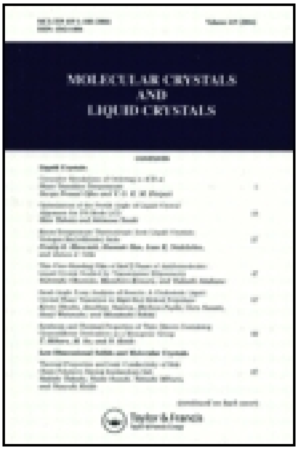


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Fabrication of Glass Fiber Reinforced Composite Films for Flexible Organic Light Emitting Diode Devices

Sang Chul Ryu [a], Jin Woo Kim [b], Quang Hung Vu [b], Hyeok Yong Kwon [c], Yun-Su Lee [c], Dong Gyu Lee [b] & Lee Soon Park [b] [c]

[a] LG Display Co., LTD., Gumi-si, Gyungsangbuk-do, Korea

[b] Department of Polymer Science, Kyungpook National University, Daegu, Korea

[c] Advanced Display Manufacturing Research Center, Kyungpook National University, Daegu, Korea

Version of record first published: 10 Nov 2009

To cite this article: Sang Chul Ryu, Jin Woo Kim, Quang Hung Vu, Hyeok Yong Kwon, Yun-Su Lee, Dong Gyu Lee & Lee Soon Park (2009): Fabrication of Glass Fiber Reinforced Composite Films for Flexible Organic Light Emitting Diode Devices, Molecular Crystals and Liquid Crystals, 514:1, 1/[331]-13/[343]

To link to this article: http://dx.doi.org/10.1080/15421400903217488

Mol. Cryst. Liq. Cryst., Vol. 514, pp. 1/[331]–13/[343], 2009
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400903217488

Fabrication of Glass Fiber Reinforced Composite Films for Flexible Organic Light Emitting Diode Devices

Sang Chul Ryu[1], Jin Woo Kim[2], Quang Hung Vu[2], Hyeok Yong Kwon[3], Yun-Su Lee[3], Dong Gyu Lee[2], and Lee Soon Park[2,3]
[1]LG Display Co., LTD., Gumi-si, Gyungsangbuk-do, Korea
[2]Department of Polymer Science, Kyungpook National University, Daegu, Korea
[3]Advanced Display Manufacturing Research Center, Kyungpook National University, Daegu, Korea

We fabricated transparent composite films which have good thermal stability, low CTE (coefficient of thermal expansion) and high mechanical properties for flexible OLED substrate. Glass fiber reinforced composite films were made by UV light induced chemical crosslinking of composite materials consisted of glass fiber and UV curable resin in film state. It was noted that the pattern of the reinforce glass fiber had important effect on the optical and mechanical properties of the resulting composite film. The performance of the composite films in the ITO thin film deposition process and subsequent OLED device fabrication was better than those of the known polymer films such as PET, PC, and PES.

Keywords: composite; CTE; display substrate; glass fiber; OLED; UV resin

INTRODUCTION

Recently there have been reported many researches on the development of new film materials that could be applied to flexible display substrate. In order to the used as flexible display substrates the materials should match properties such as high transparency, flexibility, good film forming property as well as high thermal stability

---

This research was supported by the Advanced Display Manufacturing Research Center (ADMRC), Regional Innovation Center Program of the Ministry of Knowledge Economy, Republic of Korea.

Address correspondence to Prof. Lee Soon Park, Department of Polymer Science and Engineering, Kyungpook National University, Sangyuk-dong, Buk-gu, Daegu 702-701, Korea (ROK). E-mail: lspark@knu.ac.kr

and mechanical properties. However, films made with single polymeric material were found to have limitations as substrates for flexible display, especially for flexible organic light emitting diodes (OLEDs). Films made from composite materials could be a solution for the application to the substrates for flexible displays.

