point, we synthesized bisphenol fluorene epoxy acrylate-containing unsaturated polyester (BFEA-polyester). And we identified the binder structure with ^{1}H NMR, GPC and FTIR. To compare the binder qualities of newly developed multifunctional BFEA-polyester binder and commercial acryl binder, we applied those binders to the CBR BM, and found that the synthesized BFEA-polyester binder has better photo-crosslinking capability and alkali solubility. In addition, the newly developed binder gives a good process margin, good resolution and adhesion property on glass substrate.

Experimental

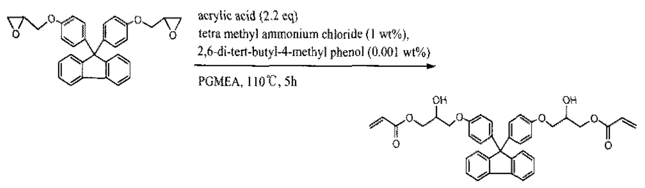
Materials. 4,4'-(9-Fluorenyildene)-diphenol, epichlorohydrin, tetramethylammonium chloride, sodium hydroxide, 4-methyl-2-pentanone, acrylic acid, propylene glycol monomethyl ether acetate, 4,4'-biphthalic anhydride, cis-1,2,3,6-tetrahydrophthalic anhydride, benzyl-triethylammonium bromide, pentaerythritol tetra acrylate (DPHA), ethanone, 1-[9-ethyl-6-(2-methyl benzoyl)-9H-carbazol-3-yl], 2-hydroxy-2-methyl-1-phenyl-1-propanone, oligo[2-hydroxy-2-methyl-1-[4-(1-methylvinyl)phenyl] propanone], 2-[4-(4'-ethylbiphenyl)]-4,6-bis(trichloromethyl)-1,3,5-triazine, carbon black (Markos 5333) were obtained from Aldrich, TCI and other commercial sources, and used without further purification. To compare pattern and other mechanical properties in the CBR BM, commercial acryl binder for negative photoresist, which consists of dicyclopentanyl methacrylate, benzyl methacrylate, methacrylic acid and other monomers, was obtained from Jooeun Co., Ltd (Korea, JEBM427, M_n 15000, acid value 120). The commercial acryl binder implies that it has no functional groups except carboxylic acid, and it does not crosslink with photo-radical in UV exposure process.

Instruments. ^{1}H NMR (500 MHz) spectrum was obtained using Varian unity inova spectrometer with internal standard reference (tetramethylsilane, TMS). FTIR spectrum was obtained using Unicam Mattson 5000 FTIR spectrometer (Model: GL-5020). Gel permeation chromatography (GPC) was performed using polystyrene standard sample. Spin coating of the CBR on glass (0.7 T) was performed with a coater from MIDAS system (SPIN-1200D). The thickness of the coated CBR was measured with KLA P-10 surface profiler. The UV (i-line) exposure equipment (Thermo-oriel Model 66902) was used for irradiation. To measure the pattern properties, we used Nikon Optiphot optical microscopy and scanning electron microscopy (SEM; Philips XL30 ESEMFEG).

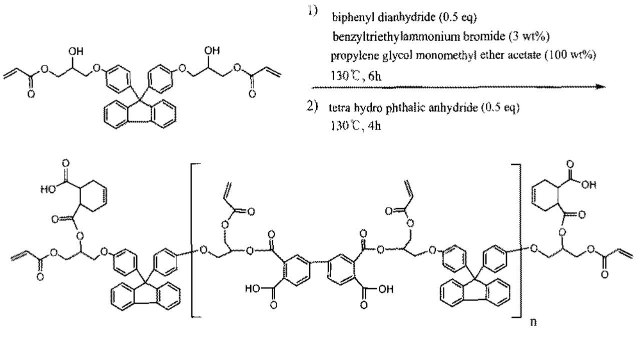
Synthesis of Epoxy Resin Containing Fluorene Moieties. Epoxy resin containing fluorene moieties was synthesized with 4,4'-(9-fluorenylidene)-diphenol and excess epichlorohydrin (Scheme 1).



