Built-In Haze Glass-Fabric Reinforced Siloxane Hybrid Film for Efficient Organic Light-Emitting Diodes (OLEDs)

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Substrates with high transmittance and high haze are desired for increasing the light outcoupling efficiency of organic light-emitting diodes (OLEDs). However, most of the polymer films used as substrate have high transmittance and low haze. Herein, a facile route to fabricate a built-in haze glass-fabric reinforced siloxane hybrid (GFRH) film having high total transmittance (≈89%) and high haze (≈89%) is reported using the scattering effect induced by refractive index contrast between the glass fabric and the siloxane hybrid (hybrimer). The hybrimer exhibiting large refractive index contrast with the glass fabric is synthesized by removing the phenyl substituents. Besides its optical properties, the hazy GFRH films exhibit smooth surface ($R_{sq} = 0.2 \text{ nm}$), low thermal expansion (13 ppm °C$^{-1}$), high chemical stability, and dimensional stability. Owing to the outstanding properties of the GFRH film, OLED is successfully fabricated onto the film exhibiting 74% external quantum efficiency enhancement. The hazy GFRH’s unique optical properties, excellent thermal stability, outstanding dimensional stability, and the ability to perform as a transparent electrode enable them as a wide ranging substrate for the flexible optoelectronic devices.

1. Introduction

Currently, most of the polymer film used as substrates for the flexible optoelectronic devices are transparent.[1] However, some electroluminescent devices such as organic light-emitting diodes (OLEDs)[2] and backlight units[3] desire polymer films having high transmission haze for enhancement of the light coupling efficiency and angular stable emission spectrum. Many researches have been studied to give the light outcoupling function to the light sources by applying the external light scattering structures such as the microlenses,[4] random structures,[5] and polymer layer with dispersed light-scattering particles.[2a,6] However, all these strategies requires additional fabrication steps, which leads to rise in cost. In addition, due to the external additive nature of such structures, the device operational stability is not necessarily warranted.

In this regard, it is useful to have a technical method to control the optical properties of the film itself without additional light scattering layer. The transmission haze of a polymer film can be increased by inserting the light scattering medium such as nanoparticles inside the film.[7] However, the use of particles inevitably results in surface protrusion, which is a detrimental feature for achieving electrical stability in the device operation. Furthermore, low uniformities induced by agglomeration of the particles are considered as other demerits of nanoparticle embedding method. As an alternative, using the fibrous materials such as cellulose or glass fabric instead of the nanoparticles can effectively solve the aggregation and uniformity issue.[2b] Furthermore, the fibrous material acts as a reinforcement inside the film, resulting in enhancement on mechanical properties such as high elastic modulus and low thermal expansion.[8] Among the fibrous materials, the glass fabric is a widely used reinforcement material for the fiber-reinforced plastics due to its high modulus, chemically inertness, low thermal expansion, and high thermal stability. However, those studies on the glass-fabric reinforced plastic films have focused on achieving high transparency.[9]

In this work, we report a glass-fabric reinforced siloxane hybrid (GFRH) substrate with high haze (≈89%) and high...
transmittance (~89%). The glass fabric was used as a light scattering material for enhancing the light outcoupling efficiency of substrate. The refractive index of the siloxane hybrid (hybrimer) was rationally modified to maximize the scattering of light at the interface of the matrix and the glass fabric, resulting in a film with high haze. In addition to the unique optical properties, the GFRH film showed low thermal expansion (CTE = 13 ppm °C⁻¹), high thermal stability, smooth surface (R_m = 0.2 nm), chemical inertness, and excellent stress resistance (E = 9.7 GPa). Furthermore, by transferring gravure-offset printed Ag grids, the GFRH films were fabricated to have embedded Ag auxiliary metal bus lines, which can contribute to achieve uniform emission. Finally, to evaluate the light extraction of high haze GFRH, OLEDs were fabricated directly on our GFRH films. The OLED fabricated on the GFRH film with high haze showed 74% increase in external quantum efficiency (EQE) compared to GFRH film with low haze. This enhancement is attributed to light scattering induced by glass fabric inside the film. The unique optical properties, excellent thermal stability, dimensional stability, and the ability to perform as a CTE allows GFRH as a substrate film for the wide range of applications for flexible optoelectronic devices.

