Optical and mechanical properties of jet printed and UV cured blue pixels with phosphated epoxy acrylate as the curing agent

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Abstract

Phosphated epoxy acrylate and phosphated imide-epoxy were synthesized and used as compositions of non-volatile (no solvent) UV curable ink for manufacturing the jet-printed LCD color filter (CF). Phosphated epoxy acrylate oligomer showed not only good solubility in UV curable monomers and pigment compatibility as ink compositions, but also good thermal and mechanical properties after curing. No receiver layer or barrier ribs are necessary to prevent the printed ink from overflowing to the neighboring area. The color inks were precisely ejected to the glass substrate and UV-cured immediately to make the stripe pattern. The printed blue stripes exhibited smooth surface, straight edge, high transparency (transmittance >84%), high nanoindentation hardness (3.94 GPa) and modulus (72.15 GPa). The influences of curable compositions on the optical properties, patterning properties, surface morphology and nanoindentation hardness of the micro-stripes were discussed.
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1. Introduction

In addition to the pigment dispersion process that is widely used for mass production, ink-jet methods are designed for manufacturing the color filter [1–4]. Inks containing the red (R), green (G) or blue (B) colorants are ejected via nozzles onto the glass substrate, and the jet-printed inks are dried to form color-filter pixels. Two kinds of ink-jet process were developed for making color filters. The first process involves an ink-receiver layer. Since the glass substrate cannot adsorb inks, the receiver layer must be coated onto the substrate before printing [5,6]. Then, the ink-jet inks can be absorbed and fixed on the glass substrate. The second process does not involve the ink-receiver layer [7]. In our previous study [8,9], aqueous UV curable ink was used to manufacture the ink-jet printed color filter. Water and cosolvent should be removed before UV curing. Patterned barrier were built on the substrate to prevent the printed ink from overflowing to the neighboring area. Inks were ejected

into the area surrounded by the barrier rib. Cho et al. [10] developed a simultaneous UV embossing method to fabricate two parallel layers with different surface properties. It could be used as barrier ribs for manufacturing of ink-jet printed color filter of a liquid crystal display.

In this study, in order to fix the printed stripes immediately after printing, inks with no volatile ingredients (non-volatile ink) were used. No solvent is necessary to dissolve the ink composition. Therefore, the phosphated oligomer or binder should be dissolved in the monomer. Phosphorus-containing groups were considered to bring improved organosolubility to high performance polyamides and polyimides [11–14]. Polyamides [11,12] and polyimides [14] with triphenylphosphine oxide groups in the polymer backbones have shown good organosolubility, good thermal and oxidative stability, and high glass transition temperatures. Moreover, phosphorus-containing groups were also incorporated into polymers for increasing the polymers' adhesive properties [14]. After curing, the color stripes of the color filter should have smooth surface and good color uniformity. The influences of curable compositions on the optical properties, patterning properties, surface morphology and nanoindentation hardness of the blue micro-stripes were discussed in this study.

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2. Experimental

Phenylphosphonic acid (PPA) and 2,2-Bis(4-glycidyloxy phenyl)-propane (DGB) were dissolved in DMF and reacted at 100 °C for 8 h to prepare the PPAD (PPA: DGB = 1:1) polymer.

The other binders were synthesized by the reaction scheme shown in Fig. 1. 4-Amino-*N*-methylphthalimide (AMP) and DGB were dissolved in DMF and refluxed at 150 °C for 6 h. PPA was mixed with the AMP–DGB solution and reacted at 100 °C for 6 h to prepare the AMPPD (AMP:DGB:PPA = 1:2:1) polymer. *N*-(2-Hydroxyethyl)phthalimide and 1,2,4-benzenetri-carboxylic anhydride (BTCA) were dissolved in DMF and reacted at 90 °C for 8 h to synthesize the BIB monomer. DGB was mixed with the BIB solution and reacted at 100 °C for 6 h. PPA was dissolved in DMF and mixed with the BIB–DGB solution. The mixed solution was reacted at 100 °C for 6 h to prepare the BIBPD (BIB:DGB:PPA = 1:2:1) polymer. PPA, 2-acryloyloxyethyl phosphate (PA) and DGB were dissolved in DMF and reacted at 90 °C for 6 h to prepare the PPADP (PPA: DGB:PA = 9:10:1) oligomer.

