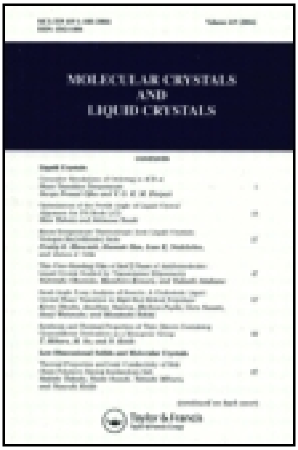

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Synthesis and Performance of Polyimide Films for the Flexible Organic Light Emitting Diodes

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Synthesis and Performance of Polyimide Films for the Flexible Organic Light Emitting Diodes

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A series of polyimide (PI) and copolyimide (Co-PI) films were prepared by two-step imidization processes from the poly(amicacid) precursors. The color and visible light transmission of the Co-PI films were much better than those of the general Kapton type PI film mainly due to the decrease of the charge transfer complex formation by the presence of the CF_3 groups both in the aromatic diamine and dianhydride monomers. In the ITO thin film deposition and subsequent OLED device fabrication, the thermal and mechanical properties of the Co-PI films were more important than the optical property of the Co-PI films.

Keywords: film; flexible OLED; flexible substrate; OLED; polyimide

INTRODUCTION

Polyimide has been known as one of most thermally stable polymers and is widely used in aerospace and electronics industries. In the electronic industry, polyimide was used for the flexible print circuit boards [1], inter-layer dielectrics [2] and as a protective coating on semiconductor devices [3,4]. Despite the excellent properties of polyimides, their widespread application was often limited due to their poor

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solubility and high processing temperature which was caused by the rigid polymer backbones and the strong interchain interactions. Another obstacle that hindered the application of polyimides was the yellow color of the film caused by the charge transfer (CT) interaction between alternating electron-donor (diamine) and electron-acceptor (dianhydride) moieties [5]. Especially, its application to the substrate for organic light-emitting diodes (OLEDs) was limited by the yellow color and stiffness of the film [6–14]. This work reports the synthesis and characterization of clear polyimide films with high thermal stability and reduced CT interactions and their application to the flexible substrate of OLEDs.

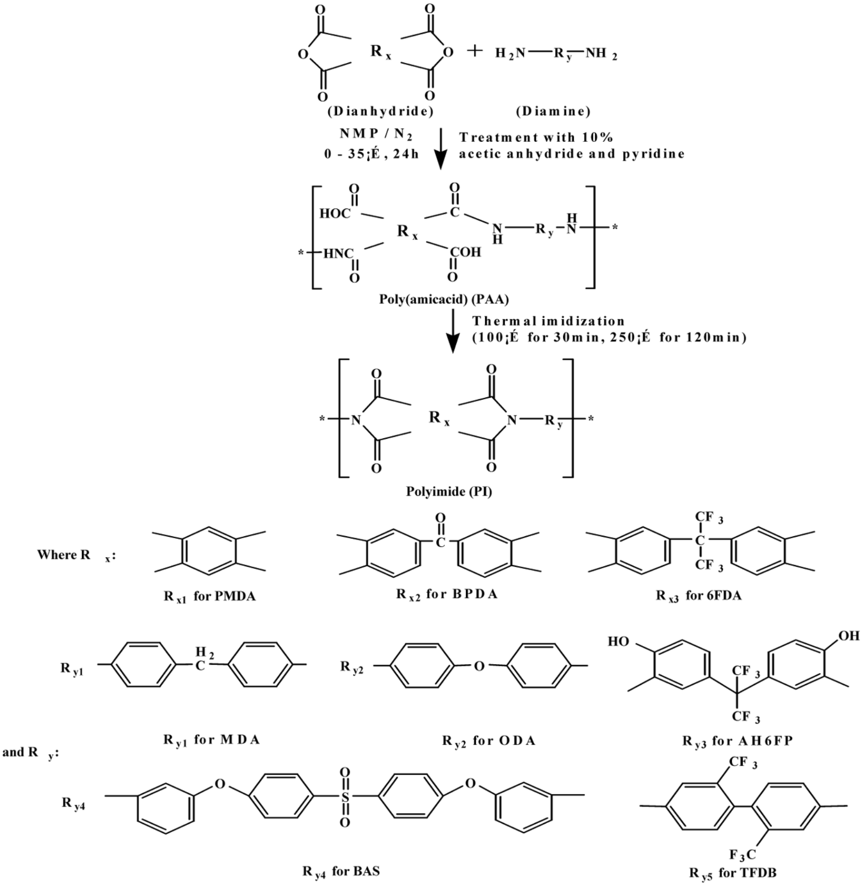
EXPERIMENTAL

Synthesis of Poly(amicacid)s (PAAs) and Copoly(amicacid)s (Co-PAAs)