2. Results and Discussion

2.1. Characterization of Hazy Glass-Fabric Reinforced Hybrimer

Figure 1a shows the schematics of the fabrication procedure for GFRH. To have easy detachment of the GFRH from the substrates, we treated substrates with trichlorooctadecylsilane to form hydrophobic self-assembly monolayer (SAM). Next, the glass fabric was placed onto the glass substrate, followed by the impregnation of oligosiloxane resin. Then, oligosiloxane impregnated glass fabric was covered with another glass and compressed via a vacuum bag pressing method. Roughly, a pressure of 0.1 MPa was applied to ensure complete impregnation and surface flatness. Then, the compressed sample was

![Figure 1. a) Schematic illustration of the fabrication procedure of GFRH. b) Schematic illustration of the light scattering by the refractive index contrast of the glass fiber and the hybrimer. Top: n_Gf and n_H denote the refractive indices of the glass fabric and the hybrimer, respectively. Bottom: Digital photographs of fabricated C-GFRH and H-GFRH. c) A cross-sectional SEM image of H-GFRH (scale bar = 50 µm). d) An AFM image obtained from the H-GFRH, showing high surface smoothness (scale bar = 1 µm).](image-url)
exposed to UV light for crosslinking the impregnated liquid oligosiloxane resin to solid hybrimer. Finally, cover glass and glass substrate are removed to fabricate the free-standing GFRH film. Figure 1b exhibits the actual images of fabricated GFRH films. We fabricated 100 µm thick GFRH films with hybrimers having refractive indices of 1.56 (left) and 1.50 (right). The refractive index of common boron-free e-glass is known to be 1.56. When GFRH was fabricated with the hybrimer having similar refractive index of the glass fabric \(n_\text{GFRH} \approx 1.56\), the clear GFRH (C-GFRH) was fabricated. On the other hand, when GFRH was fabricated with hybrimer having refractive index of 1.50, GFRH with high haze (H-GFRH) was fabricated. As shown in Figure 1b, C-GFRH showed clear letters at upper part of the film (far from the background), while letters were unrecognizable at the upper part of the H-GFRH film (far from the background) indicating that the H-GFRH has a high total transmittance at the upper part of the H-GFRH film (far from the background) due to the severe blurring. The light scattering effects of the scattering medium inside the matrix are closely related to the refractive index contrast between the scattering medium and the matrix.\cite{10} When the refractive index contrast is low, the incident light passes through the assembly film without phase lag, resulting in a film of high optical transparency.\cite{11} However, when the refractive index contrast between the glass fabric and matrix is severe, the phase lag of the light passing through fiber increases, in turn, resulting in a larger scattering angle. Although H-GFRH showed high haziness, clear letters were observed at the bottom part of the H-GFRH (attached to background) indicating that the H-GFRH has a high total transmittance. The cross-sectional scanning electron microscopy (SEM) image of the fabricated GFRH is shown in Figure 1c. The 3-µm-diameter cylindrical glass fibers in glass fabric were well impregnated inside the hybrimer matrix throughout 100 µm GFRH film. Due to the numerous glass fabric and hybrimer interface on the path of light passing through the film, the H-GFRH showed high haze even though refractive index difference was only 0.06. Figure S1 in the Supporting Information and Figure 1d shows the tilted-view SEM image of H-GFRH and surface morphology of H-GFRH, respectively. The glass fabric was well embedded inside the hybrimer matrix without protrusion on the surface. Also, H-GFRH had smooth surface exhibiting root-mean-square roughness \(R_{\text{rms}}\) of 0.2 nm, obviating additional planarization for OLED fabrication. Because the GFRH film is compressed with glass, the surface of the GFRH film follows the highly smooth surface of glass, giving such a smooth surface. The smooth surface of the H-GFRH indicates that the high haziness of H-GFRH does not originate from the scattering by the extruded glass fabric at the film surface or by the surface roughness of the film, but from the optical contrast at the fiber/matrix interface. The results of Figure 1 demonstrate the technical feasibility of equipping optical haziness to the film without disturbing the surface smoothness. The haze originates from the optical contrast present at the fiber/matrix interface. In this part, we describe the chemical aspect of controlling the refractive index of the hybrimer. To induce the refractive index contrast between the glass fabric and hybrimer, we have developed a chemical method to modify the refractive index of the hybrimer. According to the Lorentz–Lorenz equation, the refractive index of a polymer material is proportional to the polarizability of the material.