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Nanostructured Polymer/Layered Silicated Materials

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Blue-light-emitting polymer/layered silicate nanocomposites were prepared by the solution intercalation method and employed in electroluminescent device. Their photoluminescence and electroluminescence characteristics suggested that the layered material isolate the polymer chains and hinder the formation of excimers and aggregates. By reducing the excimer formation and its deleterious effects on emission efficiency, both the color purity and the luminescence stability were improved. Furthermore, the silicate nanolayers have an aspect ratio of about 500 and therefore act as efficient barriers to oxygen and moisture diffusion, which produced a dramatic increase in the device stability.

Key words: Nanocomposites, Light-emitting diodes, Stability, Excimer, Photo-oxidation

1. INTRODUCTION

Blue-light-emitting polymers are of special interest in the development of polymer light-emitting diodes (PLEDs), because they are essential to achieving the full gamut of color either in patterned RGB emitters or in optical filter-based color PLEDs.[1,2] Although many conjugated polymers have been designed that give efficient and stable blue-light emission,[3-7] only a few of these polymers are promising candidates for use in blue-light-emitting PLEDs. Polyfluorenes (PFs) were recently introduced as prospective blue-light-emitting materials for PLEDs because of their extremely high luminescence efficiencies.[8-10] Further, their thermal stabilities are superior to those of poly(*p*-phenylene vinylenes).[9] However, there are still problems that need to be circumvented if PFs are to be employed in blue-light-emitting polymer devices. Firstly, excimers can cause non-radiative decay.[11,12] Strategies to reduce the excimer emission in electroluminescent systems have been focused on two types of approaches:[13] chemical approaches such as introducing long side chains to the luminescent polymer[14] or end-capping the polymer,[15-18] and physical approaches such as tailoring the molecular weight distribution[19] and using hole-trapping molecules[20].

Another problem that must be overcome is the photo-oxidative degradation of emitting polymers triggered by the oxygen that is either residual in the polymer or released from the indium-tin-oxide (ITO) electrode.[21] Oxygen causes polymer degradation by generating aromatic ketones that quench fluorescence. Recently, Heeger's group found that low-energy emission bands are generated from the fluorenone defects that are introduced by photo-oxidation and thermal oxidation,[22] and List's group reviewed the relationship between the molecular structure and the electronic properties of π-conjugated materials.[23]

The introduction of silicate layers into polymers to create a composite material with improved mechanical properties has been widely investigated. Nanocomposites exhibit markedly better mechanical, thermal, and physico-chemical properties than neat polymers or conventional (microscale) composites.[24-26] However, studies on the effects of layered silicates on the properties of functional materials such as photo-responsive polymer nanocomposites are in their infancy. Our group[27] and Karasz's group[28] recently reported the discovery of the stable luminescence properties of polymer/clay nanocomposites. In addition, we obtained enhanced color purity and stability from polymer/nanoporous silica nanocomposite blue-light-emitting diodes.[29] In this work, we report further stabilized blue emission resulted from the use of a layered silicates.

We prepared blue-light-emitting polymer nanocomposites comprising poly(9,9'-dioctylfluorene) (PDOF) and a layered silicate (C20A) in order to simultaneously solve the two serious defects of blue-emitting polymers mentioned above. The physical aggregation of the luminescent polymer that leads to non-pure blue emission is prevented by isolating the polymer chains within the galleries of the layered silicates. Further, the layered silicates act as barriers to oxygen and moisture diffusion, leading to a large improvement in the photo-oxidation stability of the device based on the organic/inorganic nanocomposite material. In addition, luminescence characteristics of the nanocomposite PLEDs were investigated.

2. EXPERIMENTAL

A fluorene-based polymer, poly(9,9'-dioctylfluorene) (PDOF) (Mn: 11,000, PD: 2.5, yield: 90%), was synthesized via the Suzuki coupling reaction.[32] The layered silicates (C20A), which act as dielectric nanolayers, are mica-type nanoparticles that have the surfaces organically modified with dimethyl HT (hydrogenated tallow) ammonium and have a charge exchange capacity (CEC) of 95 mequiv/100 g. C20A was sonicated in trichloroethylene for 3 hrs to ensure good dispersion and then PDOF pre-dissolved in trichloroethylene was mixed with the dispersed C20A solution. The mixed solution was sonicated again for 30 min and then stirred for an additional 3 hrs to enable the intercalation of the PDOF molecules into the galleries of C20A, i.e., to enable the nanocomposite formation. The weight ratio of PDOF versus C20A in the nanocomposites was controlled to be 1:0.5, 1:1, or 1:2; the nanocomposite of PDOF/C20A with 1:0.5 weight ratio is denoted as PDOF1/C20A0.5.