Among the exiting polymer matrix composites, glass-fiberreinforced polymer matrix composites have been used widely due to their outstanding properties such as mechanical, electrical, and thermal properties. However, most of the glass fiber reinforced polymer composites have been used as structural materials. They have not been tried for application to optical films in thin film transistor (TFT) liquid crystal display or flexible substrate in OLEDs. For these applications the matching of the refractive index of matrix and glass fiber should be an essential requirement for achieving transparent composite films [1–3]. In addition to the transparency of the material, the reinforced flexible films should have low coefficient of thermal expansion (CTE) as well as high chemical and mechanical stabilities.

In this study, we tried to fabricate a glass fiber reinforced polymer film by UV light induced chemical crosslinking of composite materials consisted of glass fiber and UV curable resin in the film state. The resulting flexible substrates were subjected to the OLED device fabrication and analyzed for the necessary properties.

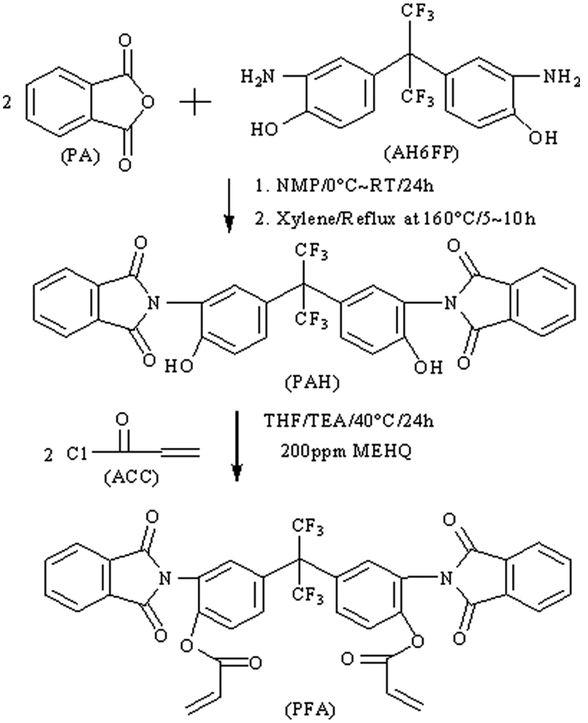
EXPERIMENTAL

Materials

Phthalic anhydride (PA), acryloyl chloride (ACC), 2,2-bis (3-amino-4-hydroxyphenyl) hexa-fluoropropane (AH6FP), triethylamine (TEA), 4-methoxyphenol (MEHQ) and triethyleneglycol dimethacrylate (TEGDMA) were obtained from Aldrich Chemical Company and used as received. Glass fiber and fabrics were received from Owens Corning Veil Netherlands B. V. and Hankuk Fiber Company in Korea. UV resins PM 472 and EB9260 were received from CCTech Inc. and SK Cytech Co. both in Korea, respectively.

Imide Monomer for UV Curable Resin

A novel imide monomer was synthesized via two-step process as shown in Scheme 1 [4–6]. Reactions were carried out in 250 ml three-neck round bottomed flask equipped with nitrogen inlet and outlet. First, intermediate with rigid imide structure (PAH) was synthesized from 2,2-bis (3-amino-4-hydroxyphenyl) hexa-fluoropropane (AH6FP) and



SCHEME 1 Synthesis of imide monomer (PFA).

phthalic anhydride (PA). The reaction was carried out in NMP solvent at room temperature for 24 h to give an amic-acid compound. After adding xylene to this amic-acid solution, the reaction mixture was refluxed at 160°C for 6 h and then cooled to room temperature. The intermediate PAH was obtained by precipitation in a water and 1 N hydroxide chloride (v/v:90/10) mixture solution, followed by filtration and drying in vacuum oven for 24 h to give 94% yield. In the second step, PAH and acryloyl chloride (ACC) were reacted in THF solvent at 40°C for 24 h with triethylamine (TEA) and 4-methoxyphenol (MEHQ) as a catalyst and polymerization inhibitor, respectively. After reaction THF solvent was removed by rotary evaporator and the imide monomer (PFA) was obtained by recrystallization in 65% yield.

