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Novel UV-curable and alkali-soluble resins for light-shielding black matrix application

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Abstract

A carbon black (CB) photo resist, comprising CB, CB dispersant, photo-curable resin, photo-initiator, and solvent, has been developed in order to prepare a light-shielding black matrix (BM) in the liquid crystal display application. In order to prepare a BM with a high opacity property or optical density (OD), the effect of CB such as its particle and concentration on light absorption property was first evaluated, and the results showed that 45 wt% CB with a particle size of about 100 nm in BM could reach an OD value of 4 μm^{-1}. Moreover, six different UV-curable and alkali-soluble resins (A1, A2, and A3; B1, B2, and B3) were synthesized as photo-curable resins. Structures of these resins were characterized by FTIR and GPC, in which concentrations of various functional groups, especially carboxylic acid and double bond, were calculated. Subsequently, Their photo-initiated polymerization rate with or without CB were measured. Finally, it was found that through a proper selection of the newly synthesized resins to prepare a carbon black photo resist, a BM with an OD of 4 μm^{-1} and a good resolution of 10 μm was successfully prepared upon low UV irradiation energy of 50 mJ/cm^2.

Keywords: Carbon black, UV-curable and alkali-soluble resins.

Introduction

Color filter (CF) is one of the important elements in display devices, such as liquid crystal displays (LCD).[1-5] It mainly comprises glass substrate, black matrix (BM)[1-3], color layer (red, green, and blue colors), and indium tin-oxide film. The role of the BM is very important as it can prevent the light leaking from the area between two color pixels to improve the color contrast of the LCD. In the past, BM was made of chrome (Cr);[1] however, Cr-BM has several disadvantages such as high cost, a complex manufacturing process, a high reflectivity, and potential environmental pollution problems.[5, 6] To solve these problems caused by Cr, carbon black (CB) is thus adopted for preparing the BM.[7]

The CB-BM is produced from a carbon black photo-resist (CB PR) which consists of CB, CB dispersant, photo-curable resin, photo-initiator (PI), and solvent. For practical use, the CB-BM with a high opacity property or optical density (OD) of 4 μm^{-1} and a good resolution of 10-30 μm is desired. As a result, a high loading and good stability of CB and a photo-curable resin with good lithographic performance in the CB PR are required.

In many studies, a stable dispersion of CB concentrate is usually prepared with the help of a surfactant or dispersant. Several kinds of dispersants have been developed so far.[8-13] For example, Jinmei et al.[13] used a water soluble poly(vinyl alcohol-styrylpyridinium) copolymer (PVA-SbQ) to prepare a stable CB dispersion in a water medium because PVA-SbQ can be adsorbed onto the surface of CB by the static interaction between the positive charge of PVA-SbQ and negative charge of CB. Kamata et al.[12] synthesized a polyacrylate dispersant having tertiary amine group as well as its quaternarized derivative for preparing CB concentrates. The influence of composition of polyacrylate dispersant on the stability of CB in organic solvent, propylene glycol monomethyl ether acetate (PGMEA), was thus evaluated.

In addition, the role of photo-curable resin in CB PR is also important. Many UV-curable and alkali-soluble resins have been proposed, which can form patterns by an alkali developer after UV-irradiation.[5, 12, 14-17] Lee[16] synthesized an UV-curable and alkali-soluble resin by the poly-condensation between bisphenolfuluorene-based epoxy acrylate and tetracarboxylic dianhydride. Kang et al.[5] disclosed various multi-functional (meth)acrylate monomers containing carboxylic acid group by the esterification between monohydroxyl multi-functional (meth)acrylates with dicarboxylic acid. The BM with a line width of 8-10 μm was prepared by using the above resins or monomers upon irradiation energy of 200-300 mJ/cm^2.

In order to prepare a high light-shielding BM with a good resolution, it is important to understand the effects of CB on the final performance of BM. Generally speaking, it is not easy to prepare a BM with both a high OD of 4 μm^{-1} and a good resolution of 10 μm in width by a low UV irradiation energy. This is because UV light is mainly absorbed by CB which leads CB PR to be less photo-cured. In addition, CB PR is generally prepared with a high concentration of CB, which is not easily soluble in the alkali developer and therefore would retard the developability of CB PR.

This work presents new CB PR systems in order to prepare a CB-BM with a high OD and a good resolution. Six different UV-curable and alkali-soluble resins were synthesized to be used in CB PR. Their photo-sensitivities were evaluated by a photo-DSC and those resins with high photo-sensitivities were then selected to prepare CB PR systems. CB dispersions containing CB, CB dispersant, and the synthesized resins in PGMEA were prepared by a ball-milling process. After adding a photo-initiator into the above CB dispersions, these CB PR systems were then irradiated with UV light of energy about 200 mJ/cm^2 or lower, and allowed by the development with an alkali developer to produce BM. The resolution of BM were then evaluated and discussed in terms of the concentration of carboxylic acid group of

synthesized resins. Finally, an appropriate mixture comprising two synthesized resins was found to give a good resolution in BM.

Experimental

Materials

2-Hydroxyethyl methacrylate (HEMA, ACROS) was free from moisture under reduced pressure prior to use. Bisphenol A epoxy diacrylate (EPA, AGI Corporation), dipentaerythritol hexaacrylate (DPHA) (Double Bond Chemical), maleic anhydride (MA, ACROS), benzophenone tetracarboxylic dianhydride (BTDA, ACROS), isophorone diisocyanate (IPDI, Lancaster), di-n-butyltin dilaurate (DBTDL, TCI), propylene glycol monomethyl ether acetate (PGMEA, Grand Chemical), tetrahydrofuran (THF, ACROS), sodium hydroxide (NaOH, SHIMAKYU), sodium hydrogen carbonate ($NaHCO_3$, SHIMAKYU), carbon black: Regal 400R (CABOT Co., Ltd), and carbon black dispersant: Disponer 9850 (DEUCHEM Co., Ltd) were all used as received. 1-[9-ethyl-6-(2-methylbenzoyl)-9H-carbazole-3-yl],-1-(O-acetyl oxime) (I242, Ciba) was used as a photo-initiator.

Synthesis of UV-curable and alkali-soluble resins

Six different UV-curable and alkali-soluble resins were synthesized as listed in Table 1. EPA and BTDA were first dissolved in PGMEA and the solid content was maintained at 40 wt%. The solution was stirred by a magnetic stirring bar and kept at 100^{o}C for 12 hr in a nitrogen atmosphere. Two resins, A1 and A2, were synthesized from different molar ratio of EPA to BTDA, 1/2 and 5/4, respectively, see Table 1. Moreover, a H-I monomer containing both isocyanate functional group and methacrylate double bond was synthesized by the reaction of an equal molar amount of HEMA and IPDI (corresponding to [OH]/[NCO]=1/2) in PGMEA solvent through urethane linkage catalyzed by the DBTDL (0.1 wt%). The reaction was conducted in an ice bath in a nitrogen atmosphere for 1 h. The detailed reaction and its structure characterization were described elsewhere.[18] Afterwards, a proper amount of the above synthesized A1 or A2 solution was added to the H-I solution for the synthesis of B1 or B2 resin, respectively, in which the total solid content in PGMEA was maintained at 40 wt%. The temperature was raised and kept at 85^{o}C and the reaction mixture was monitored by a Fourier transform infrared spectrometer (FTIR, DIGILAB FTS4000). During the reaction, carbon dioxide gas evolution was observed. The reaction product, B1 or B2, was finally obtained when the absorbance of the isocyanate group disappeared.