The optical absorption spectra of the specimens were obtained at room temperature using a Jasco V-530 UV-vis spectrometer, and the PL spectra were measured while exciting the specimens at 380 nm using an ISS PC1 spectrofluorometer equipped with a dual grating monochromator (Spex 270M) and a photomultiplier tube (Hamamatsu R928) as a detector. The absorption and PL spectra were measured with the film specimens of a 60 nm thickness that had been spin-cast onto quartz substrates. The PL decay characteristics of the pristine PDOF and the PDOF/C20A nanocomposite films were monitored under both air and N_2 atmospheres as a function of time while exciting the films with a strong 380 nm-monochromatic light from a Xenon lamp. For FT-IR measurement, the films were prepared on KBr substrates.

PLED specimens of the ITO/PVK/(emitting layer)/Li:Al structure were fabricated as follows: Indium tin oxide (ITO)-coated glass plates were washed and treated by oxygen plasma prior to the use as the substrate of PLED. On top of the substrate, a polyvinylcarbazole (PVK, M_w: 280,000) layer of a 60 nm thickness and an emitting nanocomposite layer of a 30 nm thickness were successively deposited by spin-casting from the monochlorobenzene and the tricholoroethylene solutions, respectively. Finally, Li:Al alloy cathode was deposited on the nanocomposite layer under high vacuum (10^{-6} Torr) to complete the device fabrication.

3. RESULTS AND DISCUSSION

The layered silicates (C20A), which act as dielectric nanolayers, are mica-type nanoparticles that have the surfaces organically modified with dimethyl HT (hydrogenated tallow) ammonium and have a charge exchange capacity (CEC) of 95 mequiv/100 g. C20A was sonicated in trichloroethylene for 3 hrs to ensure good dispersion and then PDOF pre-dissolved in trichloroethylene was mixed with the dispersed C20A solution. The mixed solution was sonicated again for 30 min and then stirred for an additional 3 hrs to enable the intercalation of the PDOF molecules into the galleries of C20A, i.e., to enable the nanocomposite formation. The weight ratio of PDOF versus C20A in the nanocomposites was controlled to be 1:0.5, 1:1, or 1:2; the nanocomposite of PDOF/C20A with 1:0.5 weight ratio is denoted as PDOF1/C20A0.5.

An X-ray diffraction (XRD) study was carried out to confirm the intercalation of PDOF into the C20A galleries. Figure 1 shows the XRD patterns of the specimens; the peaks are due to Bragg diffraction from the 001-lattice planes of C20A. In the figure, the diffraction peaks of the organic clay film and of the PDOF1/C20A1.0 nanocomposite film are observed at 2θ = 3.46 and 2.51, respectively. This indicates that the inter-layer d_{001}-spacing of C20A was extended from 2.5 to 3.6 nm by the intercalation of PDOF molecules into the C20A galleries. We believe that a considerable amount of PDOF molecules have become isolated within the 2-dimensional lamellar structure.

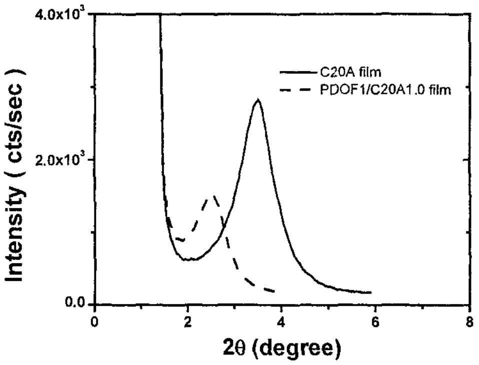
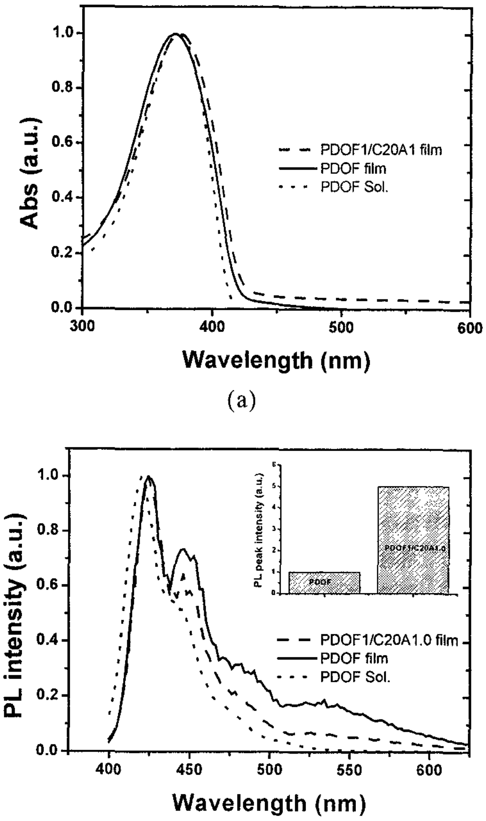


Fig. 1 XRD patterns of the organoclay (C20A) bulk and the PDOF/C20A nanocomposite films.