PAAs and Co-PAAs were synthesized via the process shown in Schemes 1 and 2. First, aromatic diamine monomer was dissolved in NMP solvent in a three-neck round bottomed flask equipped with a nitrogen inlet and outlet. The solution was cooled to 0°C and the aromatic dianhydride monomer was added and the mixture solution was stirred in the ice-water bath till it became clear. The solid content of mixture solution was 15 wt% based on total solution. The reaction mixture was then reacted for 24 hours at 35°C under nitrogen atmosphere and then the mixture solution was treated with 10 mole % acetic anhydride and 10 mole % pyridine solutions for 150 min, respectively. The treated PAAs and Co-PAAs were precipitated twice in distilled water, filtered and dried at ambient temperature in the vacuum oven for 12 h [15,16].

Film Fabrication by Thermal Imidization

Poly(amicacid) was dissolved in N,N-dimethylacetamide (DMAC) solvent to make 25 wt% solutions. The solution was stirred at room temperature for 30 min to afford a highly viscous poly(amicacid) (PAA) solution. Then PAA solution was poured on a clean and dry glass, which was coated by Automatic Film-Coating Apparatus (Comate^{TM} 3000 V) and subjected to the thermal imidization process in the IR oven. Film thickness was controlled from 40 to 140 μm by the bar diameter. The solution was heated at 100°C for 1 h to remove the solvent. The semi-dried PAA film was further dried and imidized by sequential heating from 120°C to 250°C at a heating rate of 3°C/min and further

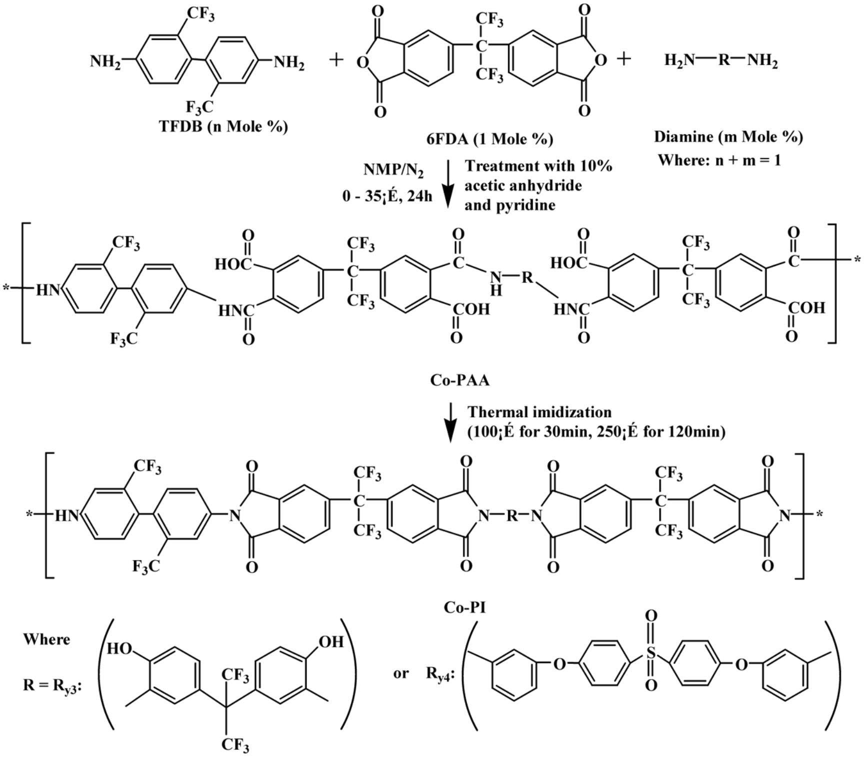


SCHEME 1 Synthesis of poly(amicacid)s and conversion to polyimide films.

heated at 250°C for 1 h. The cured polyimide film was stripped off the glass substrate by immersion in hot water followed by drying in an oven at 100°C.