In addition, another two resins, A3 and B3, were also synthesized and the experimental procedure was described as follows: EPA and MA were dissolved in PGMEA, and the solid content in PGMEA was ca. 40 wt%. The reaction mixture was stirred by a magnetic stirring bar and kept at 100^{o}C for 12hr in a nitrogen atmosphere to synthesize A3. Afterwards, a specific amount of IPDI was added into the above solution to obtain B3 resin. The molar ratio of reactants is shown in Table 1 and the total solid content in PGMEA was also maintained at 40 wt%. The reaction mixture was performed at 85^{o}C in a nitrogen atmosphere and DBTDL (0.1 wt%) was used as a catalyst. During the reaction, carbon dioxide gas evolution was observed. The reaction mixture was monitored by a FTIR until the isocyanate group was consumed completely to obtain the final product, B3. The concentrations of various functional groups and structures of these UV-curable and alkali-soluble resins are all listed in Table 1 and Figure 1, respectively.

Structure Analysis

Functional groups of UV-curable and alkali-soluble resins were characterized by a FTIR in the range of 4000-900cm^{-1}. Molecular weights were determined by gel permeation chromatography (GPC) equipped with three columns (Waters1000 Å, Phenomenex 50000 Å and 10^9 Å), and a RI detector (Shodex RI-71) under the effluent of THF solvent at a flow rate of 1 ml/min. The reported molecular weight values were based on polystyrene standards. The concentrations of carboxylic acid group in resins were identified by a titration method. 1% potassium hydroxide solution was used as a standard and the pH value was monitored by a pH meter (HORIBA F-51).

Preparation of carbon black dispersion

CB dispersion in PGMEA was prepared by a ball-milling process. CB, PGMEA, Disponer 9850, and with or without UV-curable and alkali-soluble resins were added into a vial. The mixture in vial was 10g and the composition of mixture is listed in Table 2. Approximately 15g zirconium oxide beads with diameter of 2 mm were added into the vial. The vial was rolled in the ball miller (Shin Kwang MUBM-340) at 500 rpm for one day. Particle size of CB was measured by a dynamic light scattering analyzer (DLS, MALVERN, Zetasizer 3000HS), and the morphology of CB was observed by using a scanning electron microscope (SEM, Hitachi S-2400).

Light absorption property of CB

The absorption spectra of CB dispersions were recorded by using an UV/Vis spectrophotometer (ThermoSpectronic HEλIOS). The concentration of CB in PGMEA was 0.001%. A quartz cell with a path length of 1 cm was used. The sample in the cell was subjected to UV/Vis light between 400 and 700 nm. The data interval was 1.0 nm.

Optical density of black film

CB dispersions containing 40-55 wt% CB (based on the total solid in the CB dispersion) were prepared by adding different weights of PMMA into a CB dispersion (sample 1d in Table 2). It was then dropped onto a glass substrate to prepare a black film by a spin coating process with 900 rpm for 10 s. The absorbance at 550 nm of the black film was measured by a spectrophotometer (Gretag Macbeth D2000-11). The thickness of the black film was measured by a surface profiler (TENCOR, Alpha-step). The OD value was therefore calculated according to the following equation:

$$\mathrm{OD} = \frac{-\log(I/I_0)}{d} \quad (\mu\mathrm{m}^{-1}) \ldots\ldots(1)$$

where I_0 and I are the intensity of light before and after passing through the black film at the wavelength of 550 nm, respectively, d is the film thickness.

Photo-polymerization of resins with or without CB

Photo-sensitivity of resin was studied by a photo differential scanning calorimeter (photo-DSC, Perkin-Elmer Diamond DSC coupled with EXFO OmniCure Series 2000). Sample was prepared by dissolving specific amounts of resin (10 wt%), I242 (0.1 wt%), and with (0.1 wt%) or without CB into the PGMEA solvent. Approximately 30 mg of the above solution was dropped into an aluminum pan by a micro-pipette. It was then dried at 50°C for 1 hour. The dried sample was removed into the photo-DSC, covered by a quartz glass, and equilibrated at 50°C for 10 minutes. Polymerization was initiated by the irradiation of UV light in a nitrogen atmosphere and monitored by measuring the reaction heat. The wavelength range of UV light is 250-450 nm.

In order to convert the heat flow of samples to rate of polymerization, the heat of reaction of acrylate, methacrylate, and maleate double bonds from literatures are adopted, which are 78, 56, and 60 kJ/mol,[19, 20] respectively. However, the individual heat of reaction from acrylate, methacrylate, and maleate of resin can not be separated by the photo-DSC experiment; therefore, the rate of polymerization is assumed to be an average consumption rate of acrylate, methacrylate, and maleate. The average reaction rate can be therefore defined as follows[21, 22]:

$$R_p = \frac{dx}{dt} = \frac{1}{\Delta H_{total}}(\frac{dH}{dt})_T \quad \text{………………………………………………………(2)}$$

where dx/dt (1/s) is the rate of polymerization; x is the average conversion; t (s) is the reaction time; ΔH_{total} (J) is the total exothermic heat of polymerization, defined in Eq. (3); $(dH/dt)_T$ (J/s) is the heat flow at a constant temperature recorded by the photo-DSC.

$$\Delta H_{total} = (\Delta H_1^0 \times n_1 + \Delta H_2^0 \times n_2 + \Delta H_3^0 \times n_3) \times m \quad \text{……………………………(3)}$$

where ΔH_1^0, ΔH_2^0, and ΔH_3^0 are the theoretical heat of reaction of the acrylate, methacrylate, and maleate double bond, respectively; n_1, n_2, and n_3 (mol/g) are the moles of acrylate, methacrylate, and maleate double bond per gram of resin, respectively. The n_1, n_2, and n_3 values are listed in Table 1; m (g) is the weight of resin in samples.

The curing extent (reacted C=C-mol/g) over the reaction time was thus calculated according to eq. (4).

$$\text{curing extent} = \frac{(n_1 + n_2 + n_3)}{\Delta H_{total}} \int_0^t (\frac{dH}{dt})_T dt \quad \text{……………………………………(4)}$$

Pattern formation

CB PRs were prepared by dissolving 2 wt% I242 into the CB dispersions, samples 2-4 in Table 2. It was then dropped onto a glass substrate to prepare a black film by a spin coating process with 900 rpm for 10 s. This black film was pre-baked at 50°C for 2 minutes and subsequently exposed to UV light (50-200 mJ/cm^2) with a direct contact between the 10 μm-stripe photo-mask and the black film. The BM pattern was developed by using an alkali developer ($NaHCO_3$/NaOH = 5g/1.5g in 200 ml water) for 40 s. The resulting pattern was post-baked at 200°C for 30 minutes, and was finally observed by an optical microscope (OM, Olympus MX 40) and SEM.

Results and discussion

Synthesis of UV-curable and alkali-soluble resins

In this work, A1 and A2 resins were first prepared by the esterification between OH groups of EPA and anhydride groups of BTDA at different molar ratios (see Figure 1). Their structures were confirmed by FTIR as well as GPC analysis. Table 1 lists the molar ratios of EPA to BTDA reactant and all calculated concentrations of functional groups in the A1 and A2.

A1 and A2 were further reacting with an H-I monomer to produce B1 and B2, respectively. The reaction with H-I monomer can increase the concentration of double bond which can promote the rate of polymerization as well as cross-linking density when exposed to UV irradiation. Taking B2 for an example, it was synthesized by the reaction of isocyanate group of H-I monomer to hydroxyl, carboxylic acid, and anhydride groups of A2 to produce urethane, amide, and imide groups, respectively. The structure of H-I monomer is shown in Figure 1, in which it has an isocyanate functional group and methacrylate double bond.

The structure of B2 was also confirmed by FTIR, and GPC analysis. Compared to A2, the small peak of hydroxyl group at 3500 cm^{-1} almost disappears as shown in Figure 2 because of the fast reaction with isocyanate group of H-I. The concentration of carboxylic acid measured by a titration method decreases from 2.3×10^{-3} mol/g for A2 to 1.5×10^{-3} mol/g for B2 due to the reaction with H-I. New peaks at 3375 and 1540 cm^{-1} are found and assigned to the NH stretching and bending vibration of urethane and amide groups. Besides, original anhydride group of A2 at 1780 and 1855 cm^{-1} almost disappears due to the reaction with isocyanate group in H-I, which could produce imide group. The molecular weight of B2 measured by GPC (cf. Figure 3) is found to be a little higher than that of A2 due to the introduction of H-I into B2.