\cite{12} Therefore, replacing substituents with low polarizability to high polarizability per volume can effectively increase the refractive index of the material. Among the high refractive index substituents, phenyl was used for increasing the refractive index of hybrimer.\cite{13} The high thermal stability and chemical inertness of the phenyl groups allows for the modification of the refractive indices of hybrimer without degrading thermal stability and chemical stability.\cite{14} Figure 2a shows the chemical scheme for fabricating our hybrimer. First, two silane precursors of 2-(3,4 epoxycyclohexyl)ethyltrimethoxysilane (ECTS) and diphenyldimethoxysilane (DPDMS) were reacted by a base-catalyzed hydrolytic sol–gel reaction. As the result of the sol–gel reaction, the ECTS and DPDMS were linked with siloxane bonds, resulting in a cycloaliphatic epoxy oligosiloxane (CEO) having condensed siloxane networks. Then, the CEO was polymerized via UV (Xe–Hg lamp, \(\lambda = 365\) nm) curing to form a solid cycloaliphatic epoxy hybrimer (CEH).\cite{15} The contents of phenyl groups in hybrimers were modified by changing the concentration of phenyl containing precursor, DPDMS. In this work, we have varied the concentration of DPDMS from 0 to 60 mol\%. Figure 2b shows the refractive indices \(n_\text{GFRH}\) as a function of concentration of DPDMS. Apparently, the \(n_\text{GFRH}\) is linearly proportional to the concentration. The refractive index of CEH increased from 1.50 to 1.56 as the concentration of DPDMS increased from 0 to 60 mol\%. The phenyl substituents exhibit high polarizability due to the delocalized \(\pi\) electrons.\cite{16} Therefore, as DPDMS increase from 0 to 60 mol\%, the cycloaliphatic epoxy substituents are replaced to phenyl substituents with higher polarizability, resulting in increment on refractive indices of CEH.\cite{17} To summarize, we were able to design hybrimer having the similar refractive index of glass fabric for the fabrication of C-GFRH, and hybrimer having high refractive index contrast with glass fabric for fabrication of H-GFRH by adjusting the amount of DPDMS. To examine the light scattering effect due to the optical contrast at the glass-fabric/resin interface, green laser light was irradiated to glass, C-GFRH, and H-GFRH. Figure 3a shows the actual images of light scattering effects by glass, C-GFRH, and H-GFRH. When incident light passed through the glass, light did not scatter but gave a single dot at the background. On the other hand, when light passed through the C-GFRH, unique cross-shaped scattering patterns were dimly appeared due to the small refractive index contrast lower than 0.01. The cross shape of scattering pattern of C-GFRH reflects the low-degree scattering taking place at the orthogonally woven glass-fabric surfaces. Note that four cross-shaped patterns were observed due to the four sheets of glass fabric arranged in different direction inside C-GFRH. As the refractive index contrast between glass fabric and hybrimer increases, the light scattering due to the refractive index contrast increases. In consequence, the cross-shaped patterns became thicker, resulting in a uniform diffusive scattering pattern. Figure 3b shows the direct transmittance (dot) and total transmittance (line) of glass (black), C-GFRH (red), and H-GFRH (blue). Both C-GFRH and H-GFRH showed high total transmittance of \(\approx 89\%\), similar with the transmittance of glass. This indicates that the most of the light passes through the film and light scattering by glass fabric does not trap the ongoing light. However, when the refractive index contrast between glass fabric and hybrimer...
becomes bigger, the diffuse transmittance emerges to dominate overall transmittance. In case of the H-GFRH, the diffuse transmittance of 81% was observed, while the direct transmittance was only 9%. Figure S3 in the Supporting Information shows the angular distribution of the light transmitted from the glass, C-GFRH, and H-GFRH. The transmitted light from the glass and C-GFRH showed narrow distribution, where light transmitted from H-GFRH did not. Figure 3c shows the haze of glass (black), C-GFRH (red), and H-GFRH (blue). Haze is defined as the ratio of diffusive transmittance to the total transmittance. Both glass and C-GFRH exhibited low haze close to 0% at 550 nm, meaning that most of the incident light passed without scattering. Meanwhile, H-GFRH showed high haze value of 89% indicating most of the light has changed its traveling path to