Film Fabrication by Chemical Imidization

A pot of 25 wt% PAA solution was prepared with various composition of DMAc/acetic anhydride solvent mixture. The mixture solution was heated at 80°C for 1 h for the chemical imidization and then poured on a clean and dry glass and coated by a Automatic Film-Coating Apparatus (Comate™ 3000 V). The coated film was placed in an oven at 100°C for 1 h to evaporate the solvent. The semi-dried PAA film was further dried and imidized by sequential



SCHEME 2 Synthesis of copoly(amicacid)s and conversion to copolyimide films.

heating at 100 ~ 160°C at the rate of 5°C/10 min and at 200°C for 30 min. The converted polyimide film was stripped off the glass substrate by soaking in hot water.

Measurements

Infrared spectra were obtained by using a JASCO FT-IR 620 spectrometer. Differential scanning calorimetry (DSC) and Thermogravimetric analysis (TGA) measurements were performed with a Dupont 2000 differential scanning calorimeter and a Dupont 2100 thermal gravimetric analyzer, respectively, under nitrogen atmosphere at a heating rate of 10°C/min. Mechanical properties of the films were measured on an Instron 5564 tensile tester with a 5 kg load cell. An average of at least five individual measurements was used. The optical transmittance and reflectivity of polyimide film were measured by a

UV-visible spectrometer (Jasco V-650) with a range of wavelength from 380 to 700 nm. 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 a Multimode, 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

Effects of Solvent on the Synthesis of PAAs

We used three different solvents NMP, DMAc, and DMF for the synthesis of PAAs as shown in Table 1. The results indicated that the highest reaction yields as well as the best PAA colors were obtained when using NMP as solvent. Therefore we used NMP for synthesis of all the PAAs and Co-PAAs samples.

Optical and Film Forming Properties

The imidization and film formation of various poly(amicacid)s to polyimides are shown in Table 2. The result showed that all homopolyimide films obtained except PI. 6 had yellow color and stiff film property. The polyimide film (PI. 6-3) made by chemical imidization and subsequent thermal conversion exhibited almost clear color compared to the PI films by only thermal imidization. Therefore we used PAA solutions with DMAc/acetic anhydride mixture solvent in which the mole ratio of acetic anhydride to PAA was 3 to 1 before full imidization by thermal treatment. The colorless polyimide PI. 6-3 film may be due to the reduced intra- and intermolecular CT interactions caused by the decreased electron donating property of the diamine moiety by the presence of electron-withdrawing CF_3 groups. The presence of

TABLE 1 Effect of Solvent on the PAA Synthesis

PAA name	R_x	R_y	Solvent	Yield (%)	Color
PAA 1	R_{x1}	R_{y1}	NMP	95.0	Yellow
PAA 1	R_{x1}	R_{y1}	DMAc	80.7	Yellow
PAA 1	R_{x1}	R_{y1}	DMF	82.0	Yellow
PAA 2	R_{x1}	R_{y2}	NMP	91.0	Milky
PAA 2	R_{x1}	R_{y2}	DMAc	87.5	Milky
PAA 2	R_{x1}	R_{y2}	DMF	85.0	Brown

TABLE 2 Physical Properties of Homopolymer PI Films

PI name	R_x	R_y	Imidization method	Yield (%)	Thickness (μm)	PI color
PI. 1	R_{x1}	R_{y1}	Thermal	87	80 μm	Dark Yellow
PI. 2	R_{x1}	R_{y2}	Thermal	85	80 μm	Dark Yellow
PI. 3	R_{x2}	R_{y3}	Thermal	40	80 μm	Dark Yellow
PI. 4	R_{x2}	R_{y4}	Thermal	81	80 μm	Yellow
PI. 5	R_{x3}	R_{y3}	Thermal	82	80 μm	Pale Yellow
PI. 6-1	R_{x3}	R_{y5}	Thermal	93	80 μm	Yellowish clear
PI. 6-2	R_{x3}	R_{y5}	Chemical-1[a]	91	80 μm	Yellowish clear
PI. 6-3	R_{x3}	R_{y5}	Chemical-2[b]	91	80 μm	Colorless

[a] Used acetic anhydride with same mole % of PAA.
[b] Used acetic anhydride 3 times the mole % of PAA.

bulky CF_3 groups in the dianhydride monomer should also contribute to both increased solubility and less CT formation by the steric effect.