The UV-vis absorption and PL spectra of the PDOF1/C20A1.0 nanocomposite film are compared with those obtained from the pristine PDOF film and solution in Figure 2. The onset and peak positions on the optical absorption spectrum of PDOF, that are located at 425 and 378 nm, respectively, are virtually unchanged by the intercalation. Also, the emission peak appears at ~ 420 nm irrespective of the intercalation, but the PDOF1/C20A1.0 nanocomposite exhibits a weaker vibronic emission at ~ 440 nm than the pristine PDOF film. The emission in the long-wavelength region is generally rather featureless and originates from the excimers or aggregates.[15] The PL quantum yield of excimer emission is lower than that of exciton emission.[30] Red-shifted emission and low PL efficiency can be the characteristic features of the emissions of cofacial ground state dimers and aggregates.[13]



(a)

(b)

Fig. 2 (a) UV-vis and (b) Phtoluminescence spectra of the PDOF solution (dotted lines), the pristine PDOF film (solid lines), and the PDOF/C20A nanocomposite film (dashed lines). The inset shows the PL intensities of the PDOF and the PDOF/C20A nanocomposites films.

In contrast to the excimer emission spectra, the aggregate emission spectra are often well structured and the corresponding absorption spectra exhibit characteristic red-shifts with respect to those of isolated chromophores. As the absorption spectra in Figure 2(a) demonstrate, no differences between the absorption characteristics of the pristine PDOF film and of the diluted solution were observed, indicating that the red shift in the emission spectra resulted from the excimer formation.[13] However, in the PL spectra of the PDOF1/C20A1.0 nanocomposite film shown in Figure 2(b), the long-wavelength tail due to excimers has become significantly reduced in intensity. This change in the PL spectrum implies an improvement in the color quality of blue emission and can be attributed to a reduction in interchain interactions. Isolating the conjugated polymer chains within a confined geometry prevents excitons from finding low-energy trap sites (i.e., excimer formation). The effects of isolation and of the increase in the effective excitation energy (because of the increased excitation beam path due to internal scattering or reflection within the composite film) should result in an improvement in the PL quantum yield.[27] The PDOF1/C20A1.0 nanocomposite film exhibited a PL intensity about five times stronger than that of the pristine PDOF film when the PL intensity was normalized with respect to the absorbance, as shown in the inset of Figure 2(b).

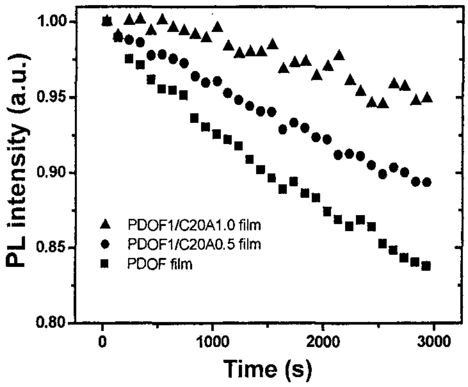


Fig. 3 Phtoluminescence intensity decay of the pristine PDOF and the PDOF/C20A nanocomposite films spin-cast on glass as a function of UV-exposure time in air.

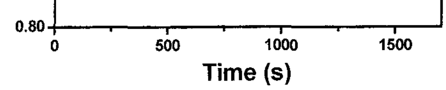


Fig. 4 Phtoluminescence intensity decay of the pristine PDOF and the PDOF/C20A nanocomposite films spin-cast on glass as a function of UV-exposure time in N_2.

Despite the remarkable improvements in the stability and color purity of PLEDs based on PF-type emitters, most of these PLEDs suffer during operation from photo-oxidation of the active layer because amorphous polymer films have sufficient free volume to allow the diffusion of oxygen atoms, which act as luminescence quenching centers.[15] To investigate the photo-stability of the PDOF/C20A nanocomposite films, the PL peak intensity was recorded under both air and nitrogen conditions as a function of time while exciting the films with a strong 380 nm-monochromatic light from a Xenon lamp. The photo-oxidation of the polymer films was observed by carrying out a PL decay experiment in air.[15] The PL intensity of the composite film in air tends to decrease more slowly with time than that of the pristine PDOF film, as shown in Figure 3. This implies that the oxidation of the polymer matrix that leads to the formation of aromatic ketones and fluorescence quenching is greatly retarded by the finely dispersed clay sheets, which are effective gas barriers.[27]

