FABRICATION OF MEH-PPV/SIO$_2$ AND MEH-PPV/TIO$_2$ NANOCOMPOSITES WITH ENHANCED LUMINESCENT STABILITIES

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Abstract. Thin films of composites made by incorporation of silicon oxide (SiO$_2$) or titanium oxide (TiO$_2$) nanoparticles into poly[2-methoxy-5-(2'-ethylhexoxy-*p*-phenylene vinylene] (MEH-PPV) were deposited by spin-coating from *p*-xylene solutions and their optical properties were investigated. SEM images showed that different extents of aggregates were formed for two kinds of nanocomposites. The UV-vis absorption spectra of MEH-PPV/SiO$_2$ and MEH-PPV/TiO$_2$ films showed a small red shift (~ 5 nm) as compared with that of pristine polymer. However, the structure of MEH-PPV was not affected as revealed by infrared and Raman experiments. This result is different from that obtained in PPV/oxide nanocomposites in which, the conjugated length of PPV main chain was reduced. Similarly, a small red shift was found in PL emission spectra with increasing the content of oxide nanoparticles. The PL degradation experiments showed that blending with SiO$_2$ nanoparticles could enhance the luminescent stability of MEH-PPV. By blending with 8% SiO$_2$ nanoparticles of 20 nm diameter, the PL intensity of MEH-PPV film attained 46% of the original one, while it decreased to 20% for pristine MEH-PPV after four weeks of exposure to ambient air. The effect of TiO$_2$ nanoparticles to stabilize MEH-PPV thin films is though less important than that of SiO$_2$.

1. INTRODUCTION

Conjugated polymers are nowadays used in several display applications [1-4], resulted from intensive research works over the last decade since the first report on polymer based light emitting diodes [5]. Among them, poly(*p*-phenylene vinylene) (PPV) and its derivatives have attracted a great deal of attention because of their particular structure and their highly interesting electroluminescent properties [6]. To enhance the performance of PPV-based devices, several studies have been carried out on composites made with polymers and nano-oxide particles such as silicon oxide (SiO$_2$) or titanium oxide (TiO$_2$). The former is found to have a good effect on the conductivity of the polymer host while the second can influence its photovoltaic properties. The use of composites is believed to increase the electrical conduction of the polymer [7] and in addition, to improve its stability [8], which is of prime importance in organic devices. When used in composites, modifications of the polymer luminescence were observed for both oxides. However, contradictory results have been reported. For example, poly(2- methoxy-5-(2'-ethylhexoxy) -1,4-phenylene vinylene) (MEH-PPV) blended with SiO$_2$ was found to have an improved conductivity as compared to the bare polymer [9], while PPV with similar nanoparticles shows a lower conductivity than the polymer alone [10].

Besides, the effects of the nanoparticles on the structure of the polymer are still a subject of research. Baraton *et al.* found that blends using TiO$_2$ nanoparticles do not break the PPV conjugation and possess the potential of gas sensing applica-

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tions [11]. Zhang *et al.* observed that the TiO_2 nano-aggregates take the form of a sphere and change into an ellipsoid as the content of TiO_2 increased [12]. From our previous report, SiO_2 nanoparticles would reduce the conjugation lengths of PPV and the reduction becomes significantly important as the content of SiO_2 increases [13]. Comparing samples having different nanoparticle sizes and a similar oxide concentration, we found that smaller nanoparticles induce larger blue shift.

The previous mentioned composites use PPV as a polymer host matrix. For this material, a thermal conversion process is required to obtain the final conjugated polymer. In this work, we have studied composites made by incorporation of SiO_2 or TiO_2 nanoparticles of different concentrations and sizes in MEH-PPV. Since MEH-PPV is a soluble conjugated polymer, one can incorporate oxide nanoparticles into MEH-PPV directly. We examine the optical properties of the hybrid materials and discuss the influence of the nature and the size of the particles on the behavior of the composites.