The color of the copolyimide (Co-PI) films was much better than that of homopolymer PI films as shown in Table 3. The Co-PI films were obtained from the comonomer compositions with 6FDA as aromatic dianhydride (100 mole %) and TFDB (80–95 mole %) and AH6FP and BAS (5–20 mole %) as aromatic diamine monomers. The removal of the yellow color from the Co-PI films might be explained as following. The increase of the irregularity of the repeat units in the copolyimides could increase the flexibility of the polymer chains which would further decrease the intra- and intermolecular CT formations. As shown in Table 3, the less comonomer was used, the better was the optical property of Co-PI films. However the Co-PI films with less than 10 mole % of comonomers became brittle and crack was seen sometimes right after conversion to PI films. When evaluated from the viewpoint of both optical quality and film forming property, the CoPIF-85:15 and CoPIS-85:15 films exhibited best performance. It should be noted that the yellow indices of 5.77 and 6.87 for CoPIF-85:15 and CoPIS-85:15 film were quite low compared to the general Kapton type homo-PI films.

The Degree of Imidization

The degree of imidization (ID) from the poly(amicacid) to polyimide was checked with the FT-IR spectrometer (Jasco FT/IR-620) according to the Eq. (1).

$$\mathrm{ID}(\%) = (A_{C-N}/A_{C=C})/(A_{C-N}/A_{C=C})_{\mathrm{fullyimidization}} \times 100 \qquad (1)$$

TABLE 3 Physical and Optical Properties of PIs and Co-PIs Films

Sample	R	n (Mole %)	m (Mole %)	Thick-ness (μm)	Yellow Index (b-value)	T_g/T_{d5} (DSC/ TGA)	Avg-Transm. (%, 380∼700 nm)	Transm. (%, 400 nm)	Yield (%)
CoPIF-80:20	Ry3	80.0	20.0	80 μm	10.19		87.88	57.32	92.3
CoPIF-85:15	Ry3	85.0	15.0	80 μm	5.77		89.29	68.66	91.5
CoPIF-90:10	Ry3	90.0	10.0	80 μm	4.49		90.58	67.27	93.1
CoPIF-95:05	Ry3	95.0	5.0	80 μm	4.85	302°C/503°C	90.13	69.51	90.7
CoPIS-60:40	Ry4	60.0	40.0	80 μm	17.54		83.16	35.21	94.4
CoPIS-70:30	Ry4	70.0	30.0	80 μm	15.11		84.04	43.53	95.8
CoPIS-80:20	Ry4	80.0	20.0	80 μm	13.62	277°C/497°C	84.41	41/00	93.7
CoPIS-85:15	Ry4	85.0	15.0	80 μm	6.87		87.04	51.45	94.5
CoPIS-90:10	Ry4	90.0	10.0	80 μm	4.90		88.51	53.35	95.3
PI. 5				≤40 μm	ND		ND	ND	82.0
PI. 6-3				80 μm	4.21		87.37	56.52	92.1

ND: Not determined; T_{d5}: the decomposition temperature at 5% weight loss.

In Eq. (1) A_{C-N}, $A_{C=C}$ were absorbance of imide C–N bond at 1385 cm^{-1} and aromatic C–C bond at 1523 cm^{-1} in the polyimide backbone, respectively [20]. A typical FT-IR spectrum of PI. 5 homopolyimide film is shown in Figure 1. The degree of imidization was followed both according to the imidization temperature (under constant time of 40 min) and to the heat treating time (at constant temperature of 250°C). As shown in Figure 2, high degree of imidization (ID = 94%) was obtained under the condition of baking at 250°C for 120 min after pre-baking at 100°C for 30 min.