Scheme 1. Synthesis of epoxy resin containing fluorene moieties.



Scheme 2. Synthesis of bisphenol fluorene epoxy acrylate.



Scheme 3. Condensation polymerization of bisphenol fluorene epoxy acrylate with 4,4′-biphthalic anhydride.

In a 250 mL round bottomed flask, we added 4,4′-(9-fluorenylidene)-diphenol (25 g, 0.071 mol), epichlorohydrin (79 g, 0.854 mol), tetramethylammonium chloride (0.75 g) and dimethyl sulfoxide (25 g, 100 wt% based on diphenol), and the mixture was heated to 100 ℃ and stirred with a teflon magnetic stirring bar. After the complete dissolution of the whole mixture, we added sodium hydroxide (3.72 g, 0.093 mol) slowly for 1 hr. The mixture was further stirred for 6 hrs. The excess epichlorohydrin and dimethyl sulfoxide solvent were removed under reduced pressure. For epoxy ring closure reaction, we dissolved the crude reaction mixture in 4-methyl-2-pentanone (25 g, 100 wt% based on diphenol), and added 30% aq. NaOH (0.5 eq) and stirred for 6 hrs at room temperature. At the end of the reaction, the reaction mixture was washed several times with DI water to remove salt, and the 4-methyl-2-pentanone layer was separated and diluted with excess hexane. The resulting white precipitate solid was filtered and dried at reduced pressure to give bis-epoxy containing fluorene moiety (Yield: 85%).

Synthesis of Bisphenol Fluorene Epoxy Acrylate. To impart the photosensitivity and cross-linking ability, we introduced acryl groups on both sides of the epoxy resin containing fluorene moiety (Scheme 2).

In a 250 mL round bottomed flask, we added epoxy resin containing fluorene moieties (25.5 g, 0.055 mol), acrylic acid (8.712 g, 0.121 mol) and propylene glycol monomethyl ether acetate (25.5 g), and the mixture was stirred with a teflon magnetic stirring bar to give a homogeneous solution. Then, we added tetramethyl ammonium chloride (0.255 g, 1 wt%) and 2,6-di-tert-butyl-4-methyl phenol (0.03 g), and the reaction mixture was heated to 110 ℃ and stirred for 5 hrs. The reaction was monitored by checking the exhaustion of the raw material with thin layer chromatography. The crude mixture was washed several times with DI water to remove the excess acrylic acid, and concentrated. The crude mixture was diluted with a large amount of hexane to give slightly yellowish precipitate, and the product was filtered and dried under vacuum (Yield: 76%).

Condensation Polymerization of Bisphenol Fluorene Epoxy Acrylate with 4,4′-Biphthalic Anhydride. We copolymerized bisphenol fluorene epoxy acrylate with 4,4′-biphthalic anhydride to obtain the final binder polymer, i.e. alternated polyester, which has di-acrylate groups and di-carboxylic acid groups (Scheme 3). In a 250 mL round bottomed flask, we added bisphenol fluorene epoxy acrylate (25 g, 0.041 mol) and propylene glycol monomethyl ether acetate (25 g, 100 wt%), and the mixture was stirred with a teflon magnetic stirring bar for 30 min. Then, we added benzyltriethylammonium bromide (0.75 g, 3 wt%) as catalyst and 4,4′-biphthalic anhydride (6.1 g, 0.021 mol), and the mixture was heated to 130 ℃ and stirred for 4 hrs. The polymerization was monitored by checking the exhaustion of the anhydride groups with FTIR. After the complete consumption of 4,4′-biphthalic anhydride, we added tetrahydrophthalic anhydride (3.2 g, 0.021 mol), and stirred for 4 hrs at 130 ℃.

The reaction mixture was washed several times with DI water to remove salt, and the organic layer was separated and precipitated with excess methanol. The resulting yellowish powder was filtered and dried at reduced pressure to give the binder polymer (Yield: 87%, GPC M_n: 3050).