Composite Film Fabrication

To fabricate composite films, glass fiber or fabric was first immersed in the UV curable resin solution (Table 1) which was made by mixing

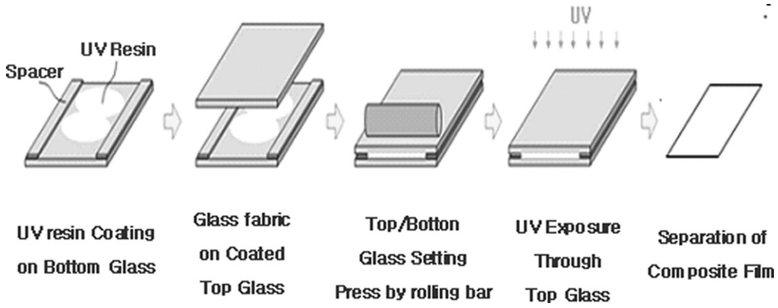
TABLE 1 Composition of UV Curable Resins used as Polymer Matrix

	Weight ratio (%)				
Sample	PM 472 (%)	EB 9260 (%)	TEGDMA (%)	PFA (%)	PI (%)
KUV-0	100				0.0
KUV-1		30.0	69.5		0.5
KUV-2		50.0	49.5		0.5
KUV-3		70.0	29.5		0.5
KUV-Co	79.5			20	0.5

such necessary components as UV resin (PM 472), UV oligomer (EB9260), monomer (TEGDMA), imide monomer (PFA) and photoinitiator (Irgacure 819). Second the UV curable resin was coated on the glass substrate to about 50 μm thickness and then the UV resin immersed glass fabric was layered on top of it, followed by setting of top glass which was also coated with UV curable resin. The gap between the bottom and top cover glasses was controlled by spacers in the range of 130 μm to 350 μm. Finally the UV light was exposed through the top glass and the composite film was obtained by immersing the UV cured glass set in hot aqueous solution and separating the glasses as shown in Scheme 2.

Measurements

Infrared and ^{1}H-NMR spectra were obtained by using a JASCO FT-IR 620 spectrometer and a Bruker 400 NMR spectrometer. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed with a Dupont 2000 differential scanning calorimeter and a Dupont 2100 thermal gravimetric analyzer, respectively, under



SCHEME 2 Process of composite film fabrication.

a nitrogen atmosphere at a heating rate of 10°C/min. The CTE of the films wae measured by thermomechanical analyzer (Perkin Elmer, Diamond TMA) at a heating rate of 5°C/min in 100~200°C range. Mechanical properties of the films were measured on an Instron 5564 tensile tester with a 5 kg load cell. The optical transmittance and reflectivity of the films were measured by a UV-visible spectrometer (Jasco V-650) from 380 to 700 nm range. The value of color (L) and chromaticity (a, b) of specular inclusion (SCI) were obtained by a Minolta CM-2600d under a D50 condition in day light and color temperature of 5003 K. The SEM and AFM micrographs were obtained with a Hitachi S-4300 and a NanoScope III system, respectively. Current and luminance vs. voltage profiles were obtained by using a dc power supply connected with model 8092A digital multimeter (Hyun Chang Product Co. Ltd.).

RESULTS AND DISCUSSION

Analysis of Imide Monomer

The synthesis of imide monomer (PFA) was confirmed by FT-IR (JASCO FT/IR-620 spectrophotometer), ^{1}H-NMR (Bruker Avance Digital 400) and GC-mass (Finnigan QCQ) spectroscopy. As shown in Figure 1, FT-IR spectrum showed the absorption peaks at 1728 cm^{-1} (C=O symmetric stretching), 1377 cm^{-1} (C–N stretching),