Other Physical Properties

In order to be used as flexible substrate of OLED devices, the polyimide film needs to be thermally stable and highly transparent in the visible region with low yellow index. The thermal stability of the Co-PI films was checked by TGA and DSC. The TGA thermograms of Co-PI films (CoPIF-95:05 and CoPIS-80:20) exhibited 5% weight loss at about 503°C and 497°C, respectively as shown in Figure 3. The glass transition temperatures (T_g) of CoPIF-95:05 and CoPIS-80:20 films were 302°C and 277°C, respectively from the DSC measurement.

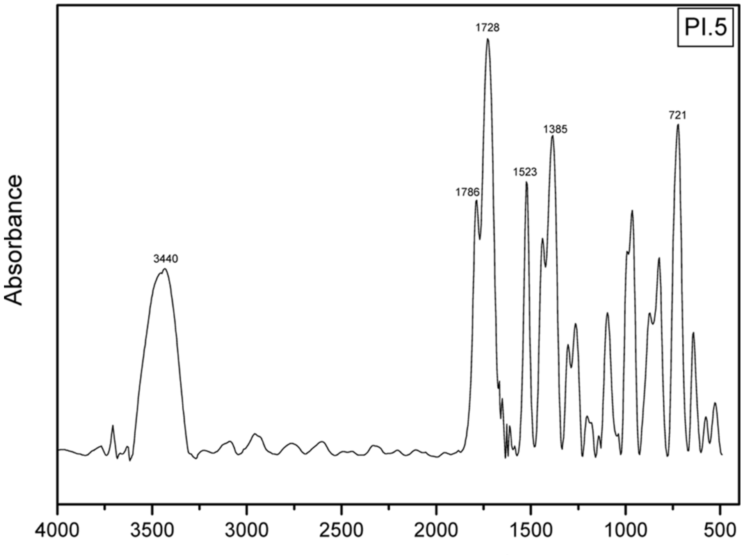


FIGURE 1 FT-IR spectrum of PI. 5 film.

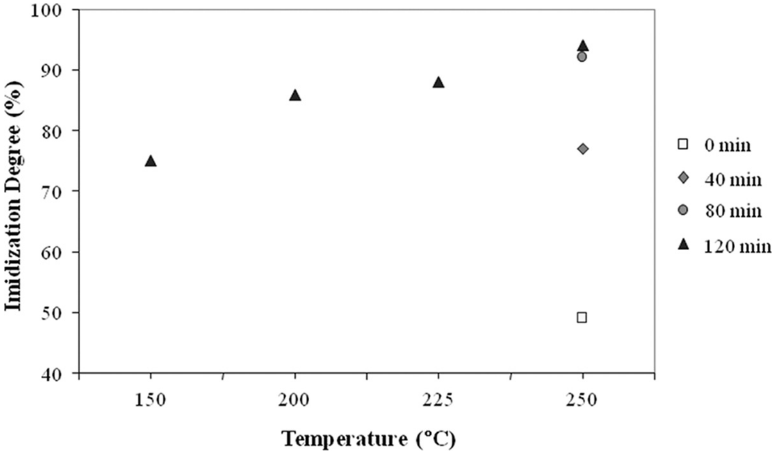


FIGURE 2 Imidization degree of polyimide sample PI. 5 plotted imidization temperature.

The transmittance of the Co-PI films was measured with the UV-Vis spectrometer (Jasco V-650 Spectrometer). As shown in Table 3, the CoPIF-85:15 film exhibited average transmittance of 89.29%