Another resin, A3, was prepared by the esterification between OH group of EPA and anhydride group of MA at 100^{o}C. In addition, B3 resin was prepared by the further reaction of carboxylic acid or hydroxyl group of A3 to isocyanate group of IPDI. Structure of A3 and B3 are shown in Figure 1.

Figure 4 shows the FTIR spectra of A3 and B3. Compared to A3, the FTIR spectrum of B3 shows that the small peak of hydroxyl group at 3500 cm^{-1} almost disappears which implies that the hydroxyl group of A3 was completely reacted with the isocyanate group of IPDI. This is because the relative reactivity of isocyanate group to hydroxyl group is higher than that to carboxylic acid group.[23] This figure also shows that the original absorbance of carboxylic acid group of A3 between 2500 and 3300cm^{-1} is not obvious in B3 due to the reaction with isocyanate group of IPDI. The concentration of carboxylic acid, determined from a titration method is found to decrease from 3.0×10^{-3}mol/g for A3 to 1.7×10^{-3}mol/g for B3. New peaks at 3375 and 1540 cm^{-1} are observed and assigned to the NH stretching and bending vibration of urethane and amide groups. Figure 5 also shows that the molecular weight of B3 is broad and higher than that of A3, which also confirms the condensation reaction between A3 and IPDI.

Influence of dispersant and resins on the particle size of CB

Because CB is prone to aggregate,[8, 24] the aggregate of CB is often needed to be broken down by a dispersion process for practical applications. Therefore, the surface treatment of CB in dispersion is required. In many studies, a stable dispersion of CB concentrate is usually prepared by a surfactant or dispersant. In this work, a CB dispersant, Disponer 9850, was used in order to obtain a stable CB dispersion because it can be adsorbed onto the surfaces of CB by the interaction between the amino group of Disponer 9850 and the carboxylic acid group on the surfaces of CB. The dispersion ability of dispersant is to examine the particle size of CB in dispersion, i.e., the smaller particle size of CB, the better dispersion ability of dispersant. Also, a good dispersant would maintain the stability of dispersion. The concentration of dispersant used in this work is listed in Table 2 and the particle size of CB dispersed by this CB dispersant was determined by a DLS and a SEM.

Figure 6 shows the relationship between the concentration of dispersant in PGMEA solution and the particle size of CB. The particle size of CB is defined at the point of 50% of accumulated distribution. Apparently, as the concentration of dispersant in CB dispersion is lower than 1%, the particle size of CB is greater than 280nm and a high viscous CB dispersion was observed. In addition, sedimentation of CB in PGMEA was observed after one day. On the other hand, when the concentration of dispersant is not less than 1.5%, the particle size of CB can reach to about 100 nm. Besides, no sedimentation behavior was observed even though the storage time is longer than three months.

The prepared dispersion dropped on glass substrate was also observed by a SEM as shown in Figure 7. It shows that the CB with a small and uniform particle size is well-dispersed when the concentration of dispersant is at least 1.5%. On the contrary, as the concentration of dispersant is less than 1%, the aggregation of CB becomes more and more severe as shown in Figure 7(a) and (b). This implies that the amount of dispersant required is at least 1.5% to prevent CB from aggregation.

The effect of different resins on the particle size of CB is also discussed. As illustrated in Table 2, interestingly, the particle size of CB in sample 3b is only 110 nm although it was dispersed by 1 wt% of dispersant. This is because B1 resin used in sample 3b can be adsorbed onto CB by the hydrogen bonding between urethane, amide, or imide anchoring groups of B1 and the surface carboxylic acid groups of CB, which can prevent the aggregation of CB particles.[25] In addition, compared with sample 3b, the particle sizes of CB in samples 4a-4c are even smaller, about 90 nm.

This is because B2 resin not only has urethane, amide, and imide anchoring groups but also possess a longer polymer chain, providing hydrogen bonding with CB and sufficient steric repulsion force to prevent CB from aggregation.

Optical density

In general, a CB-BM with a high OD of 4 μm^{-1} is required for practical use. In view of this, the CB in BM with high light-shielding property is desired. Two factors are thought to be important to influence the OD of BM: the light absorption property of CB and the concentration of CB.

It is known that the blackness of CB is normally a function of particle size [13]. Therefore, the light absorption property of CB with different particle sizes needs to be discussed. CB of 0.001 wt% in PGMEA was measured by an UV/Vis spectrophotometer. Figure 8 shows the absorbance spectra of CB dispersions 1a-1d. Apparently, the light absorption of CB increases as the particle size of CB decreases, indicating that light is easily absorbed by CB with a smaller particle size due to its larger specific surface area. In addition, Table 2 also shows the absorbance of different dispersions at 550 nm, and it is found that CB with the particle size of 90-110 nm exhibits the highest absorbance of about 0.48, indicating that samples 2-4 are suitable for BM application.

Another important factor, the concentration of CB is also discussed by comparing the OD of black films containing different concentrations of CB. The black films were prepared from sample 1d with the addition of different amounts of PMMA. As shown in Figure 9, the OD of black film increases as the concentration of CB increases. This figure also shows that the OD is close to 4 μm^{-1} as the concentration of CB is 45 wt% (based on the weight of black film), indicating that the concentration of CB is required at least 45 wt% for practical use.

Photo sensitivity of resins

In order to produce a BM with low energy consumption, the photo-sensitivity of CB PR is very important. The photo-initiator used in this study is I242 because it exhibits a stronger and broader absorption band in the range of 250-380 nm than other PIs and has been reported to be suitable for CB curing systems.[26] The photo-sensitivity of six resins added with 1 wt% I242 (based on the weight of resin) was thus monitored by a photo-DSC and the results are shown in Figure 10. The irradiation energy is 1.3 mW/cm^2. It is found that the curing extent of resins decreases in the order of B2>B3>B1>A2>A3>A1, i.e., decreasing with an increase in the concentration of carboxylic acid group in resin. This is because the carboxylic acid group of resin can form ionic complex with the tertiary amine group of primary radicals produced from I242, thus decreasing the mobility of primary radicals and initiator efficiency. According to the experimental results, B series resins were selected for the following studies because they have higher photo-sensitivities than A series resins.

Effect of the particle size of CB on the photo-sensitivity of CB PR

As mentioned above, the light absorption property of CB changes with its particle size; therefore, it is believed that the photo-sensitivity of CB PR is also affected by the particle size of CB. In this part, 1 wt% CB (based on the weight of B2 resin) with different particle sizes taken from samples 1a-1d in Table 2 was added into B2, and the rate of polymerization of CB/B2 mixtures initiated by I242 was then monitored by a photo-DSC. The results are shown in Figure 11. It is found that the curing extent of B2 increases as the particle size of CB increases. For instance, the final curing extent of B2 containing CB with the particle size of 100 nm is about

2.7×10^{-4} (mol-C=C/g), which is smaller than that of B2 with CB particle size of 460 nm. Because CB can absorb light, and the smaller, the larger of the absorbance; a large portion of incident light is thus absorbed by CB rather than PI.[18] Therefore, the rate of initiation is decreased and thus decreasing the curing extent of resin. Yet, CB with the particle size of about 100 nm is needed for being an effective light-shielding material; the preparation of a BM with both a high optical density and a good resolution is not an easy task.

Resolution of BM

In this study, the BM patterns were produced from the CB PRs by adding 2 wt% I242 into CB dispersions of samples 2-4. The concentration of CB (based on the total solid in the CB PR) was maintained at 45 wt% in order to produce a BM with an OD of 4 μm^{-1}. Unfortunately, it is not easy to produce a BM with both a high OD and a good resolution because the lithographic performance of CB PR is largely influenced by CB. In view of this, the UV-curable and alkali-soluble resin becomes the key material to affect the resolution of BM. Both the photo-sensitivity of exposed area and the solubility of unexposed area in alkali developer would affect the final resolution of BM, which would be discussed in the following sections.