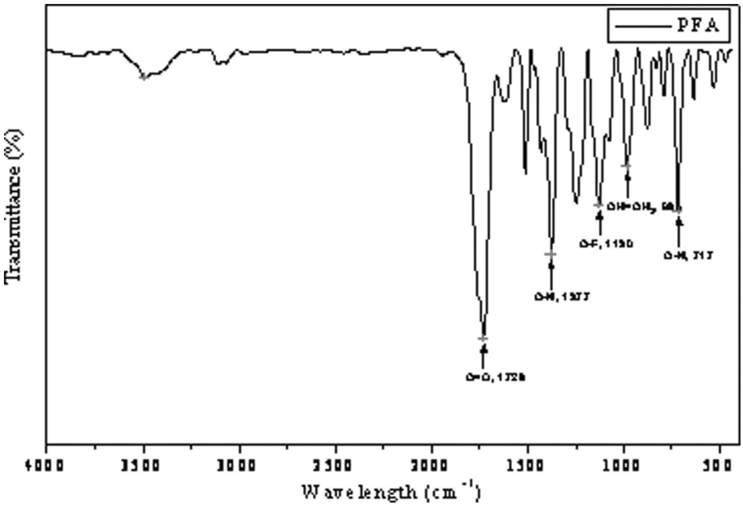


FIGURE 1 FT-IR spectrum of imide monomer PFA.

1130 cm^{-1} (C–F multiple stretch bonding), 984 cm^{-1} (CH=CH$_2$), and 717 cm^{-1} (C–N bonding) corresponding to the characteristic peaks of PFA imide monomer. The disappearance of absorption band at 1720 cm^{-1} corresponding to C=O stretching of carboxylic acid and at 1660 cm^{-1} corresponding to C=O amide stretching indicated that full imidization was achieved from the PAH amic-acid intermediate to the imide monomer [7–10].

The ^{1}H-NMR spectrum in Figure 2 also revealed the full imidization of the imide monomer. In addition to IR and ^{1}H-NMR spectra, the mass spectral analysis of PFA confirmed the molecular peak at 735.6 in good agreement with the calculated value for the proposed structure.

Composite Film Fabrication and Film Properties

It was a difficult choice to select the best combination of reinforce phase and matrix phase because several factors such as optical, mechanical, and film forming properties should be considered. Table 1 shows the composition of UV curable resin which will be converted to the polymer matrix of the composite film after UV exposure.

Several composite films and pure polymer films were prepared in order to compare the necessary physical properties utilizing the formulation shown in Table 2. First the transparency of the composite films was compared with the unreinforced matrix films (M-0 and

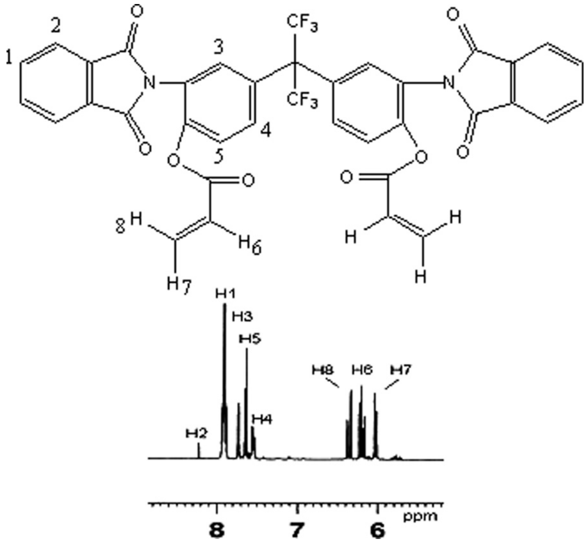


FIGURE 2 ^{1}H-NMR spectrum of imide monomer (PFA) in DMSO-d6.