Blue pigment (Clariant) containing 50% phthalocyanine pigment in a vinyl chloride/vinyl acetate copolymer carrier material was added as colorant. The ingredients of the PPADP3 ink included blue pigment (0.25 g), tetrahydrofurfuryl methac-rylate (4.05 g), PPADP (0.3 g), ITX/907 (0.2 g), pentaerythritol triacrylate (2.5 g) and dipentaerythritol hexnacrylate (2.7 g). The BIBPDI ink was prepared by similar ingredients except PPADP and pentaerythritol triacrylate were replaced by BIBPD (0.1 g) and pentaerythritol triacrylate (2.7 g).

Thermogravimetric analysis (TGA) was carried out using a TGA2950 apparatus from TA Instruments at a scan rate of
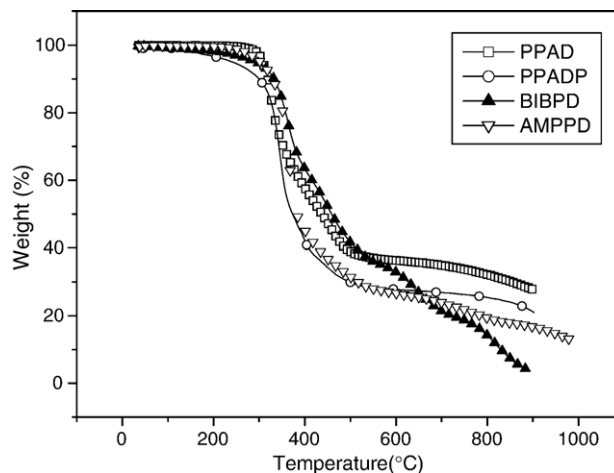
Fig. 2. Thermogravimetric analysis thermograms of the binders.