BM pattern from B1/DPHA mixture

As mentioned above in Figure 10, B series resins were selected as photo-curable agents to prepare the BM due to their higher reactivities. At first, B1 was used; however, the photo-sensitivity of B1 is not as high as those of B2 and B3, therefore, we believe photo-sensitivity of CB PR is low when using B1 as the photo-curable agent. In order to solve this problem, B1/DPHA mixture was used because DPHA is a small monomer containing six acrylate groups and its extremely fast curing rate can improve the photo-sensitivity of CB PR.

The CB PRs were prepared by adding 2 wt% of I242 into CB dispersions. The effect of different resins on the resolution of BM is discussed by observing the appearance of black pattern. Figure 12 shows the OM image of pattern prepared from sample 2a by using a 25 μm-stripe photo mask. The UV irradiation energy was 200 mJ/cm^2 and the development time was 40 s. Although pattern was produced, the boundary of the pattern was coarse. This can be explained by two factors: On is that the concentration of carboxylic acid group in sample 2a is 6.2×10^{-4} mol/g (shown in Table 2), which is too low to provide a sufficient solubility of unexposed area in the alkali developer. The other one is that DPHA exhibiting a fast curing rate probably induces unnecessary polymerization in a small portion of unexposed area near the boundary of pattern, which would reduce the solubility of unexposed area in the alkali developer. In addition, a pattern with a smaller line-width like 10 μm was tried and could not be successfully prepared from the CB PR of sample 2a due to the same reason mentioned above. According to the experimental results, sample 2a of B1/DPHA is not suitable to prepare BM with a good resolution.

BM pattern from B1/B3 mixture

In order to improve the solubility of unexposed area in the alkali developer, the concentration of carboxylic acid group in CB PR needs to be increased. Therefore, a mixture of two resins, B1 and B3, was used to replace B1/DPHA, because both B1 and B3 contain carboxylic acid group. Figure 13(a) shows the SEM image of the pattern prepared from sample 3a (B1/B3=4.4/3.6). The irradiation energy was 200 mJ/cm^2 and the development time was 40 s. Compared with sample 2a, the pattern can be successfully prepared from sample 3a by using a 10 μm-stripe photo mask and the unexposed area is completely washed out. Because the concentration of carboxylic acid group in sample 3a increases to 7.9×10^{-4} mol/g, providing a good solubility of unexposed area in the alkali developer.

In addition, the effect of irradiation energy on the appearance of pattern is also discussed by observing the SEM images shown in Figure 13(a)-(c). Obviously, the line-width of pattern prepared upon UV irradiation of 50 mJ/cm^2 decreases to about 7 μm and surface of the pattern is very rough. We believe that the curing extent of exposed area upon UV irradiation of 50 mJ /cm^2 is too low to produce a good pattern. The surface and line-width of patterns prepared upon UV irradiation of 100 and 200 mJ/cm^2 are smoother and larger than the pattern prepared upon 50 mJ/cm^2, respectively, indicating that the irradiation energy is required at least 100 mJ/cm^2. However, the boundaries of these two patterns are not absolutely straight; moreover, the line-width of patterns prepared upon UV irradiation of 100 and 200 mJ/cm^2 are approximately 8-9 μm, which are slightly smaller than the line-width of 10 μm on photo-mask. It seems that a small portion of exposed area near the boundary of pattern was removed by the alkali developer. We believe that increasing the amount of resins in CB PR can improve the curing extent of exposed area to solve this problem.

This deduction was confirmed by using sample 3b to prepare a pattern because the concentration of B1/B3 in sample 3b is larger than that in sample 3a. A 10 μm-stripe photo mask was used and the UV irradiation energy was 100 mJ/cm^2. Compared with the pattern prepared from sample 3a in Figure 13(b), the boundary of the resulting pattern from sample 3b seems straighter (shown in Figure 13(d)); in addition, the line-width of pattern is close to 10 μm. This implies that increasing the amount of resins in CB PR is a good way to prepare a pattern with good appearance.

BM pattern from B2/B3 mixture

As mentioned above, the photo-sensitivity of B1 is not as high as those of B2 and B3. In order to prepare a BM with low energy consumption, B2/B3 was thus prepared to replace B1/B3. Three CB PRs (samples 4a-4c in Table 2) with different ratios of B2/B3 were prepared in order to adjust the concentration of carboxylic acid group to a proper value that would give the final pattern with good appearance. The compositions of samples 4a-4c are listed in Table 2 and the patterns prepared from these three CB PRs are shown in Figure 14(a)-(c). Compared with the pattern produced from sample 3b, the UV irradiation energy of 50 mJ/cm^2 is sufficient to produce patterns from samples 4a-4c, which also confirms that photo-sensitivity of B2/B3 is higher than that of B1/B3. In addition, the effect of the concentration of carboxylic acid group in CB PR on the appearance of pattern can also be understood. A very clean and straight pattern of 10 μm in width produced from sample 4c is clearly observed. However, the patterns produced from samples 4a and 4b, both of which contain less carboxylic acid groups than sample 4c, are not so perfect since the unexposed area is not completely washed out during development. This implies that B2/B3 with a weight ratio of 2.2/6.8 having the concentration of carboxylic acid group at 7.4×10^{-4} mol/g in sample 4c is appropriate to prepare a good pattern.

Conclusions

The CB-BM having a high OD of 4 μm^{-1} and a good resolution of 10 μm was successfully produced from the CB PR prepared in this work. The roles of CB and resins in CB PR are important because they strongly influence the OD and the pattern appearance of CB-BM, respectively. To have a high light absorption property as a good light-shielding material, the CB should have a particle size of about 100nm. By using the CB of about 100nm, it is found that 45 wt% CB (based on the total solid in the CB PR) is sufficient to produce a black film with a high OD of 4 μm^{-1}. Finally, the CB-BM pattern was prepared from CB PR through an UV-lithography process. According to the SEM and OM observation, it is found that the appearance of the pattern is strongly affected by the photo-sensitivity and the concentration of carboxylic acid group of resins in CB PR. In addition, B2 and B3 are found to be the best two photo-curable resins in the CB PR because of their high photo-sensitivities. By using a CB PR containing B2/B3 with a weight ratio of 2.2/6.8, a good CB-BM pattern was successfully prepared upon UV irradiation at a low energy of 50 mJ/cm^2.

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Table 1. Functional group concentrations of resins, A1, A2, A3, B1, B2, and B3

Resin code	Components	Molar ratio	Carboxylic acid (mol/g)[a]	Acrylate (mol/g)[b]	Methacrylate (mol/g)[c]	Maleate (mol/g)[d]
A1	EPA:BTDA	1:2	5.1×10^{-3}	1.7×10^{-3}	0	0
A2	EPA:BTDA	5:4	2.3×10^{-3}	2.6×10^{-3}	0	0
A3	EPA:MA	1:2	3.0×10^{-3}	2.8×10^{-3}	0	2.8×10^{-3}
B1	EPA:BTDA:H-I	1:2:2	2.2×10^{-3}	1.1×10^{-3}	1.1×10^{-3}	0
B2	EPA:BTDA: H-I	5:4:2.67	1.5×10^{-3}	2.1×10^{-3}	0.6×10^{-3}	0
B3	EPA:MA:IPDI	1:2:0.8	1.7×10^{-3}	2.5×10^{-3}	0	2.5×10^{-3}

[a] concentration of COOH group was determined by a titration method.

[b, c, d] concentration of acrylate, methacrylate, and maleate groups are calculated from composition, respectively.