2. EXPERIMENTAL

The light-emitting polymer MEH-PPV was prepared according to previous method in the literature [14]. SiO_2 nanoparticles dispersed in ethylene glycol (EG) were provided from SPCI S.A. and TiO_2 nanoparticles from Degussa. SiO_2 nanoparticles were obtained by heating the dispersed EG solution under vacuum to remove the solvent.

Four solutions of MEH-PPV in *p*-xylene were mixed with diameter 20 nm SiO_2/xylene solutions in different weight ratios (1%, 2%, 4%, and 8%). The mixtures were prepared under ultrasonication for 1 hr, filtered with 10 μm filter, and then spin-coated on the pre-cleaned glass substrates. Four other MEH-PPV/SiO_2 nanocomposites (100 nm, 1%, 2%, 4%, and 8%) and four MEH-PPV/TiO_2 nanocomposites (20 nm, 1%, 2%, 4%, and 8%) were prepared by the similar procedure.

UV-vis absorption spectra of the samples were measured with a CARY 5G spectrophotometer. Raman and infrared experiments were performed by using a BRUKER RFS 100 and a BRUKER IFS 28 spectrophotometer, respectively. Photoluminescence (PL) spectra were obtained with a Fluorolog 3 spectrophotometer. All the measurements were performed in air and at room temperature. Scanning Electron Microscopy (SEM) images were obtained by using a Jeol 6800 SEM apparatus.
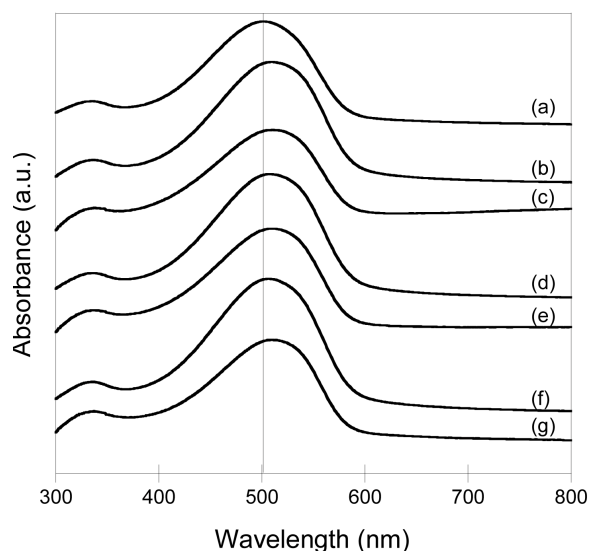

Fig. 1. UV-vis absorption spectra of MEH-PPV and nanocomposite thin films: (a) MEH-PPV; (b) MEH-PPV/SiO_2 (20 nm, 1%); (c) MEH-PPV/SiO_2 (20 nm, 4%); (d) MEH-PPV/SiO_2 (100 nm, 1%); (e) MEH-PPV/SiO_2 (100 nm, 4%); (f) MEH-PPV/TiO_2 (20 nm, 1%); (g) MEH-PPV/TiO_2 (20 nm, 4%). The vertical line indicates the absorption band maximum of MEH-PPV.