Formulation of CBR. We prepared two kinds of CBRs. Formula 1 contains multifunctional novel BFEA-polyester binder, and formula 2 contains the commercial acryl binder. The preparative methods of two formulas are as follows. For formula 1, in a 200 mL round bottomed flask, we added 2-hydroxy-2-methyl-1-phenyl-1-propanone (0.3 g), oligo [2-hydroxy-2-methyl-1-[4-(1-methylvinyl)phenyl] propanone (0.3 g), 2-[4-(4′-ethylbiphenyl)]-4,6-bis(trichloromethyl)-1,3,5-triazine (0.6 g), and propylene glycol monomethyl ether acetate (PGMEA; 83.8 g), and the mixture was stirred with a teflon magnetic stirring bar at room temperature. After complete dissolution, we added pentaerythritol tetraacrylate (DPHA; 2 g) and BFEA-polyester binder (BFEA; 4 g), and stirred for 2 hrs. Then, we added carbon black powder (9 g) and stirred for 4 hrs. The formula 2 was obtained using commercial acryl binder instead of the BFEA-polyester binder with the same quantity.

BM Pattern Formation with CBR. We prepared the CBR BM, so-called Black Matrix (BM), to study the pattern straightness, residue property, photo-sensitivity, and resolution. The prepared CBR was coated on glass (0.7 T thickness) with a spin coater for 5 sec at 540 rpm. And coated samples were pre-baked at 90 ℃ for 90 sec. And UV exposure experiments under patterned photo-mask were performed with the irradiation energy of 80, 120 and 150 mj, respectively. Those samples were developed with aqueous KOH solution (0.05%). The developing conditions were as follows. The temperature was 20 ℃, and the developing pressure was 1.2 kgf/cm^2. Under the same condition, we employed different developing times (70, 75, 80, and 85 sec) to study the process margin. After we clean the CBR BM with DI water (pressure; 5.0 kgf/cm^2, time; 30 sec), the patterned CBR BM was post-baked at 220 ℃ for 20 min. The final thickness of CBR BM was about 1.2 μm. We studied the photo-sensitivity, process margin, adhesion property, pattern straightness, residue property, and peel off phenomena using optical microscopy and SEM.

Adhesion Properties of CBR BM. The adhesion property was measured by cross-cut test in the coated layer and peeling using a tape. The specific method was as follows. The prepared CBR was coated on glass with spin coater for 5 sec at 540 rpm. And the coated sample was pre-baked at 90 ℃ for 90 sec. After pre-bake, we irradiated overall UV exposure (120 mj and without photo-mask). It was developed with developer for 80 sec. Other developing conditions and DI rinsing conditions were the same as the former conditions. Then, the sample was post-baked at 220 ℃ for 20 min. We scratched the coated layer with a razor blade. Scratch shape was mosaic pattern with 1 mm^2 dimension size. The number of square pattern is one hundred. And we put the prepared samples in the thermo-hygrostat box for 2 days. The temperature was 90 ℃, and the humidity was 90%. Finally, we performed a cross-cut test by adhering the 3M hard adhesive tape (model: #5029) onto the surface of prepared samples followed by peeling off the tape instantly. We counted the number of the left square patterns with optical microscopy.

Results and Discussion

Synthesis of BFEA-Polyester Binder Polymer. Epoxy resin containing fluorene moieties was synthesized from 4,4′-(9-fluorenylidene)-diphenol and excess epichlorohydrin (Scheme 1). To impart the photosensitivity and cross-linking ability, we introduced acryl groups on both sides of the epoxy resin containing fluorene moiety to give the corresponding di-acrylates (i.e., bisphenol fluorene epoxy acrylate (BEFA)) (Scheme 2). ^{1}H NMR study showed that we successfully introduced epoxy functional groups onto 4,4′-(9-fluorenylidene)-diphenol (Figure 1(a)), and the corresponding bisphenol fluorene epoxy acrylate (BEFA) resin showed the typical proton peaks of acrylate functional groups in the range of 5.8~6.4 ppm (Figure 1(b)). Since BEFA resin contains two reactive secondary alcohols, we copolymerized BEFA