Table 2. The composition of CB dispersion, properties of CB, and the concentration of carboxylic acid group

Sample codes	CB (wt%)	dispersant (wt%)	Resins (wt%)		PGMEA (wt%)	Particle size of CB (nm)[a]	Absorbance of CB at 550 nm[b]	Concentration of COOH (mol/g)[c]
1a	10	0.5	0		89.5	430	0.15	0
1b	10	1	0		89	280	0.33	0
1c	10	1.5	0		88.5	100	0.48	0
1d	10	2	0		88	100	0.48	0
			Resin B1	DPHA				
2a	10	2	5.6	2.4	80	90	0.48	6.2×10^{-4}
			Resin B1	Resin B3				
3a	10	2	4.4	3.6	80	90	0.48	7.9×10^{-4}
3b	10	1	5	4	80	110	0.47	8.9×10^{-4}
			Resin B2	Resin B3				
4a	10	1	7.6	1.4	80	90	0.48	6.9×10^{-4}
4b	10	1	5	4	80	90	0.48	7.2×10^{-4}
4c	10	1	2.2	6.8	80	90	0.48	7.4×10^{-4}

[a] particle size of CB is determined by a DLS and defined at the point of 50% of accumulated distribution.

[b] absorbance of CB at 550 nm is determined by an UV/Vis spectrophotometer. The concentration of CB in PGMEA was maintained at 0.001%.

[c] concentration of carboxylic acid group is calculated from the mole of carboxylic acid group divided by the weight of total solid in CB dispersion.

Figure captions

Figure 1. Synthesis and structures of resins, A1, A2, A3, B1, B2, and B3

Figure 2. FTIR spectra of EPA/BTDA mixture, A2, and B2

Figure 3. GPC curves of EPA, BTDA, A2, and B2

Figure 4. FTIR spectra of EPA, A3, and B3

Figure 5. GPC curves of EPA, MA, IPDI, A3, and B3

Figure 6. Influence of amount of CB dispersant, Disponer 9850, on the particle size of CB determined by DLS

Figure 7. SEM pictures of CB dispersions with different amounts of dispersant (a)0.5 wt%, (b)1.0 wt%, (c)1.5 wt%, and (d)2.0wt%

Figure 8. The absorbance spectra of samples 1a to 1d. The concentration of CB in PGMEA is 0.001 wt%.

Figure 9. The relationship between the concentration of CB and the OD of black film

Figure 10. The curing extent of resins determined by a photo-DSC. The polymerization was initiated by 1 wt% I242 upon the UV irradiation with energy of 1.3 mW/cm^2.

Figure 11. The effect of the particle size of CB on the curing extent of resin B2. The polymerization was initiated by 1 wt% I242 upon the UV irradiation with energy of 1.3 mW/cm^2.

Figure 12. The OM image of pattern prepared from sample 2a by using a 25 μm-stripe photo mask. The UV irradiation energy was 200 mJ/cm^2 and the development time was 40 s.

Figure 13. The SEM images of the pattern prepared from (a) sample 3a irradiated by UV with 200 mJ/cm^2, (b) sample 3a irradiated by UV with 100 mJ/cm^2, (c) sample 3a irradiated by UV with 50 mJ/cm^2, and (d) sample 3b irradiated by UV with 100 mJ/cm^2. The development time was 40 s.

Figure 14. The SEM images of the pattern prepared from (a) sample 4a irradiated by UV with 50 mJ/cm^2, (b) sample 4b irradiated by UV with 50 mJ/cm^2, and (c) sample 4c irradiated by UV with 50 mJ/cm^2. The development time was 40 s.

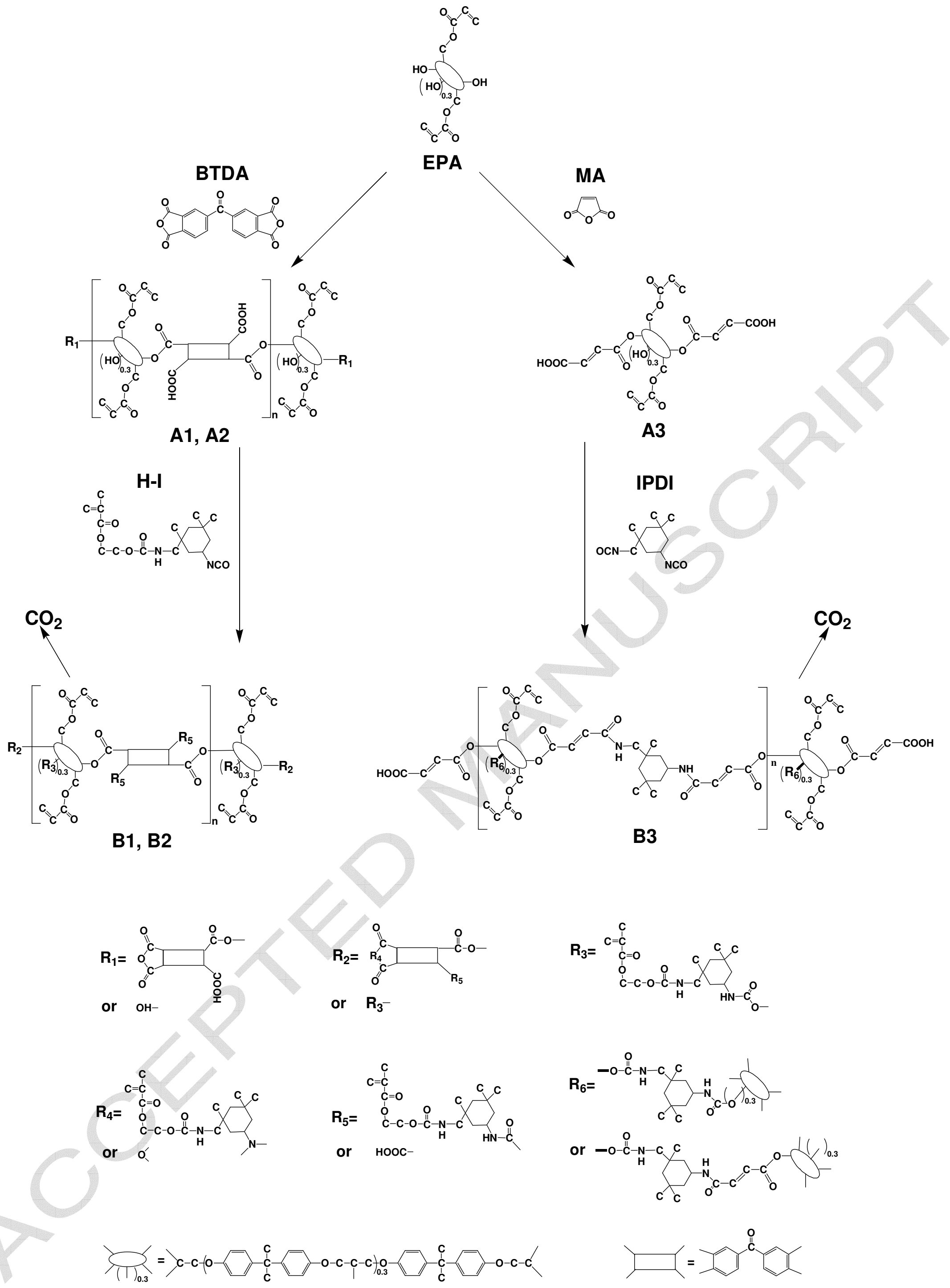
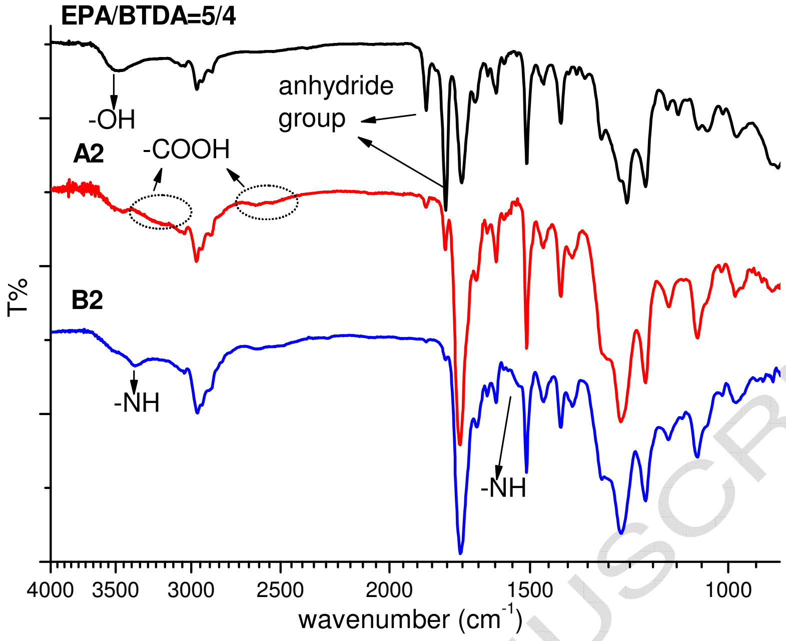

EPA
BTDA
MA
A1, A2
A3
H-I
IPDI
CO_2
CO_2
B1, B2
B3
R_1=
or OH–
R_2=
or R_3–
R_3=
R_4=
or
R_5=
or HOOC–
R_6=
or

Figure 1.