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**Figure 2.** a) Schematic illustration of the synthesis procedure of CEO and CEH. b) The refractive indices of CEH as a function of DPDMS concentration.

**Figure 3.** a) A real image of the visual effect of light scattering effects by glass, H-GFRH, and C-GFRH. b) Total transmittance (line) and direct transmittance (dot) of glass (black), C-GFRH (red), and H-GFRH (blue). c) Transmission haze of glass (black), C-GFRH (red), and H-GFRH (blue).
give a diffuse light profile due to the high refractive index contrast. Also, haze behavior of the C-GFRH at short wavelength can be explained by refractive index contrast. Glass fabric and hybridmer has different optical dispersion properties, resulting in refractive index contrast at shorter wavelength even though refractive indices are matched in 550 nm. As a consequence, increase in haze of C-GFRH is observed at short-wavelength region. In summary, by adjusting the chemical composition, we were able to fabricate a translucent film with high haze and high total transparency.

In the context of using the H-GFRH as a substrate, high thermal stability is a critical issue. The substrates are often exposed to high-temperature processes during the fabrication process of OLED devices. For example, typical annealing temperature of indium tin oxide (ITO) for anode exceeds 150 °C, which is high enough to disintegrate most of existing conventional polymer films. To compare the thermal expansion of the H-GFRH with the conventional polymers, the polyethylene terephthalate (PET), polyethylene naphthalate (PEN), and H-GFRH were analyzed with thermomechanical analysis (TMA). Figure 4a shows the TMA profiles of PET, PEN, and H-GFRH. The coefficients of thermal expansion (CTE) of both PET and PEN were increased rapidly at temperatures higher than 80 and 120 °C, respectively. The change in CTE of conventional polymer films at high temperatures originates from the glass-transition behavior of the polymeric materials. However, H-GFRH maintained low CTE (13 ppm °C⁻¹) up to 180 °C. The low CTE property of H-GFRH originates from the low thermal expansion of the glass fabric (5 ppm °C⁻¹). To clearly identify the glass transition behavior of the PET, PEN, and H-GFRH, we conducted dynamic mechanical analysis (DMA) on those films. The glass-transition behavior of polymer films can be identified by the sudden change in tan δ, which represents the ratio of loss modulus (E″) to storage modulus (E′) energy in the material. As seen in Figure 4b, PEN and PET films showed abrupt storage modulus (line) drop and increment of tan δ (dot) at 80 and 120 °C, respectively. Meanwhile, H-GFRH showed negligible change on the storage modulus or tan δ, indicating that H-GFRH exhibits negligibly weak glass transition behavior. As a result, the H-GFRH can maintain its mechanical properties and low thermal expansion in a wide range of temperature. Furthermore, the H-GFRH’s optical properties including high total transmittance and low absorbance were maintained after heat treatment at 200 °C for 1 h in vacuum environment (Figure 4c). These results indicate that optical properties of H-GFRH do not degrade by the 200 °C heat-treatment process. Note that the H-GFRH also showed no deformation or curl after the heat treatment. The excellent thermal stability of H-GFRH enables the implementation of various processes in a stable manner at elevated temperature, which is essential for fabrication of high-performance OLEDs.