3. RESULTS AND DISCUSSION

3.1. UV-vis spectra

Fig. 1 shows the UV-vis absorption spectra of pristine MEH-PPV and its nanocomposite films. For pristine MEH-PPV films, the absorption band maximum was located at 503 nm. For MEH-PPV/oxide nanoparticles thin films, the maxima of UV-vis absorption bands were located at ca. 508 nm showing a slight red-shift as compared to that of the pristine polymer. Red shift in absorption is associated with long conjugation segments that have lower optical bandgap. The shift was found for all the nanocomposite films and may be explained by the temperature effect induced by the use of ultrasonic bath for preparing the composite solutions. Indeed, in order to disperse the oxide nanoparticles homogeneously inside the polymer layer, a ultrasonic bath was applied to the polymer/nanoparticle solution for 1 hr before depositing thin films. Increasing temperature of the solution would increase the conjugation length of polymer chains slightly, resulting from the annealing effect of the film [15,16]. The choice of *p*-xylene as the solvent is
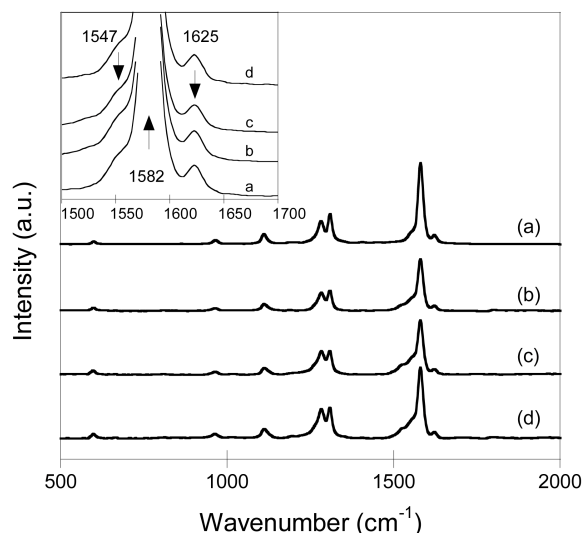
Fig. 2. Raman spectra of MEH-PPV and nanocomposite thin films: (a) MEH-PPV; (b) MEH-PPV/SiO$_2$ (20 nm, 2%); (c) MEH-PPV/SiO$_2$ (100 nm, 2%); (d) MEH-PPV/TiO$_2$ (20 nm, 2%). Inset: details of Raman triplet for the films.

3.2. Raman and infrared spectra

Fig. 2 shows the Raman spectra of MEH-PPV and some nanocomposites. All spectra show the characteristic bands of MEH-PPV: 1112 cm^{-1} (mixtures of C-C stretching and C-H in-plane-bending vibration), 1282 cm^{-1} (C=C stretching band of benzene ring), 1582 cm^{-1} (C-C stretching band of benzene ring), and 1623 cm^{-1} (C=C stretching band of vinyl group). No significant shift of these bands is observed in polymer and composites, suggesting that the conjugation length is similar in the studied materials [17]. In PPV-based derivatives, the distribution of the triplet band between 1500 and 1700 cm^{-1} offers the information of conjugation length of polymer chains [18]. When the conjugation length is reduced, the band at 1625 cm^{-1} grows stronger than the one at 1548 cm^{-1}. The observation in PPV/oxide nanocomposites is pretty clear [13]. For MEH-PPV and its nanocomposites, however, two bands at 1547 and 1582 cm^{-1} merge; the change of this triplet band is difficult to observe.

Though the conjugation length evolution of MEH-PPV and its nanocomposites could not be clearly estimated from the spectra, we notice that no new band is formed in composite films and that there is no significant change in the shape and intensity of the polymer spectrum upon incorporation of particles. This reveals that the chemical structure of MEH-PPV is not affected by the incorporation of SiO$_2$ or TiO$_2$ nanoparticles.

3.3. SEM micrographs

Fig. 3 shows the SEM images of some MEH-PPV nanocomposites. It can be seen that both SiO$_2$ and TiO$_2$ nanoparticles form aggregated regions. Aggregation of TiO$_2$ nanoparticles seems more important than SiO$_2$. SiO$_2$ and TiO$_2$ nanoparticles can be dispersed homogeneously in hydroxy-containing solvents such as EG and glycerol, since there are many hydroxyl groups on the surface of oxide nanoparticles. In this work, *p*-xylene is chosen as the solvent and oxide nanoparticles aggregate. From the dispersion point of view, homogeneous thin films can be obtained by adding some wetting agent into polymer/oxide solutions.