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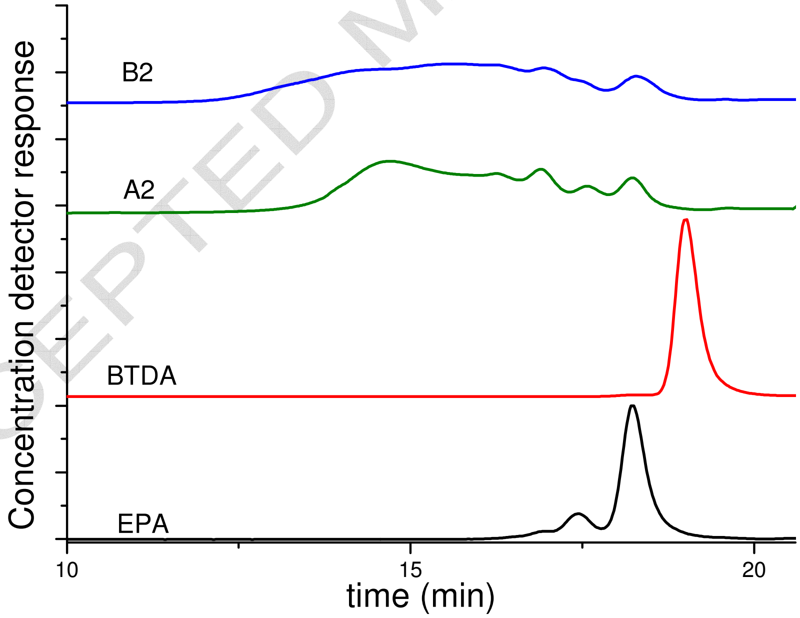

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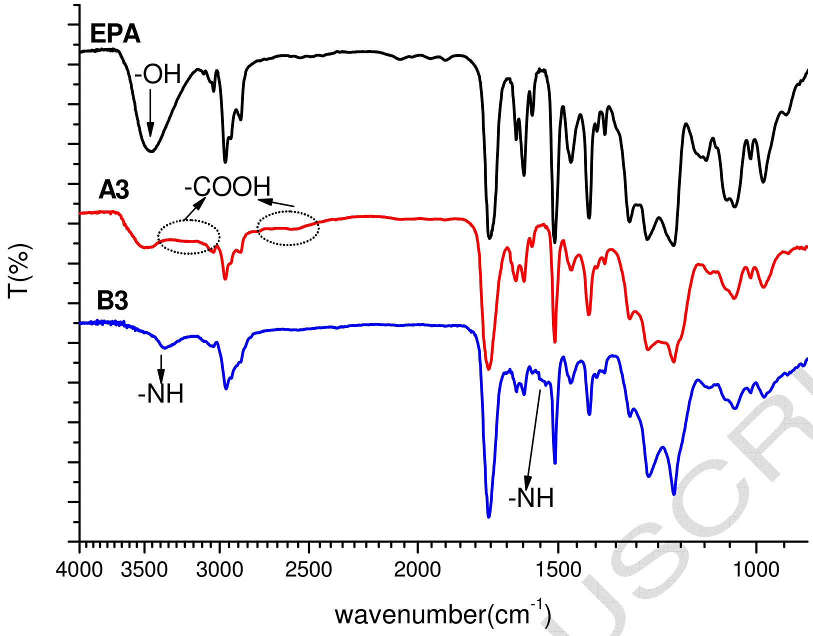

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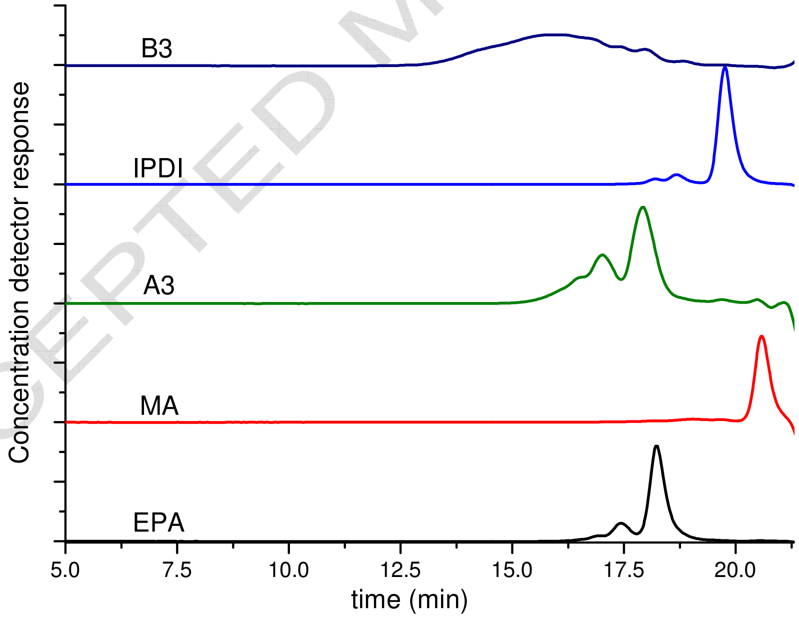