10 °C/min under nitrogen atmosphere. The transmittance spectra of the films were recorded by a UV–Vis spectropho-tometer (Hitachi UV-3000). SEM measurements were con-ducted with a HITACHI S3000 Vacuum SEM Spectrometer. The mechanical properties of different cured films were investigated by the nanoindentation test using a TriboScope (Hysitron Inc.) nanoindentor. The load was applied to the surface with 5 s hold period at the maximum applied load. The nanoindentation test involved indentations with maximum load at 1000 µN of 300–400 nm in depth. The mechanical properties of the printed stripes were investigated by the nanoindentation test using a MTS Nano-Indenter XP system. It can make well-defined indentation impressions on the tiny stripe. The
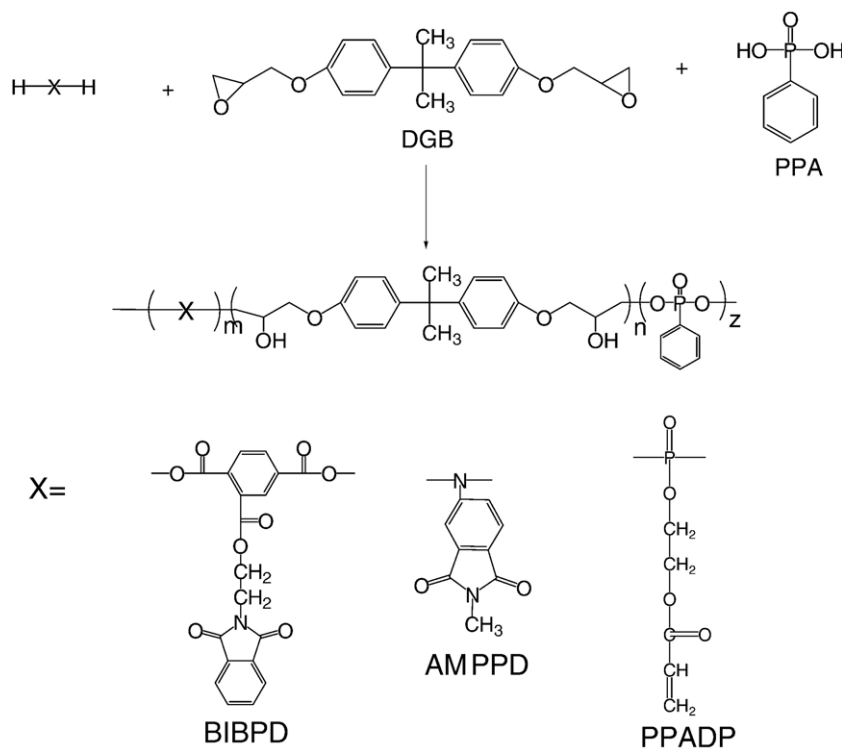
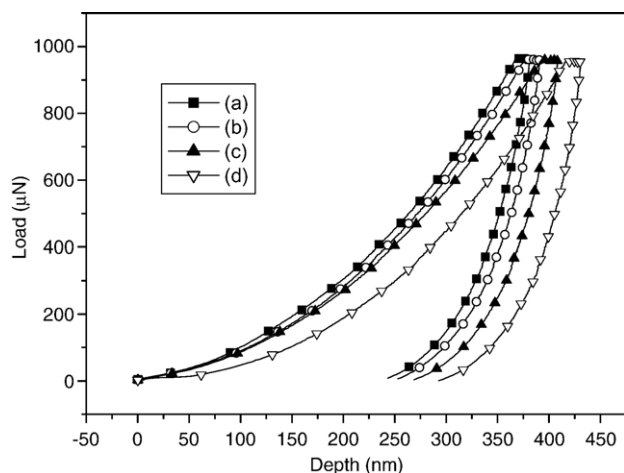Fig. 1. Reaction scheme of synthesizing BIBPD, AMPPD and PPADP binders.

Fig. 3. Nanoindentation loading–hold–unloading curves of the binders (a) AMPPD, (b) BIBPD, (c) PPADA and (d) PPAD.

Fig. 4. UV–Vis spectra of the binders and cured film of PPADP3 blue ink.

nanoindentation test involved indentations with maximum depth at 1000 nm.

3. Results and discussion

The thermal stability and degradation behavior of the phosphorus binder and UV cured polymer were evaluated by TGA. Td represents the temperature at 5% weight loss. As shown in Fig. 2, Td of the PPAD binder consisted of phenyl phosphorus segments is 320 °C. Td of the UV cured PPADP is 230 °C. PPAD had the highest char yield (30 %) at 900 °C. PPADP has similar structure with PPAD except that 10% (mole ratio) phenyl phosphoric acid is replaced by the phosphoric acrylate group. The phosphoric acrylate group may break at higher temperature. Char yield of the cured PPADP (PPA:DGB: PA=0.9:1:0.1) is 24%. The phenyl phosphoric acid structure favored the formation of more char at high temperature than the phosphoric acrylate did. For AMPPD and BIBPD, pendent phthalimide segments were introduced into the polymer chain to evaluate their influences on the thermal stability. However, compared with the TGA curves of cured PPADP and PPAD, introducing pendent phthalimide groups did not lead to large improvement in the thermal stability. AMPPD, BIBPD and PPAD showed similar Td. The temperature of rapid weight loss of BIBPD shifted to higher temperature region. The TGA curve dropped rapidly after 600 °C. AMPPD, BIBPD and PPAD showed better thermal resistant properties than the cured PPADP. However, all binders (with Td ≥ 230 °C) can be used in the CF application.