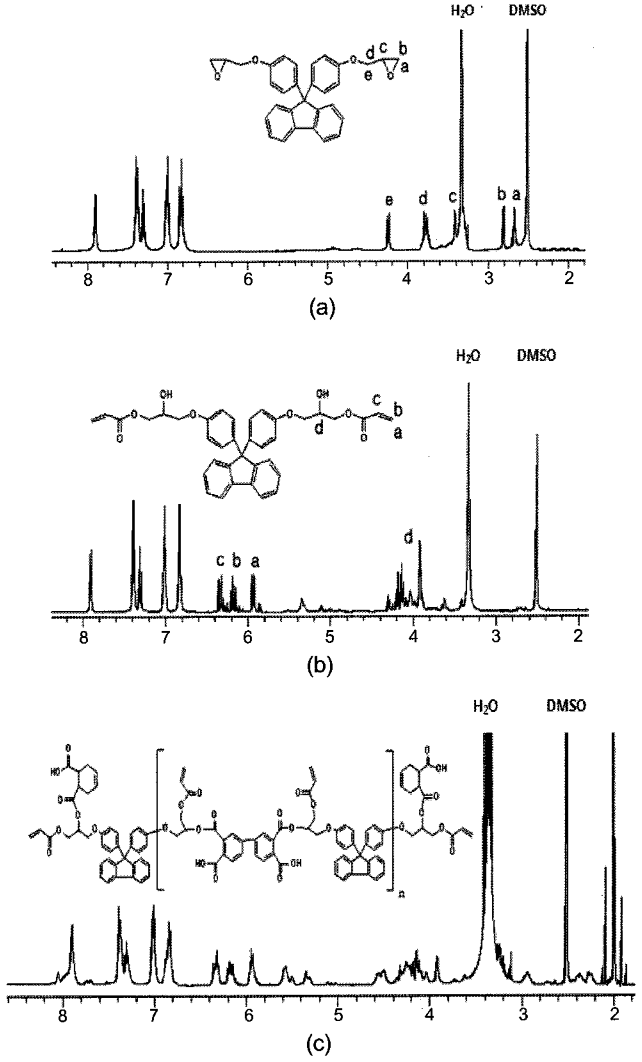


Figure 1. ^{1}H NMR spectra of (a) epoxy resin containing fluorene moieties; (b) bisphenol fluorene epoxy acrylate; (c) copolymer of bisphenol fluorene epoxy acrylate with biphthalic anhydride.

with 4,4′-biphthalic anhydride via condensation polymerization to obtain the final BEFA-polyester binder polymer, i.e. alternated polyester, which has di-acrylate groups and di-carboxylic acid groups (Scheme 3).

The polymerization was monitored by checking the exhaustion of the anhydride groups of 4,4′-biphthalic anhydride using FTIR. Figure 2 shows the FTIR spectrum of the reaction mixture indicating the disappearance of typical 4,4′-biphthalic anhydride peaks (1770 and 1850 cm^{-1}) during the copolymerization reaction. After the complete consumption of 4,4′-biphthalic anhydride, we added tetrahydrophthalic anhydride as a quencher, and stirred for 4 hrs at 130 ℃. Figure 1(c) shows the ^1H NMR spectrum of the final BEFA-polyester binder polymer.

GPC trace of the copolymer of bisphenol fluorene epoxy acrylate with biphthalic anhydride (Figure 3) showed a polydisperse chromatogram (PDI=2.23) with the peak molecular weights of 3403, 2085, 1276 and 824, respectively. As we expected, the molecular weight of BFEA-polyester binder was much lower than the commercial acryl binder (M_n 20000~30000). For the CBR BM application, relatively low molecular weight binder has several advantages such as easiness for slit coating and thin film formation. However, relatively high molecular weight binder gives higher viscosity, poor coating uniformity and stain, etc.