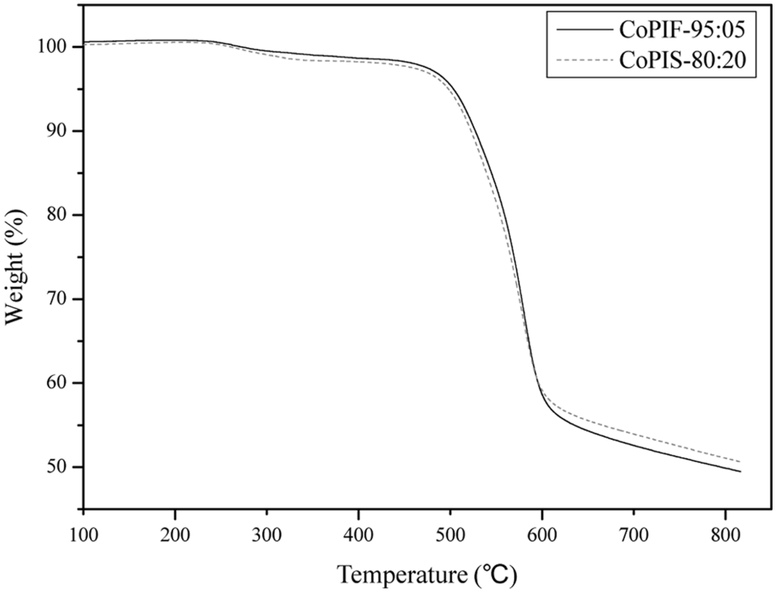
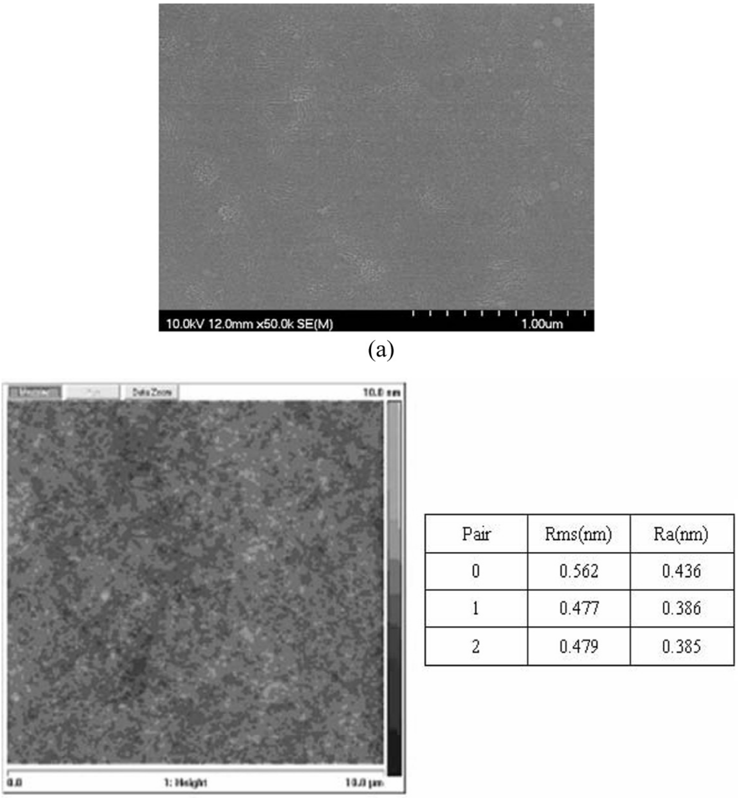


FIGURE 3 TGA curves of Co-PI films.