TABLE 2 Composition of Composite Materials and Physical Properties of Films

Film	Reinforce phase	Matrix phase	Physical properties of films			
			Thickness	Ave-trans (%, 380∼700 nm)	Trans (%, 440 nm)	Color
M-0	–	KUV-0	170 μm	89.9	88.86	Transparent
M-Co	–	KUV-Co	120 μm	87.19	83.96	Transparent
Com-C1	M524-C64	KUV-0	130 μm	90.38	89.50	Transparent
Com-C2	M524-C64	KUV-Co	150 μm	80.94	75.43	Transparent
Com-C3	M524-C64	KUV-1	150 μm	89.90	88.95	Transparent
Com-H1	Hankuk Veil	KUV-0	170 μm	87.73	86.27	Transparent
Com-H2	Hankuk Veil	KUV-Co	140 μm	83.4	78.61	Transparent
Com-H3	Hankuk Veil	KUV-1	140 μm	88.59	87.65	Transparent
Com-G1	Glass Fiber	KUV-1	150 μm	86.6	82.85	Transparent

M-Co). As shown in Table 2 most of the composite films apparently exhibited nearly same transmittance as the unreinforced matrix films in the visible region. This may be due to the good compatibility and matching of refractive indices between the matrix and reinforce phases [1,2].

When UV-Vis spectra of the films were compared, it was noted that unreinforced matrix film M-0 showed better transmittance than M-Co film which contained synthesized imide monomer (PFA) in the UV crosslinkable resin formulation. This was considered to be due to the chromophores present in the imide monomer.

Thermal and Mechanical Properties

In addition to the optical clarity, composite films should meet the thermal and mechanical requirements. The coefficient of thermal expansion (CTE) and glass transition temperature (T_g) data of the unreinforced and composite films are shown in Table 3. It was noted that the CTEs of composite film were much lower than those of unreinforced polymer matrix films. The CTE values in 13∼18 ppm range could be hardly observed in the commercial polymer films which are usually made by extrusion process utilizing single component polymeric materials [12–14]. As for the glass transition temperature (T_g) data, the films made with UV curable resin(KUV-0 formulation) did not show Tg values, which was attributed to the extensive crosslinking reactions during the UV exposure. The films made with KUV-2 and KUV-3 resins in Table 1 gave cracked films after UV curing. The films made with KUV-1 and KUV-Co resins as shown in Table 3 gave

TABLE 3 Thermal Properties of Unreinforced and Composite Films

Film name	Reinforced phase	Matrix phase	T_g (°C) (DSC)	CTE ($\times 10^{-6}$/°C) (20–160°C)
M-0	–	KUV-0	ND	182.2
M-Co	–	KUV-Co	189	172.0
Com-C1	M524-C64	KUV-0	ND	17.2
Com-C2	M524-C64	KUV-Co	192	–
Com-C3	M524-C64	KUV-1	198	18.1
Com-H1	Hankuk Veil	KUV-0	ND	33.6
Com-H2	Hankuk Veil	KUV-Co	191	13.4
Com-H3	Hankuk Veil	KUV-1	199	16.5
Com-G1	Glass Fiber	KUV-1	196	15.2
PES	–	–	223	55.0

ND: Not determined.

TABLE 4 Mechanical Properties of Composite Films

Film name	Max. Load (kgf)	Tensile strain at break (%)	Tensile stress (kgf/cm^2)	Molulus (Auto-Young's) (kgf/cm^2)	Thickness (μm)
Com-C1	9.18	2.66	573	28,563	160
Com-C2	14.36	4.06	845	28,949	170
Com-C3	11.86	4.86	659	23,922	180
Com-H1	5.63	2.06	352	22,879	170
Com-H2	5.60	2.35	407	30,015	170
Com-H3	5.43	2.84	286	20,777	190
Com-G1	21.95	4.52	1097	42,042	200
PES	17.26	153.2	690	16,587	250

composite films with high T_g and low CTE values which could be used as the flexible substrate for the flexible displays.