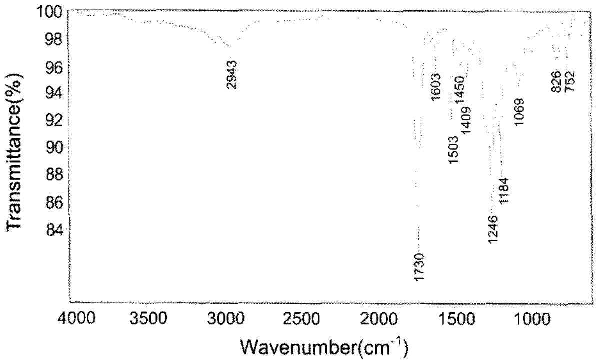


Figure 2. FTIR spectrum of copolymer of bisphenol fluorene epoxy acrylate with biphthalic anhydride.

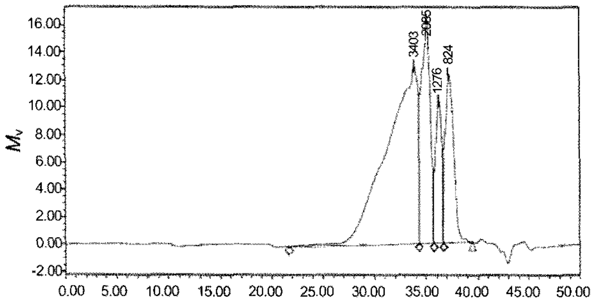


Figure 3. GPC trace of copolymer of bisphenol fluorene epoxy acrylate with biphthalic anhydride.

Photo-Sensitivity of CBR BM. In given developing conditions (developing time; 80 sec, temperature; 20 ℃), we prepared two types of CBR BMs (formula 1 with BFEA-polyester binder and formula 2 with commercial acryl binder). The photo-sensitivity of formula 1 is better than formula 2 since with the same UV exposure quantity, the critical dimension (CD; the width of pattern) of (a) is bigger than (b) (Figure 4). It means that the unsaturated BFEA-polyester binder enhanced the photo-crosslink density during the UV exposure process, and that led a side-spreading crosslink and CD expansion.

Under the same UV exposure quantity, the bigger CD value is very useful in the commercial process line of color filter fabrication since we are able to obtain the target CD value with low UV exposure quantity (i.e. cost reduction). In addition, BFEA-polyester binder showed that as we changed the exposure quantity from 80 to 150 mj, the deviation value of CDs was very small compared to commercial acryl binder (Figure 4). For BFEA-polyester binder, the deviation value of CDs was Δ0.057 μm/mj (29.2 μm → 33.2 μm; Figure 4(a)), however for acryl binder using the same recipe, the deviation value of CDs was Δ0.129 μm/mj (17.1 μm → 26.1 μm; Figure 4(b)). Since UV exposure intensity generally decreases with time, the small deviation of CDs with variation of UV exposure intensity increases the available period of UV lamp.

Process Margin and Resolution of CBR BM. In the process of CBR BM formation, we employed various developing times. Generally, the CD of clear photoresist with no pigment and/or carbon does not easily change with developing times. However, the CD of CBR BM changes easily with developing time. The reason is that carbon black cuts the UV irradiation and decreases the photo-crosslink density. And it also leads to the shallow photo-crosslink at the surface. The shallow photo-crosslink layer is easily attacked by developer, and this leads to the change of CD with developing time. For the process margin with developing time, formula 1 was far

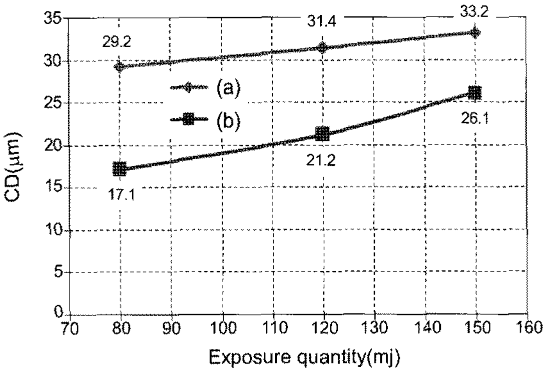


Figure 4. The variation of CDs with exposure quantity: (a) formula 1; (b) formula 2.