Table 1
Solubility of the oligomer and binders in different solvent and monomer

	AMPPD	BIBPD	PPAD	PPADP
THF	O	X	X	O
DMF	O	O	O	O
DMSO	O	O	O	O
THF methacrylate	X	X	X	O

O: Soluble; X: Insoluble.

The nanoindentation technique is a useful tool for the determination of the mechanical properties of thin films, including polymers.[15,16] The force–depth curves (Fig. 3) showed a typical remaining plastic deformation of the four binders during indentation. The hardness of AMPPD, BIBPD, PPADP and PPAD (at max load=1000 μN) were 0.28, 0.27, 0.24 and 0.22 GPa respectively. However, the films showed
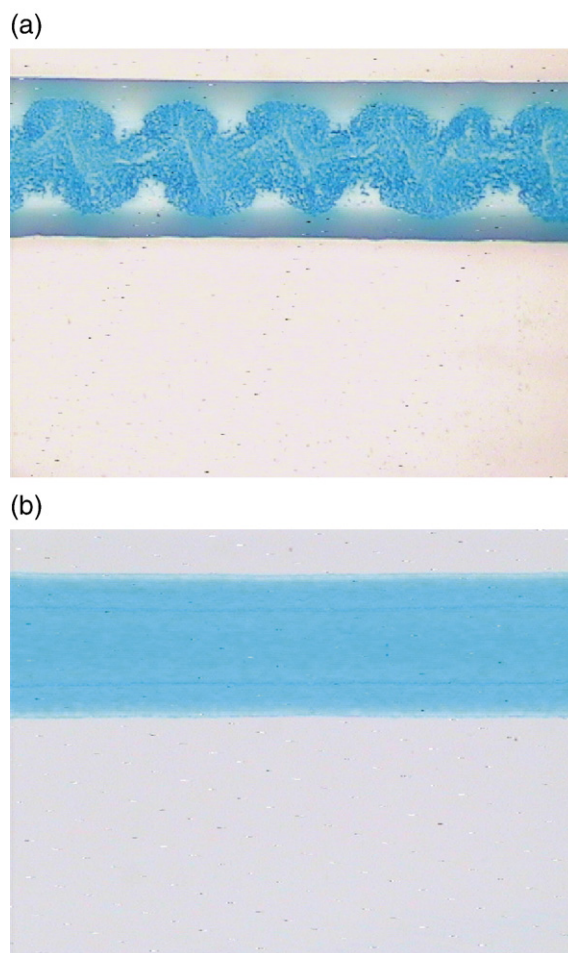
(a)

(b)

Fig. 5. OM images of (a) the cured BIBPDI stripe and (b) the cured PPADP3 stripe.
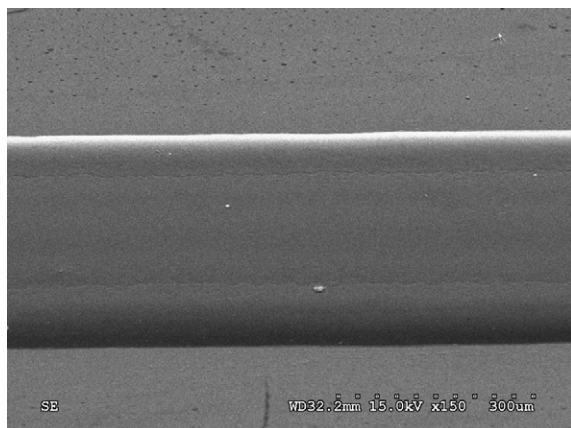
Fig. 6. SEM images of the cured PPADP3 stripe.

nearly the same modulus. The modulus of AMPPD, BIBPD, PPADP and PPAD were 7.6, 7.8, 7.7 and 7.7 GPa respectively. AMPPD polymer with bulky phenylphosphonic and phthalimide side chain showed the highest hardness of all films. The phthalimide group of AMPPD is directly attached on the main polymer chain. The phthalimide group of BIBPD is attached on the main polymer chain through a short flexible aliphatic ester spacer. Although the cured PPADP is a crosslinked polymer, the aliphatic acryloyloxyethyl side chain may increase the free volume of the polymer and lead to lower hardness than the AMPPD film. The high hardness and modulus exhibited by AMPPD film in nanoindentation evaluations indicate their greater resistance to plastic deformation and local penetration on application of external force.