The mechanical properties of composite films are shown in Table 4. It was noted that the composite films made with glass fabric by Owens Corning and Hankuk Fiber Co. exhibited nearly same tensile stress and modulus values. The composite film Com-G1 which was made with the glass fiber as reinforced phase in the crossed pattern showed much higher tensile stress and modulus than the ones made with glass fabric as reinforced materials. The composite film Com-G1 exhibited both low CTE and excellent mechanical properties compared to the

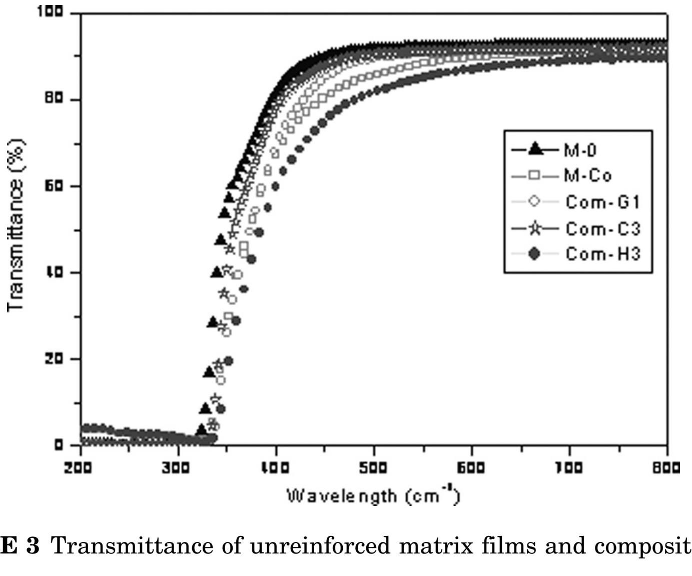
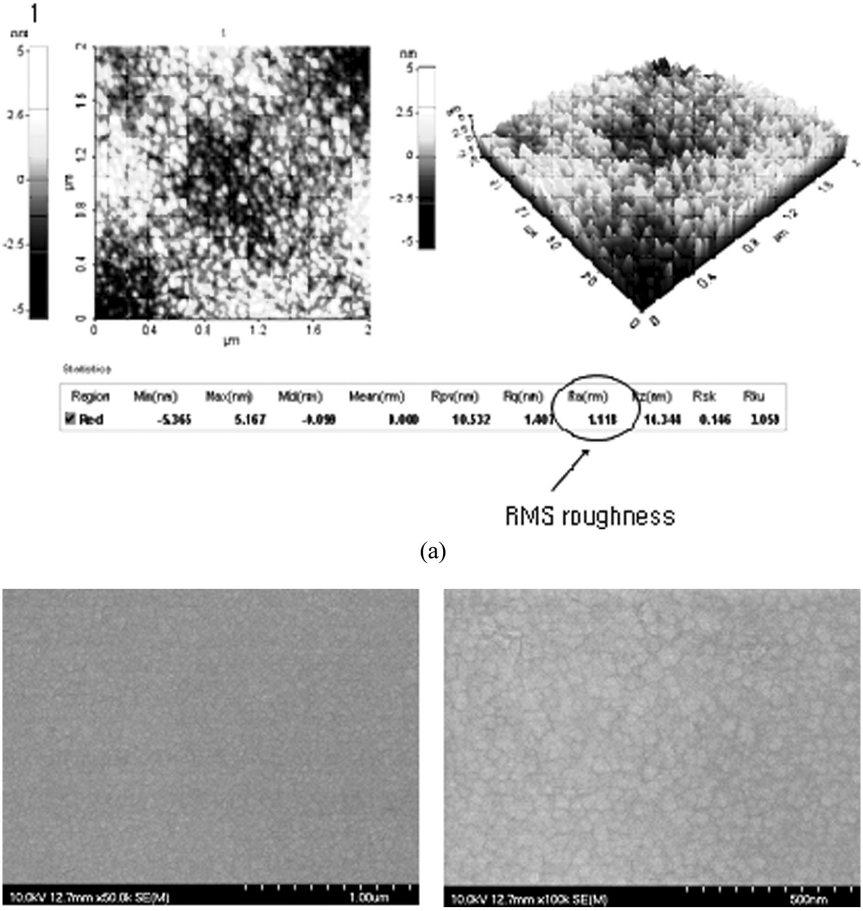


FIGURE 3 Transmittance of unreinforced matrix films and composite films.

poly(ether sulfone)(PES) film which is regarded as a potential candidate for flexible substrate. These results indicated that the pattern of reinforced phase had important effect on the optical and mechanical properties of the composite films.