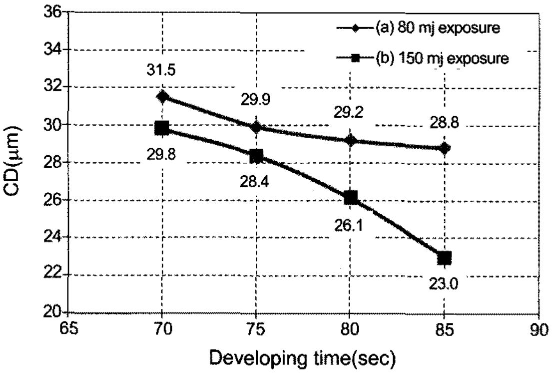
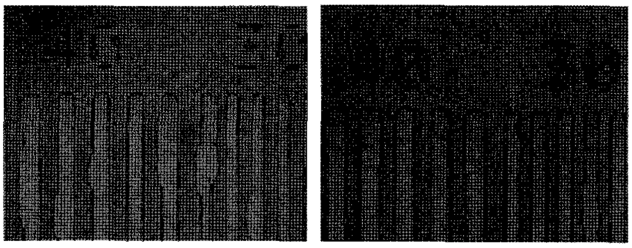


Figure 5. The variation of CDs with developing time: (a) formula 1; (b) formula 2.



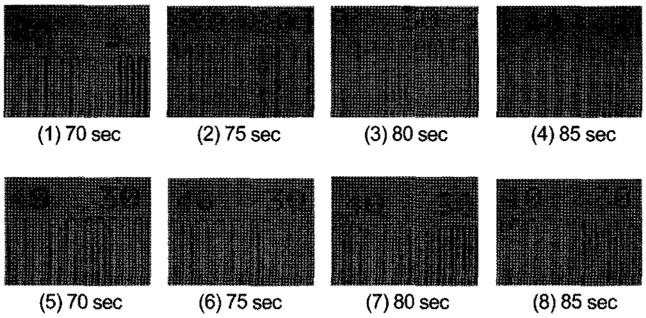
(a) (b)

Figure 6. BM pattern properties with different UV exposure quantities and CD values: (a) CD 17.1 μm (80 mj applied onto the formula 2 coated film); (b) CD 26.1 μm (150 mj applied onto the formula 2 coated film).

superior to formula 2 (Figure 5).

In spite of the same carbon black quantity employed, we supplied higher UV irradiation onto the formula 2 sample film than the formula 1 sample film since the pattern properties depend on the CD value (Figure 6). Thus we applied different UV exposure quantities (formula 1 sample film; 80 mj & formula 2 sample film; 150 mj) to obtain the similar CD and pattern properties. Under this condition, we obtained the process margin data of formula 1 & 2. For BFEA-polyester binder (formula 1), the deviation value of CDs was Δ0.18 μm/sec (31.5 μm → 28.8 μm; Figure 5(a)), however for commercial acryl binder (formula 2) using the same recipe, the deviation value of CDs was Δ0.45 μm/sec (29.8 μm →23.0 μm; Figure 5(b)).

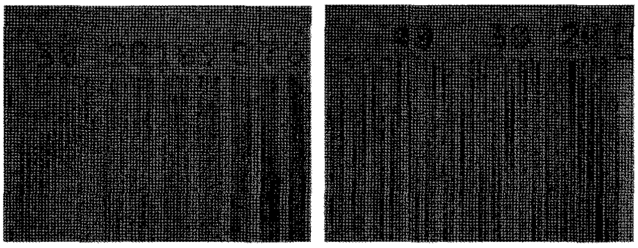
We also observed the pattern shapes of both formulas using optical microscopy (Figure 7). The straightness of formula 1 pattern edge was superior to that of formula 2 pattern edge. In the view of Figure 7(1) & (5), there were residues of pattern edge. When the developing time was not enough, residues of pattern edge remain. In the pattern properties of formula 2 sample, when we applied 75 sec developing time (Figure 7(6)), residue amount was decreased even though not perfectly. When we tried to remove residues completely with additional developing time over 75 sec, the pattern quality went from bad to worse.