Besides the thermal stability, chemical stability of the substrate is another important issue on fabrication of OLED devices. The substrate is exposed to various chemicals during the cleaning and ITO patterning processes. Therefore, the chemical inertness of the substrate is essential for fabrication of the OLEDs. We tested the chemical stability of H-GFRH on methanol, acetone, and ITO etchant. As seen in Figure 5a, the H-GFRH films maintained their shapes and surface morphologies after dipping into methanol, acetone, and ITO etchant for 1 h. Figure 5b shows the atomic force microscopy (AFM) images of H-GFRH before and after dipped into various solvents for 1 h. Compared to the initial surface roughness of H-GFRH (Rrms = 0.2 nm), H-GFRH
after dipping into methanol ($R_{\text{rms}} = 0.2$ nm), acetone ($R_{\text{rms}} = 0.3$ nm), and ITO etchant ($R_{\text{rms}} = 0.2$ nm) showed negligible roughness change. The excellent chemical stability of H-GFRH originates from the highly crosslinked structure and the chemical inertness of the siloxane backbone. The excellent chemical stability of H-GFRH enables the etching process of photoresists and ITO on the substrates. In addition to the neat chemical stability, H-GFRH showed superior tensile strength compared to other common polymer films (Table S1, Supporting Information). The excellent mechanical properties of H-GFRH originate from the reinforcement by glass fabric, which bears high modulus compared to polymeric materials. Furthermore, the H-GFRH showed good surface pencil hardness value of 5H attributed to the high hardness and resilient characteristics of the siloxane hybrid material used as the matrix. These results indicate that H-GFRH exhibits excellent dimensional stability to scratches, and impacts. The chemical inertness and dimensional stability of H-GFRH against various harsh actions strongly imply its applicability in existing display fabrication technology.

2.2. Fabrication of OLEDs on H-GFRH

To verify the light outcoupling enhancement capacity of H-GFRH, we fabricated OLEDs directly on H-GFRH and C-GFRH. For the fabrication of OLEDs with high emission uniformity, current density of the anode must be uniform. Therefore, the low sheet resistance of the electrode is essential for fabrication of uniform OLED lightings. However, the mostly used anode material, transparent conducting oxide (TCO), does not have enough low sheet resistance required for the large-area OLED. Therefore, to reduce the resistance of the TCO, auxiliary metal electrodes are often used. In this work, we applied the Ag grids onto the surface of the GFRH by using a transferring method from the glass. The fabrication procedures of Ag grid embedded GFRH are illustrated in Figure 6a. i) First, Ag grid was printed on the glass substrate by a gravure-offset printing method. To facilitate the detachment of the substrate and the printed Ag grid, the glass substrate was treated to have a hydrophobic SAM (Figure S5, Supporting Information). ii) Then, the glass fabric was placed onto the Ag grid followed by impregnation of oligosiloxane resin. iii) The sample was covered with cover glass and was compressed by vacuum bag molding method. The compressed sample was exposed to UV light. iv) Finally, the cover glass and glass substrate were removed. Figure 6b shows the image of fabricated Ag-grid embedded H-GFRH film. Due to the hydrophobic SAM, all Ag grids were successfully transferred to the surface of the GFRH without disconnections. As seen in Figure 6c, the Ag-grid embedded H-GFRH showed lower total transmittance (~84%) compared to the H-GFRH (~89%) due to the Ag grids at the surface. However, the embedment of the Ag grids alternatively increased the haze of the H-GFRH. The Ag grid embedded GFRHs exhibited low sheet resistance of approximately 8 Ω sq$^{-1}$ (Figure S6a, Supporting Information). To verify the extrusion or disconnection of the transferred Ag grid, the Ag grid embedded H-GFRH was analyzed with SEM analysis. Figure 6d exhibits the tilted cross-sectional SEM image of the Ag-grid embedded H-GFRH. The Ag grid was well transferred to the surface of H-GFRH without any extrusion or disconnection. The partially buried Ag grids were observed using SEM analysis (Figure S6b, Supporting Information). Therefore, we successfully fabricated GFRHs having characteristics of transparent conducting electrodes.