There is also a change in the PL intensity in the absence of oxygen that cannot be completely explained by the oxygen-induced chemical changes;[15] hence we also need to consider the relationship between the physical changes in the polymer, such as excimer formation, and the PL stability. To investigate the relationship between physical degradation and excimer formation,[15] the PL intensity decay of the pristine and nanocomposite films was monitored as a function of excitation time in a N_2 atmosphere. In the initial stage, the PL intensity decay was faster for the pristine PDOF film than for the PDOF1/C20A1.0 nanocomposite film as shown in Figure 4. On further excitation, however, it was very interesting to observe that the PL decay rates of both specimens begin to decrease and then fall towards zero. The decrease in PL intensity is thought to originate from a physical degradation due to excimer formation, but the degree of PL decay of the PDOF/C20A nanocomposite film was somewhat smaller than that of the pristine PDOF film. The enhanced photo-stability of the PDOF1/C20A1.0 nanocomposite film can be explained by the inhibited excimer formation. Excimer formation is hindered by the reduction in interchain interaction that is produced by intercalating the polymer chains between the silicate nanolayers, and thus the aggregate-related fluorescence is reduced. Aggregate growth is expected to occur in both the bulk polymer and the polymer/clay nanocomposite phases simultaneously with photochemical oxidation, but these effects become diminished and saturated upon further UV exposure.

FT-IR spectroscopy was used to probe the chemical change of the specimens that results from the UV irradiation in air. Figure 5 shows the infrared spectra of the pristine PDOF and the PDOF1/C20A1 nanocomposite films before and after a 2 hrs' UV exposure in air. For both the films, two new IR-absorption bands appeared around 1717 and 1606 cm^{-1} but the growth of the two peaks was remarkable for the pristine PDOF film. The former peak is attributed to carbonyl stretch of an aromatic ketone or ester and the latter may be interpreted as a stretching mode of an asymmetrically substituted benzene ring.[31] Development of these two peaks is considered to result from the photo-oxidation of PDOF and the intensities of the peaks were much weaker for the nanocomposite film demonstrating its enhanced photo-stability.

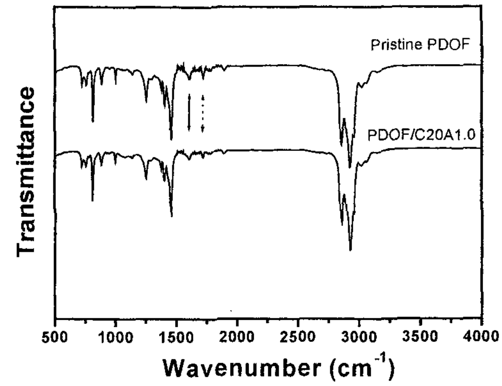


Fig. 5 FT-IR transmittance spectra of the PDOF and the PDOF1/C20A1.0 films after photo-oxidation in air for 8 hr: 1606 cm^{-1} (solid arrow) and 1717 cm^{-1} (dotted arrow)

Figure 6 shows the normalized EL spectra of the ITO/PVK/(PDOF/C20A)/Li:Al devices with different emitting layer compositions. The excimer formation decreased with increasing C20A content due to the polymer chain isolation effect.

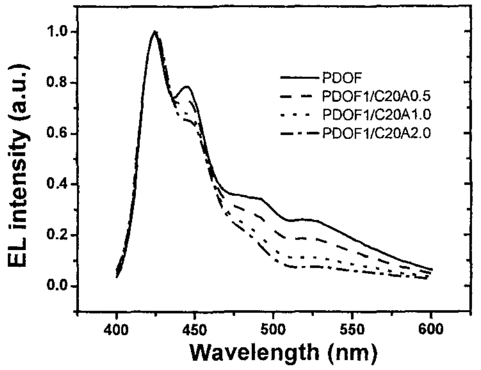


Fig. 6 Electroluminescence spectra of the ITO/PVK/(PDOF/C20A)/Li:Al devices with different emitting layer compositions.

4. Conclusions

In the present study, a new approach that retards both the chemical and the physical degradation processes of polyfluorenes in PLEDs was introduced. Specifically, films of nanolayer nanocomposites comprising a blue-emitting polyfluorene (PDOF) and a layered silicate (C20A) were prepared. The PDOF/C20A nanocomposite films exhibited narrow emission spectra with smaller long-wavelength tails and better stability in both air and nitrogen atmospheres. The enhanced emission color purity of the nanocomposite films is attributed to the reduced interchain interactions achieved by isolating the conjugated polymer chains within the confined geometry of the dielectric nanolayers. The nanolayers in the nanocomposite films not only inhibit the photochemical oxidation of PDOF by blocking the oxygen penetration but also prevent the excimer formation by their steric hindrance; these two effects are combined to improve the photo-stability of the films. In addition, the nanocomposite films demonstrated markedly enhanced PL and EL quantum efficiencies. The PDOF/C20A nanocomposites can be a promising candidate for the blue-light-emitting material in PLEDs due to their high emission color quality, better long-term stability, and enhanced luminescence properties.

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