TABLE 4 Mechanical Properties of Co-PIs Films

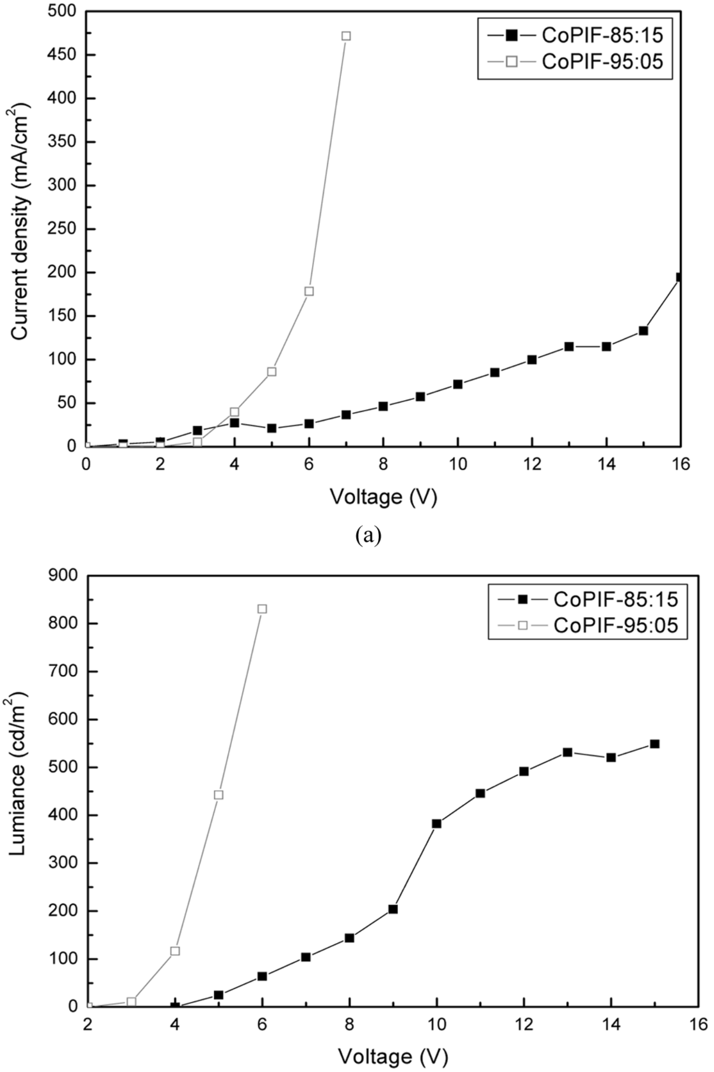
Sample	Max Load (kgf)	Tensile strain at break (%)	Tensile stress (kgf/cm^2)	Modulus (Auto-Young's, kgf/cm^2)
CoPIF-80:20	6.84	2.99	570	21,859
CoPIF-85:15	8.15	4.65	1019	28,494
CoPIF-90:10	7.12	4.16	890	26,958
CoPIF-95:05	9.66	5.15	1207	32,442
CoPIS-60:40	9.34	4.52	1168	33,210
CoPIS-70:30	8.24	3.99	915	29,299
CoPIS-80:20	7.63	3.36	953	33,990
CoPIS-85:15	8.32	4.92	1040	27,099
CoPIS-90:10	3.80	2.88	951	39,504



Pair	Rms(nm)	Ra(nm)
0	0.562	0.436
1	0.477	0.386
2	0.479	0.385

(b)

FIGURE 4 The SEM (a) and AFM (b) images of ITO coated CoPIF-95:05 film.



(a)

(b)

FIGURE 5 (a) The current density (J)-voltage (V) and (b) luminance (L)-voltage (V) curves of OLEDs on ITO coated CoPIF films.

in the 380–700 nm region and 68.66% at 400 nm. These values were comparable to those of optical films used in the liquid crystal display devices.

The mechanical properties of Co-PIs films are shown in Table 4. As shown in Table 4 the mechanical and optical properties did not match well. Although the yellow index and transmittance to visible light were good for the CoPIF-85:15 and CoPIS-85:15 films, the mechanical property of the Co-PI film was best in the case of CoPIF-95:05 sample.

ITO Thin Film Deposition and OLED Device Properties

The deposition of Indium Tin Oxide (ITO) thin film on the Co-PI films was conducted with the RF magnetron sputter under the condition of RF power 1000 W, Ar gas 130 sccm, O_2 gas 2 sccm and working pressure of 1 mtorr. The sheet resistance values of the ITO coated CoPIF-85:15 and coPIF-95:05 films were 40 and 35 Ω/sq, respectively as measured with 4 point probemeter. The SEM and AFM micrographs of the CoPIF-95:05 film are shown in Figure 4 in which the rms and Ra roughness of the film were 0.48 and 0.39 nm.

The fabrication of OLED on the ITO coated CoPIF-85:15 and CoPIF-95:05 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 two CoPIF film are shown in Figure 5. The performance data in Table 3, 4, and Figure 5 shows that CoPIF-95:05 film performed better in the OLED device than that of CoPIF-85:15 film while the optical property was on the opposite. These results suggest that the thermal property is more important than optical property in the ITO thin film coating flexible substrate and subsequent OLED device fabrication.

CONCLUSIONS

In the synthesis of Copoly(amicacid)s and subsequent conversion to Co-PI films, the choice of monomer combination was very important for the clear polyimide film with low yellow index. The combination of 6FDA (100 mole %) aromatic anhydride and TFDB:AH6FP (85:15 mole %) aromatic diamine monomers gave low yellow index, good film formation and high transmittance in the visible range. In the ITO thin film deposition on the Co-PI films and subsequent OLED device fabrication, the mechanical property was found more important than the optical properties as shown in the OLED device with the CoPIF-95:05 film as flexible substrate.

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