ITO Thin Film Deposition and OLED Device Properties

The deposition of Indium Tin Oxide (ITO) thin film on the composite films was conducted with the RF magnetron sputter under the



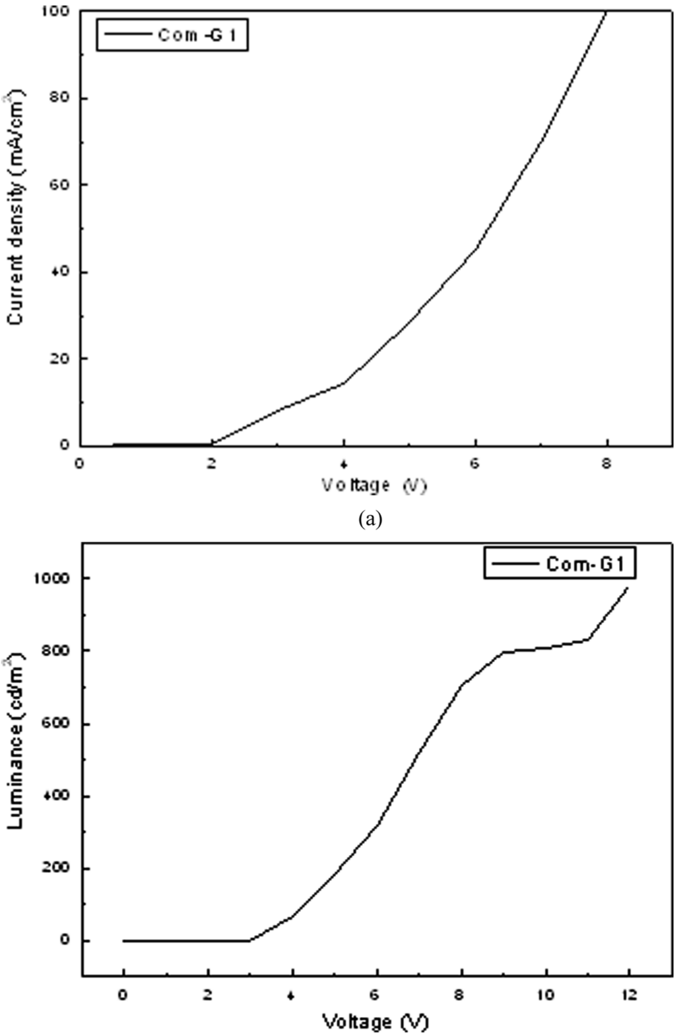
Region	Min(nm)	Max(nm)	Mid(nm)	Mean(nm)	Rpv(nm)	Rq(nm)	Ra(nm)	Rz(nm)	Rsk	Rku
☑ Red	-5.365	5.167	-0.098	0.000	10.532	1.407	1.118	14.344	0.146	3.050

(a)

(b)

FIGURE 4 (a) The AFM and (b) SEM images of ITO coated composite film Com-G1.

condition of RF power 1000 W, Ar gas 130 sccm, O_2 gas 2 sccm and working pressure of 1 mtorr. The surface roughness of the ITO thin layer on the flexible film is very important because the rough ITO surface may cause an electrical failure in the OLED devices which are operated under the high electric field strength. The SEM and



(a)

(b)

FIGURE 5 (a) The current density (J)-voltage (V); and (b) luminance (L)-voltage (V) curves of OLED fabricated with Com-G1 composite film.

TABLE 5 Performance of the OLED Devices Fabricated on Various Flexible Substrates

Sample	Turn on voltage (V)	Maximum voltage (V)	Brightness (cd/m^2)	Efficiency (lm/W)
Com-C3	3	8	881	0.468
Com-H3	4	8	486	0.326
Com-G1	4	12	982	0.405
PC	3	6	593	0.351
PEN	3	7	581	0.445
PES	4	9	508	0.334

AFM micrographs of the ITO coated Com-G1 composite film is shown in Figure 4 in which the rms surface roughness of the ITO layer was about 1.12 nm.