3.4. PL spectra and degradation

From literature, we know that MEH-PPV is easily photo-oxidized [19]. The photo and photo-oxidative reactions in PPV derivatives are similar to those occurring in PPV [20]. In particular, in MEH-PPV, degradation of the polymer would result from a
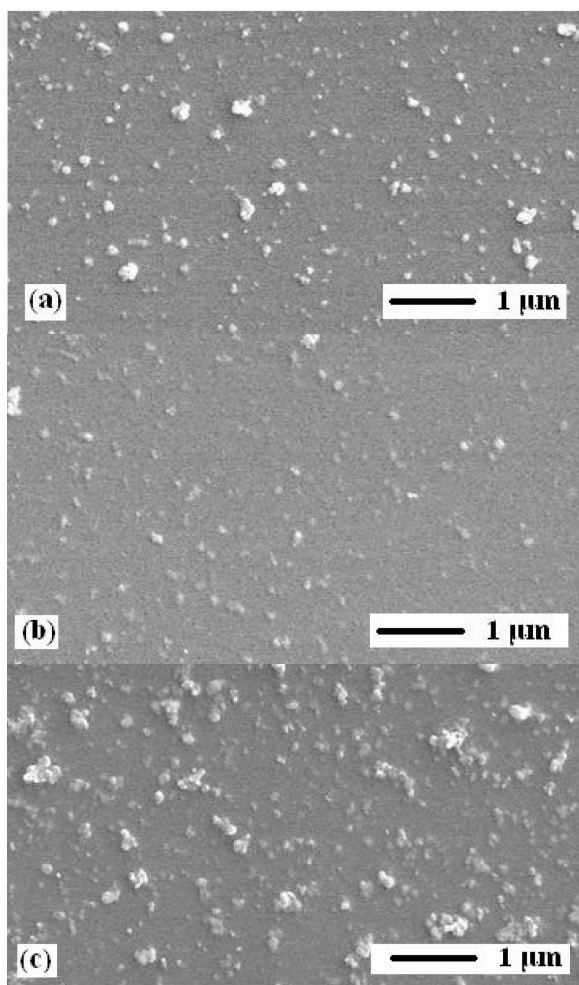
due to its high boiling point, which can prevent the change in the polymer concentration with raised temperature. We conclude that the incorporation of oxide nanoparticles does not reduce the conjugation length of MEH-PPV. The result is different from what we found for PPV/SiO$_2$ nanocomposites [13]. The previous experiments showed that SiO$_2$ nanoparticles reduced the conjugation lengths of PPV chains, and the reduction of conjugation length was more noticeable on increasing the oxide concentration or on decreasing the particle size. The difference between composites may be understood by the formation process. In fact, the thermal conversion is essential for the formation of fully conjugated PPV. When oxide nanoparticles are added into PPV precursor solution, they can insert into precursor polymer chains and the formation of vinyl bonds would be hindered by those nanoparticles and thus, the final conjugation length of PPV is reduced after the conversion process. On the contrary, as MEH-PPV is a soluble, its conjugation length is determined at the stage of synthesis. Therefore, incorporation of oxide nanoparticles will not affect its structure and hence its optical properties.

Fig. 3. SEM images of MEH-PPV nanocomposites films: (a) MEH-PPV/SiO$_2$ (20 nm, 2%); (b) MEH-PPV/SiO$_2$ (100 nm, 2%); (c) MEH-PPV/TiO$_2$ (20 nm, 2%).

carbonyl functional group into the polymer, when exposed to air and visible light. This group breaks the carbon double bond, and destroys the extended conjugation of the polymer chain [21]. Consequently, the chain segmentation leads to a blue shift of the photoluminescence spectrum, and formation of luminescence quenching defects results in a decrease of its intensity. Several investigations have shown that the use of nanoparticles leads to enhancement of optical, electrical properties and stability [22]. Incorporation of oxide nanoparticles into MEH-PPV would stabilize the composite materials. To study the stabilization of the polymer films, we have performed the following aging (deg-

radation) experiment. After their fabrication, the nanocomposite films were placed in ambient air, without protection and their PL spectra were periodically measured within four weeks. Analyses of the films by absorption, Raman and infrared spectroscopy did not show significant changes in the polymer structure except a slight increase in intensity of the IR bands located at 1690 and 1590 cm^{-1}, which are attributed to the carbonyl and phenylene bonds respectively. This variation suggests a loss of symmetry of C=C bonds in the backbone, and an oxidation induced by ambient air. However, compared to PPV, the oxidation observed here is of rather weak intensity. In composites films, the corresponding bands have a weak intensity and are not affected by the air exposure.