Although cured PPADP showed lower heat resistance than the AMPPD, BIBPD and PPAD binder, PPADP oligomer exhibited better solubility in THF solvent than the other binders. As listed in Table 1, only the PPADP oligomer can be dissolved in tetrahydrofurfuryl methacrylate. The enhanced solubility was attributed to the aliphatic pendent phosphated acrylate chain. In this study, patterns were prepared by jetting and curing of non-volatile UV curable ink. After printing, the ink can be fixed immediately by UV curing reaction. In order to make a stable dispersed color ink, the binder must be dissolved in the monomer. Otherwise, some solvent should be added in the ink to prevent the phase separation problem. Therefore, PPADP was selected for the printing test.

The optical properties of the materials are critical to their application in manufacturing color filter. The transmittance of the visible light should be as high as possible. Fig. 4 illustrates the UV–Vis spectra of the polymer films. PPAD and BIBPD films showed higher transparency than PPADP. AMPPD films exhibited the lowest transmittance at the visible light range. In the range of 400–700 nm wavelengths, more than 90% transmittance for PPAD and BIBPD films were observed. PPADP showed acceptable transmittance at the transmitting wavelength of the blue pigment. More than 84% transmittance was observed for the cured blue PPADP3 film.

Fig. 5(a) showed OM images of the blue stripe printed by the BIBDPI ink. There were spiral-shaped pigment aggregates at the central region of the printed stripe. The spiral aggregates were similar to the instable flow behavior of polymer melt observed in the extrusion processing when both the extrusion rate and viscosity were too high [17]. Besides, the edge of the stripes consisted of only the UV-curable resin and binder. BIBPD was not compatible with the blue pigment. BIBPD cannot be used as the ink composition for the non-volatile jet-printed ink for CF manufacturing. The OM image of the blue stripe printed by PPADP3 ink was shown in Fig. 5(b). Stripes with straight edges and good color uniformity were prepared on the glass substrate. The surface morphology of the printed stripe was measured by SEM. The SEM image of the stripe was shown in Fig. 6. The stripe showed smooth surface and straight line edge. The outer regions near the two edges are slightly higher than the central region. The mechanical properties of the printed stripes were investigated by the nanoindentation test. Well-defined indentation impressions were made on the tiny stripe to detect the hardness and modulus. The hardness and modulus at max load are 3.94 and 72.15 GPa respectively.

4. Conclusions

Phosphated epoxy acrylate PPADP oligomer with pendent phosphated acrylate exhibited good solubility in the UV curable monomer and excellent pigment compatibility. It can be used as compositions of non-volatile UV curable ink for manufacturing the jet-printed LCD color filter. No receiver layer or barrier ribs are necessary to prevent the printed ink from overflowing to the neighboring area. The color inks were precisely ejected to the glass substrate and UV-cured immediately to make the stripe pattern. The printed stripes exhibited smooth surface, straight edge, high transparency (transmittance >84%), good thermal properties, high nanoindentation hardness (3.94 GPa) and modulus (72.15 GPa). BIBPD with pendent phthalimide segments as thermal resistant binder showed poor solubility in monomer and poor pigment compatibility. There were spiral-shaped pigment aggregates at the central region of the printed stripe. The chemical structure of the oligomer for jet printed CF should be properly designed to meet the requirements of good solubility in monomer, together with high transparency, good thermal and mechanical properties after curing.

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