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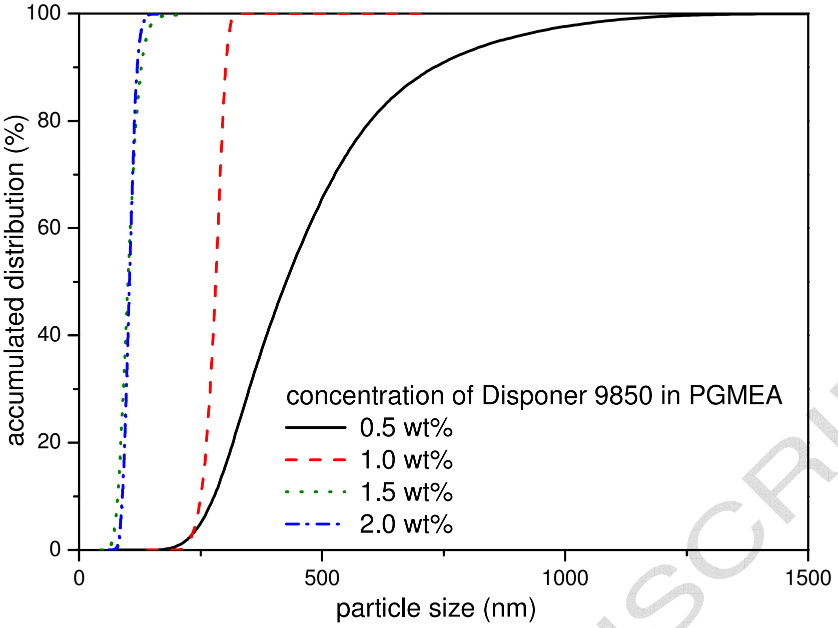
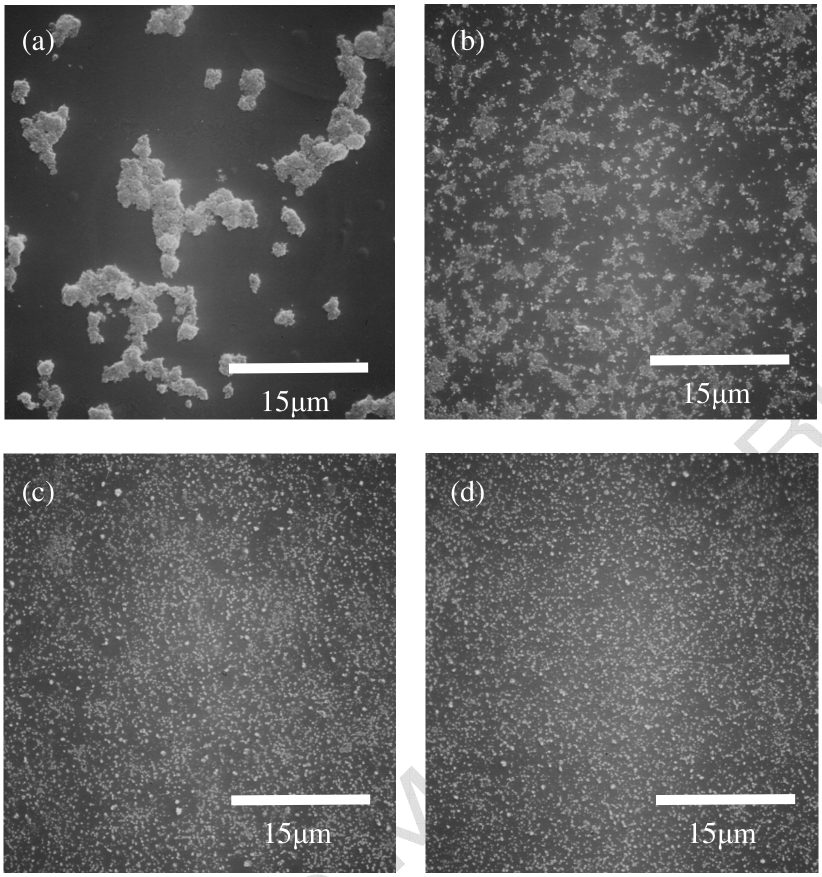

accumulated distribution (%)
0
20
40
60
80
100
particle size (nm)
0
500
1000
1500
concentration of Disponer 9850 in PGMEA
0.5 wt%
1.0 wt%
1.5 wt%
2.0 wt%

Figure 6.



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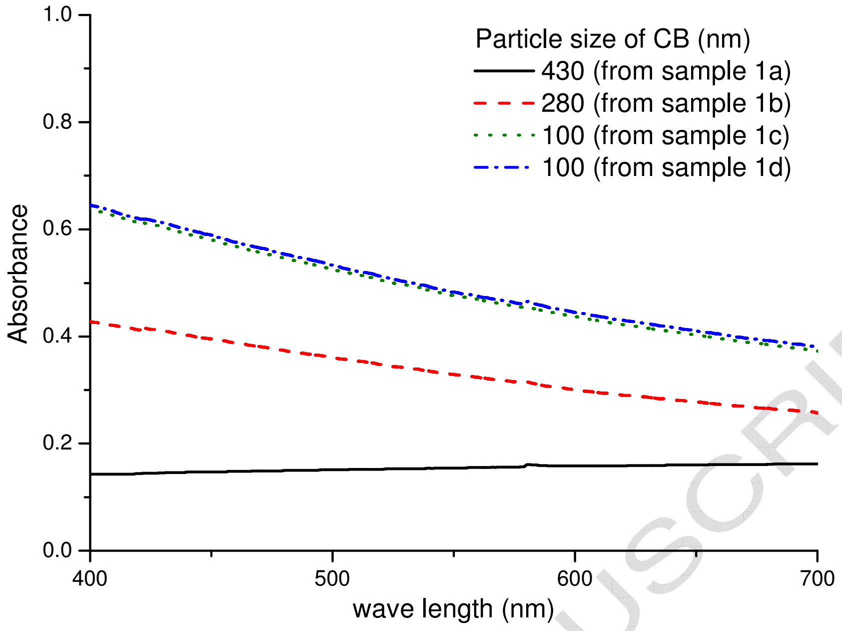

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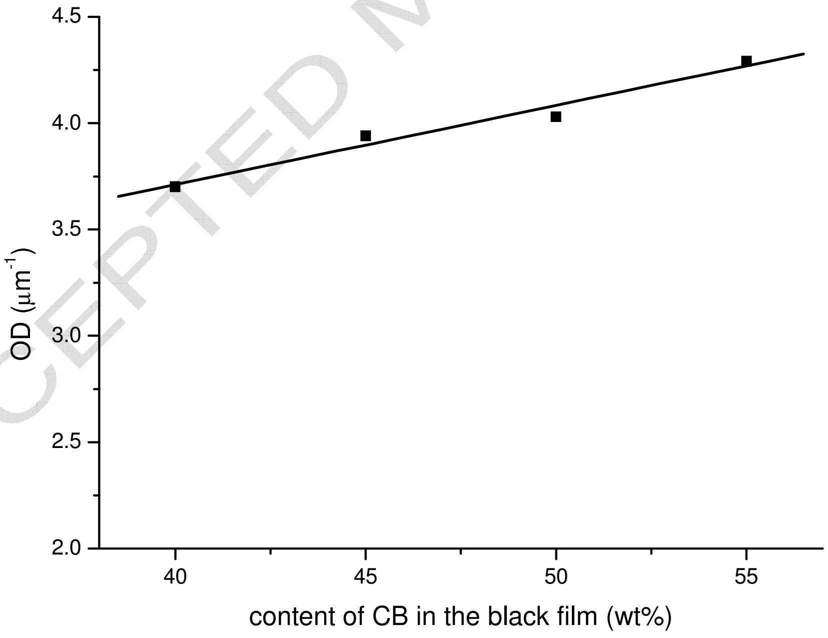

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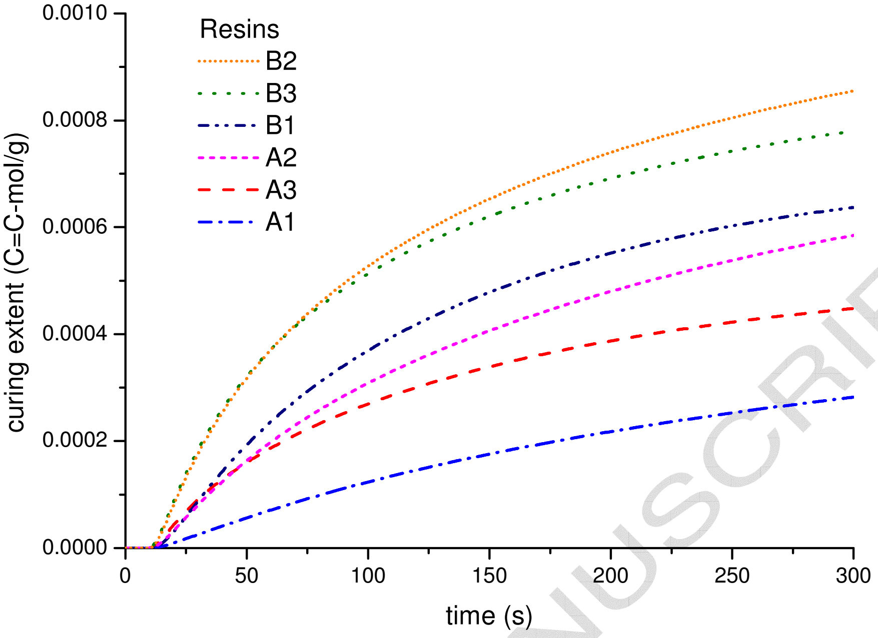
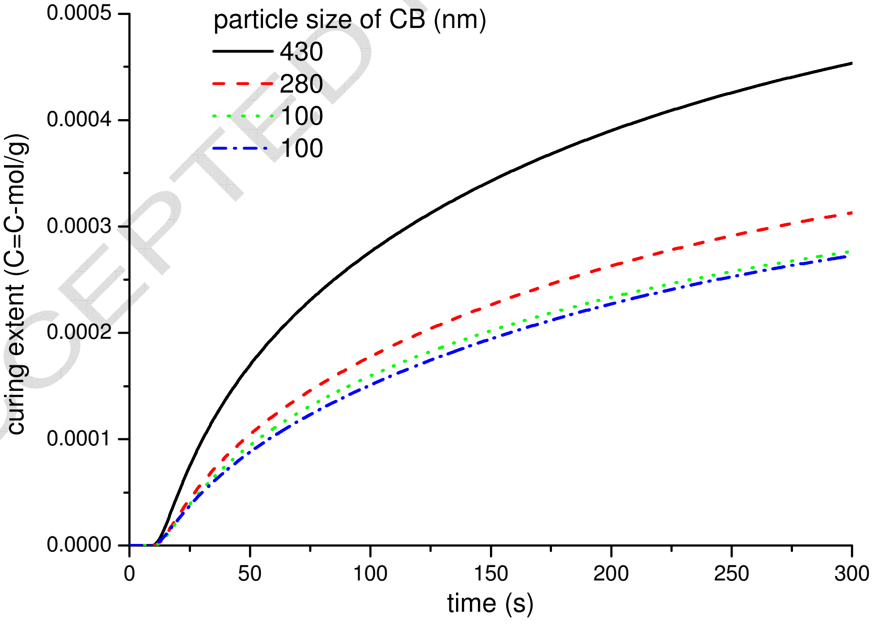