Fig. 4 shows the PL spectra evolution of MEH-PPV and its nanocomposite films for a period of four weeks. In Fig. 4a, the main emission band of a freshly prepared (or pristine) MEH-PPV film is located at 592 nm, with a shoulder band at 640 nm. After one week of exposure, the intensity of the emission band decreased dramatically to 35% of the fresh sample, and decayed to 20% after four week. The color of MEH-PPV thin film also changed from orange-red to yellow by the naked eye.

Figs. 4b shows the PL spectra of MEH-PPV/SiO$_2$ (20 nm, 2%), those of MEH-PPV/SiO$_2$ (100 nm, 2%), and MEH- PPV/TiO$_2$ (20 nm, 2%) are not shown. Several observations can be made from the composite spectra. First, a slight PL red shift of the emission band is found as compared to MEH-PPV. This shift is consistent with the result of UV-vis absorption. Second, the intensity of emission band is decreasing with the exposure time but the decrease is lesser than that obtained in pristine MEH-PPV. For example, the PL intensity of MEH-PPV/SiO$_2$ (20 nm) film attained 60% of the initial one after one week of exposure while for MEH-PPV/SiO$_2$ (100 nm) composite, the PL intensity decreased to 48% of its initial value for the same duration. Therefore, incorporation of SiO$_2$ nanoparticles into the polymer can retard the photo-oxidation of MEH-PPV. A similar result was also reported by Lim *et al.* [23,24]. They found that the incorporation of SiO$_2$ nanoparticles with diameter 400 nm into PPV could reduce the photo-oxidation and enhanced the stability of PPV.

To examine the influence of the oxide particle nature and size, we plot in figure 5 the PL intensity ratio L/L_0 (L_0 denotes the initial intensity of the emission band maximum, and L its intensity after exposure) as a function of time. We note that all the
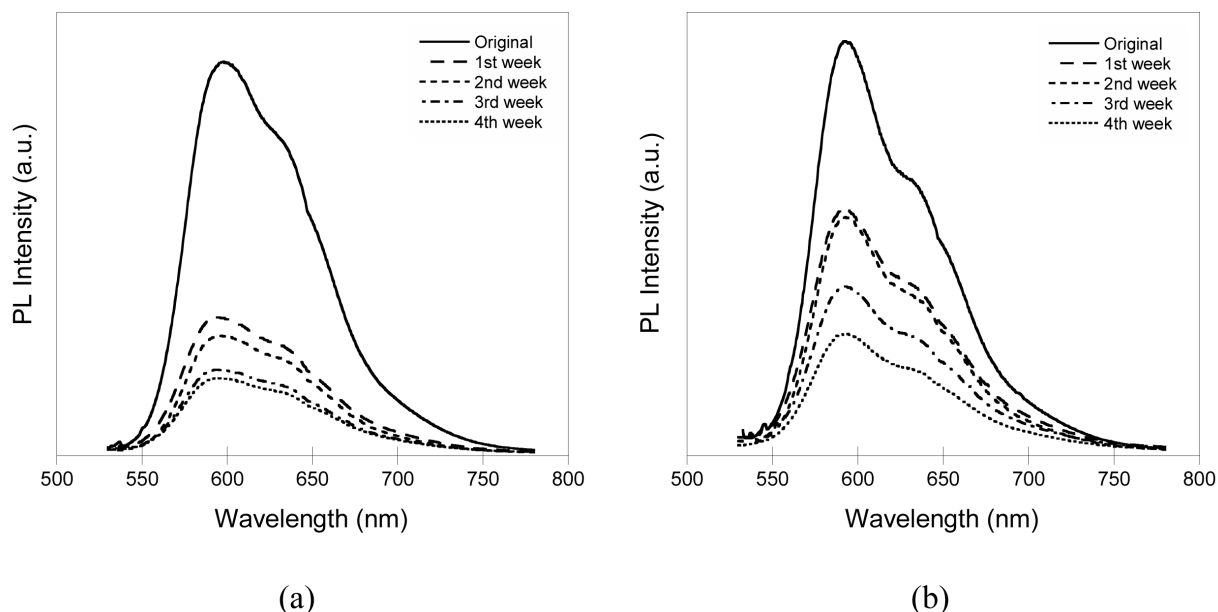
(a)   (b)