Figure 7a shows the EQE of the OLEDs on the C-GFRH and H-GFRH. The EQE values are almost constant in the luminance range of 5000–15000 cd m$^{-2}$. At luminance of 2000 cd m$^{-2}$, the EQE of C-GFRH showed value of 13.3% where H-GFRH exhibited EQE value of 23.2% having an increment of 74%. Furthermore, OLEDs fabricated on H-GFRH showed wider angular emission range compared to the OLEDs on C-GFRH (Figure 7b). To be specific, noticeable light extraction in the higher angle (>40°) were observed. For instance, C-GFRH showed only 40% light intensity at angle of 60° compared to the light intensity at angle of 0°. On the other hand, H-GFRH showed 65% light intensity at angle of 60° compared...
to the light intensity at angle of 0°. The widened distribution of H-GFRH OLED is in accordance with the results of Figure 3. Figure 7c shows the electronluminescence (EL) spectra of OLEDs on C-GFRH (left) and H-GFRH (right) as a function of viewing angle. The EL spectra of OLEDs on H-GFRH showed negligible difference from the EL spectra of OLEDs built on
C-GFRH. Also, the full width at half maximum of H-GFRH did not change as the viewing angle decrease. These results imply enhancement of light extraction by the haze in H-GFRH has negligible angle dependence, resulting in stable EL spectra. Because the original EL spectrum is preserved in a stable manner, there original OLED organic stack structure can be used without modification. Such feature is very attractive in the OLEDs in which more than one emissive layer is present.

3. Conclusion

To conclude, we report a reliable route to fabricate a robust manner, there original OLED organic stack structure can be fabricated in a stable EL spectra. Because the original EL spectrum is preserved in a stable manner, there original OLED organic stack structure can be used without modification. Such feature is very attractive in the OLEDs in which more than one emissive layer is present.

4. Experimental Section

Characterization of OLEDs on GFRH: The ITO anode of the OLED was prepared on the GFRH film by using RF-DC sputtering process (HanaPlasma, Sputter system HS-PL200S) to a thickness of 100 nm. The OLED stack and cathode were deposited by a thermal evaporation method in a high-vacuum chamber below 6.7 × 10⁻⁵ Pa. The phosphorescent green OLED was fabricated on the GFRH film (embedded Ag auxiliary electrode)/ITO (100 nm). 1,4,5,8,9,11-hexaazatriphenylene-hexacarbonitrile (Hat-CN, 10 nm)/N,N'-bis(naphthalen-1-yl)-N,N'-bis(phenyl)benzidine (NPB, 40 nm)/Hat-CN (10 nm)/NPB (40 nm)/Hat-CN (10 nm)/NPB (40 nm)/4,4',4'-tris(carbazol-9-yl)triphenylamine (TCTA, 10 nm) were used as hole transport layer. The emission layer was used 2,6-bis-[30-[N-carbazole phenyl] pyridine doped with 7% of tris [2-phenylpyridinato-C2,N] iridium (III) (DCzppyIrrppy, 20 nm). 1,3-bis-(3,5-diprop-3-yl-phenyl)benzene (BmPyPB, 60 nm) was used for electron transport layer. LiF (1 nm)/Al (100 nm) were deposited as a cathode electrode.

Evaluation of OLEDs on GFRH: The fabricated OLEDs were characterized using a current/voltage source unit (Keithley 2400) in a nitrogen-filled glove box. The angular spectrum and intensity of the OLEDs were tested using fiber optic spectrometer (EPP2000, Stellarnet) and a calibrated Si photodiode (FDS100, Thorlabs) mounted on a motorized goniometer system.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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