(1) 70 sec (2) 75 sec (3) 80 sec (4) 85 sec

(5) 70 sec (6) 75 sec (7) 80 sec (8) 85 sec

Figure 7. BM pattern straightness with different developing times: (1)~(4); formula 1, (5)~(8); formula 2.



(a) Formula 1 (b) Formula 2

Figure 8. Optical micrographs of BM patterns of (a) formula 1;. (b) formula 2.

On the other hand, the pattern properties of formula 1 sample were generally satisfactory except the developing time of 70 sec (Figure 7(1)). Good CBR BM with proper process margin makes the good pattern properties with a small deviation of CDs with developing time. The pattern straightness, no residue formation and no peel off are the key points of CBR BM. And the main role of BM excludes the light from the back light unit in TFT-LCD. Therefore, when the pattern straightness is bad, the contrast and color coordinate of TFT-LCD are very unstable.

Regarding the pattern resolution, this is also a very important factor in the color filter process. BM is the first step in color resist pattern process, and they mark the sheet align key with BM for the next continuous process. Normally, align key requires very fine resolution (under 10 μm). Therefore we should obtain the resolution under 10 μm at the optimal developing time. Considering the proper pattern properties and process margin, 75 sec developing time was the best for both formulas. At 75 sec, formula 1 gave a 6 μm pattern, but formula 2 gave a 20 μm pattern (Figures 8 & 9).

Adhesion Properties of CBR BM. Generally, epoxy acrylate type resin has good adhesion properties and mechanical properties.[4] With aforementioned method (vide supra), we had an adhesion test on CBR BM samples. We performed a cross-cut test by adhering the 3M hard adhesive tape (model:

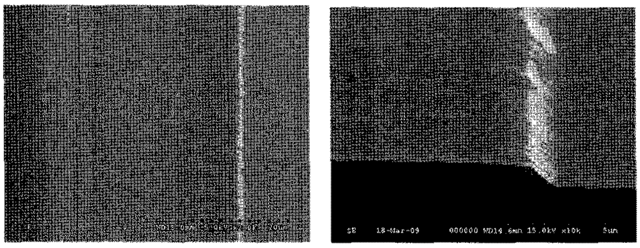


Figure 9. SEM images of CBR BM employing formula 1.

Table 1. The Cross-cut Test Results of CBR

	Number of fully peel–off squares	Number of semi peel–off squares
Formula 1	0	2
Formula 2	3	46

#5029) onto the surface of prepared samples followed by peeling off the tape instantly. We counted the number of the left square patterns with optical microscopy. It was found that the formula 1 gives the better adhesion property than the formula 2 (Table 1).

For the coated CBR BM sample with formula 2, about the half of the mosaic patterns (49/100) were come off. However, in the case of formula 1, most of them remained (98/100). From this test, we confirmed that epoxy acrylate–type BFEA–polyester binder resin has a good adhesion property on the glass.

Conclusions

In this research, in order to obtain the multifunction of the binder polymer, we successfully synthesized bisphenol fluorene epoxy acrylate–containing unsaturated polyester (i.e. BFEA–polyester) and identified the binder polymer structure with ^{1}H NMR, GPC and FTIR. We also developed fluorene–containing multifunctional binder polymer for LCD color filter resist, and employing the binder polymer carbon black based black photoresist (CBR) was prepared in order to apply it to the black matrix (BM). From the BM lithography test, we found that the synthesized BFEA–polyester binder has better photo–crosslinking capability and alkali solubility than the commercial acryl binder. In addition, the newly developed binder gives a good process margin, good resolution and adhesion property on glass substrate.

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