Fig. 4. Evolution of photoluminescence spectra of MEH-PPV and nanocomposite films as a function of exposure time: (a) MEH-PPV; (b) MEH-PPV/SiO$_2$ (20 nm, 2%).
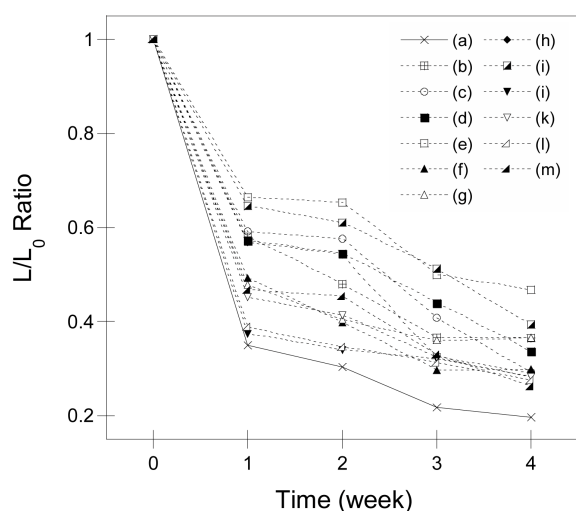

Fig. 5. Variation of L/L$_0$ ratio as a function of time: (a) MEH-PPV; (b) MEH-PPV/SiO$_2$ (20 nm, 1%); (c) MEH-PPV/SiO$_2$ (20 nm, 2%); (d) MEH-PPV/SiO$_2$ (20 nm, 4%); (e) MEH-PPV/SiO$_2$ (20 nm, 8%); (f) MEH-PPV/SiO$_2$ (100 nm, 1%); (g) MEH-PPV/SiO$_2$ (100 nm, 2%); (h) MEH-PPV/SiO$_2$ (100 nm, 4%); (i) MEH-PPV/SiO$_2$ (100 nm, 8%); (j) MEH-PPV/TiO$_2$ (20 nm, 1%); (k) MEH-PPV/TiO$_2$ (20 nm, 2%); (l) MEH-PPV/TiO$_2$ (20 nm, 4%); (m) MEH-PPV/TiO$_2$ (20 nm, 8%).

composite films show better emission stability than bare MEH-PPV films. On the other hand, composites with SiO$_2$ nanoparticles are more stable than those made with TiO$_2$ nanoparticles. For any oxide concentration, the decrease in emission is less than that measured in TiO$_2$ based composites. In addition, for a given particle type, the emission stability is improved when using a higher oxide concentration. Finally, the influence of the particle size could not be clearly established from the obtained results. It can be suggested that small size particles may offer a better luminescence stability by comparing the behaviour of different composites containing SiO$_2$ particles of 20 and 100 nm sizes.

4. CONCLUSION

In this work, we have investigated the optical properties of MEH-PPV and its nanocomposites made by incorporating SiO$_2$ and TiO$_2$ nanoparticles into polymer layer. We have shown that the conjugation length of the polymer is not affected by the presence of the particles, whatever their concentration (up to 8%) and their nature, in contrast to results obtained in PPV/oxide nanocomposites. We show furthermore that the studied composites present a higher stability in emission characteristics compared to bare polymer films. We explain this stability as a consequence of the reduction of the formation of carbonyl type groups in MEH-PPV,

resulted from the presence of the nanoparticles. It is probable that the conservation of the conjugation length plays an important role in the stability of the polymer but it is also obvious that the particles limit or even reduce the formation and diffusion of oxygen inside the polymer matrix. The high stability of the composites makes them attractive for fabrication of photoactive devices, especially for TiO$_2$ based composites, which can be used in polymer photovoltaic cells.

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