The resistance value of the ITO coated Com-G1 composite film was as low as 50 Ω/sq. The fabrication of OLED device on the ITO coated composite films was carried out with the Sunic EL Plus 200, a cluster type OLED panel fabrication system. The OLED device had configuration of ITO/α-NPD (600 Å)/Alq$_3$ (400 Å)/LiF (5 Å)/Al (1200 Å). The J-V and L-V curves of the OLEDs obtained with Alq$_3$ as emitting layer on the composite films are shown in Figure 5 and Table 5. The data on Table 5 showed that Com-G1 and Com-C3 films performed better in the ITO thin film coating and subsequent OLED devices than commercial films such as PC, PEN and PES. This may be due to the improved thermal and mechanical properties of the composite films compared to the commercial films.

CONCLUSIONS

Glass fiber reinforced composite films were made by UV light induced chemical crosslinking of composite materials consisted of glass fiber and UV curable resin in film state. The transparency of the composite film as was comparable to the unreinforced matrix films with careful matching of the refractive indicies. The composite films exhibited high thermal stability and low coefficient of thermal expansion in the 13–18 ppm range. It was also noted that the pattern of the reinforce phase exhibited important effect on the optical and mechanical properties of the film. The performance of the composite films on the ITO thin film deposition and subsequent OLED device was better than those of the known polymer films such as PET, PC, and PES.

REFERENCES

[1] Boccaccini, Aldo R., Atiq, Shbbar, & Helsch, Gundula. (2003). *Comp. Sci. and Tech.*, *63*, 779–783.

[2] Smeacetto, F., Salvo, M., Ferraris, M., Casalegno, V., & Asinari, P. (2008). *J. European Ceram. Soci.*, *28*, 611–616.

[3] Iba, H., Chang, T., & Kagawa, Y. (2002). *Comp. Sci. and Tech.*, *62*, 2043–2053.

[4] Chen, T.-A., Jen, A. K.-Y., & Cai, Y. (1996). *Macromolecules*, *29*, 535.

[5] Whitmore, F. C. & Singleton, W. F. (1941). (Ed.). *Organic Synthesis*, John Wiley and Sons: New York, Collective Vol. 1, 410.

[6] Ichimura, K. & Oohara, N. J. (1987). *Polym. Sci., Polym. Chem. Ed.*, *25*, 3063.

[7] Zhai, Yan, Yang, Qin, Zhu, Rongqi, & Gu, Yi. (2008). *J. Mater. Sci.*, *43*, 338–344.

[8] Gao, Hong, Wang, Dong, Guan, Shaowei, Jiang, Wei, Jiang, Zhenhua, Gao, Weinan, & Zhang, Daming. (2007). *Macromol. Rapid Coomun.*, *28*, 252–259.

[9] Yang, S. Y., Ge, Z. Y., Yin, D. X., Liu, J. G., Li, Y. F., & Fan, L. (2004). *J. Polym. Sci. Part A: Polym. Chem.*, *42*, 4143–4152.

[10] Vora, Rohitkumar H. & Goh, Suat Hong. (2006). *Mater. Sci. and Eng., B*, *132*, 24–33.

[11] Iba, H., Naganuma, T., Matsumura, K., & Kagawa, Y. (1999). *J. Mater. Sci.*, *34*, 5701–5705.

[12] Chen, Xin-Gui, Guo, Jing-Dong, Zheng, Bing, Li, Yuan-Qing, Fu, Shao-Yun, & He, Guan-Hu. (2007). *Comp. Sci. and Tech.*, *67*, 3006–3013.

[13] Seino, Hiroshi, Haba, Osamu, Ueda, Mitsuru, Mochizuki, Amane. (1999). *Polymer*, *40*, 551–558.

[14] Kelly, A., Stearn, R. J., & McCartney, L. N. (2006). *Comp. Sci. and Tech.*, *66*, 154–159.