Figure 10.



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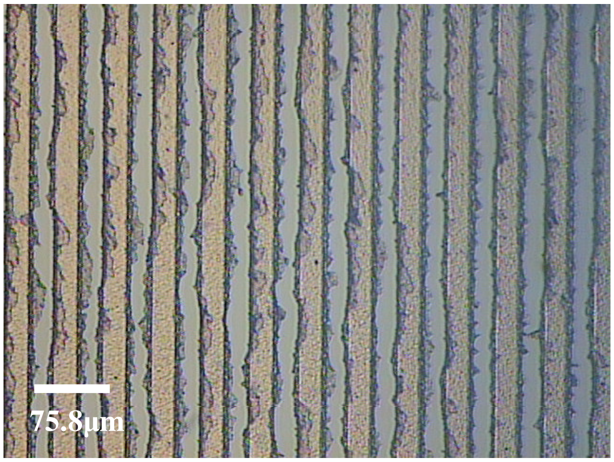

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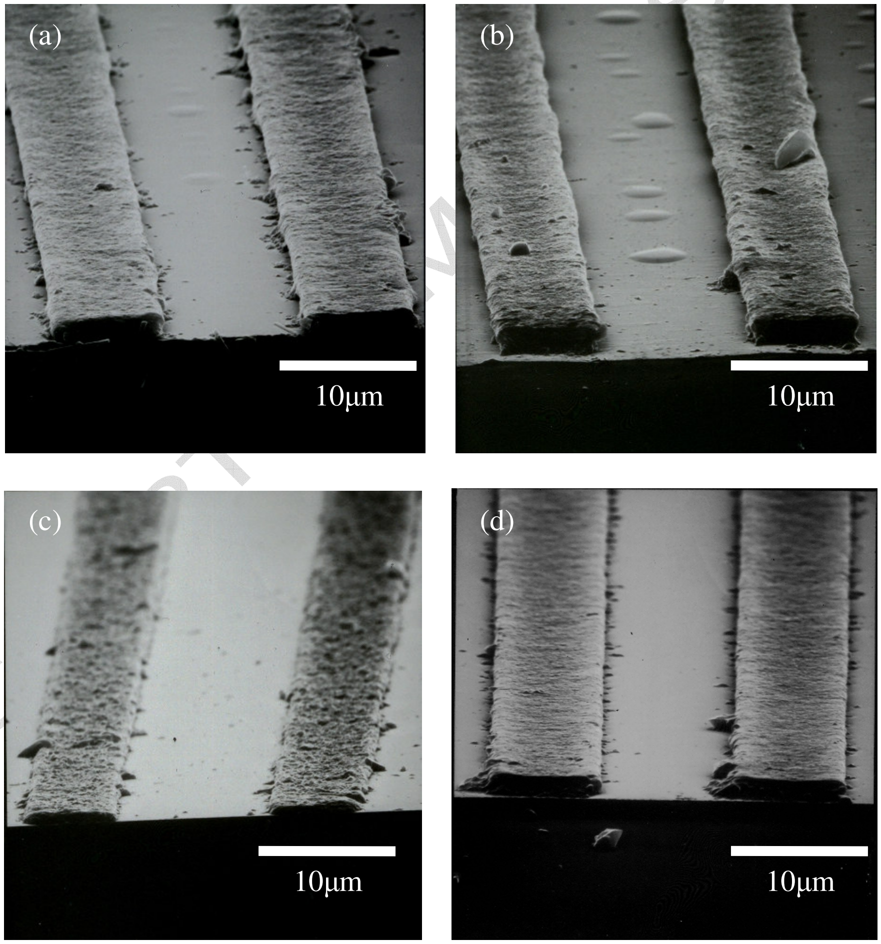

Figure 13.

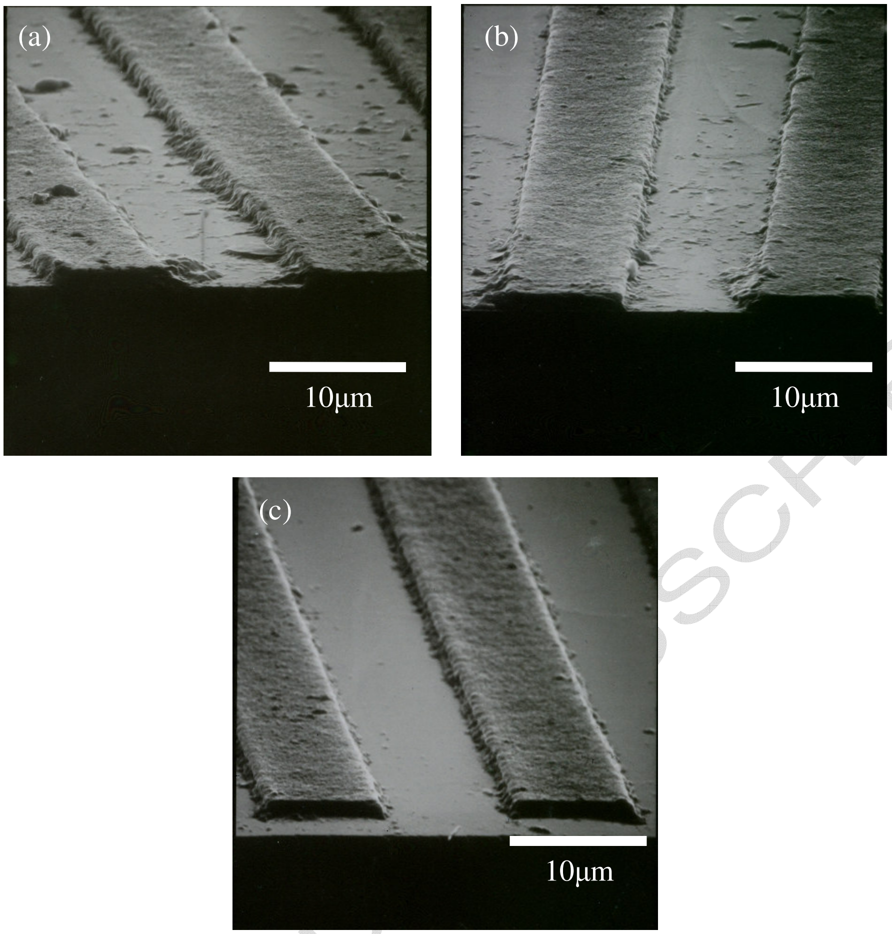

Figure 14.