

Optical and electrical investigations of poly(*p*-phenylene vinylene)/silicon oxide and poly(*p*-phenylene vinylene)/titanium oxide nanocomposites

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Abstract

Composites made by incorporation of silicon oxide (SiO₂) or titanium (TiO₂) nanoparticles into poly(*p*-phenylene vinylene) (PPV) have been fabricated and their electrical and optical properties have been investigated. The UV-vis absorption and Raman spectra showed that SiO₂ nanoparticles reduced the conjugation lengths of PPV chains, while TiO₂ nanoparticles did not. In the case of SiO₂ nanoparticles, the reduction of conjugation length was more noticeable on increasing the oxide concentration or on decreasing the particle size. Fourier transform infrared (FT-IR) spectra showed that both types of nanoparticles also reduced the formation of carbonyl groups in PPV main chains. Current-voltage characteristics measured in the indium tin oxide (ITO)–composite–MgAg diodes exhibit different electrical behavior to the composites depending on the particle size and the nature of the used oxide. The composite–electrode contact morphology, the polymer–dielectric particle contact, and the change in the polymer chain length are the possible explanations for these changes in behavior of the diodes.

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1. Introduction

Since the first report on polymer light-emitting diodes [1], a number of π -conjugated polymers have been intensively investigated in order to fabricate devices for industrial applications [2–5]. Among them, poly(*p*-phenylene vinylene) (PPV) and its derivatives have attracted a great deal of attention in recent years because of their particular structure and their highly interesting electroluminescent properties [6]. To enhance the performance of PPV-based devices, both chemical and physical methods can be used, improving the quality of the polymer, and hence, its behavior in devices. Using chemical methods, the structure of the polymer can be changed by adding functional groups to the backbone, which improve the solubility or modify the band gap of the material [7,8]. Chemical techniques generally lead to good results but they strongly depend on the synthesis of the

polymer. Using physical methods, the properties of the polymer can be improved by adding inorganic nanoparticles to the host material. This process is believed to increase the electrical conduction of the polymer [9], and in addition, to improve its stability [10], which is of prime importance in devices. Several studies have been carried out on composites made with PPV or its derivatives and nano-oxide particles, such as silicon oxide (SiO₂) or titanium oxide (TiO₂). The former is found to have a good effect on the conductivity of the polymer host while the second can influence its photovoltaic properties. In both cases, modification of the polymer luminescence is observed. It should be noted, however, that contradictory results were obtained in very similar materials. For instance, poly(2-methoxy-5(2'-ethyl) hexoxy-phenylene vinylene) blended with SiO₂ was found to have an improved conductivity as compared to the bare polymer [11] while PPV with similar nanoparticles shows a lower conductivity than the polymer alone [12]. Besides, the influence of the nanoparticles on the structure of the polymer is still a subject of discussion. Some workers reported that the conjugation length of the polymer could be altered by the incorporation of the nanoparticles, modifying

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Table 1

The composition and wavelength of the maximum absorption peak of PPV nanocomposites

Sample	Nanoparticle size (nm)	Nanoparticle ratio (wt.%)	UV λ_{max} (nm)
PPV	X	0	433
PPV/SiO ₂ -A	100	1	430
PPV/SiO ₂ -B	100	2	430
PPV/SiO ₂ -C	100	4	422
PPV/SiO ₂ -D	100	8	419
PPV/SiO ₂ -E	20	1	426
PPV/SiO ₂ -F	20	2	415
PPV/SiO ₂ -G	20	4	403
PPV/SiO ₂ -H	20	8	402
PPV/TiO ₂ -A	20	1	429
PPV/TiO ₂ -B	20	2	427
PPV/TiO ₂ -C	20	4	427
PPV/TiO ₂ -D	20	8	426

its optical and electrical properties [13]. Others found no structural change in the composites, suggesting that the added particles preserve the conjugation length [14]. It should be emphasized that the polymers used in these works were not synthesized by the same technique and discrepancies in the analysis results may partially be derived from the quality of the polymer materials.

In this work, we have studied some composites made by incorporation of silicon oxide (SiO₂) or titanium oxide (TiO₂) particles of different concentrations and sizes in PPV. We have examined the optical and electrical properties of the hybrid materials using the same polymer host in order to check the influence of the nature and the size effect of the particles on the behavior of the composites.

2. Experimental details

The precursor polymer of PPV was prepared by the classical Wessling–Zimmermann method. Details of the synthesis have been reported previously [15]. SiO₂ nanoparticles dispersed in ethylene glycol (EG) were provided from SPCI S.A. The trade name were NYACOL DP5820 (particles of 20 nm diameter) and DP5540 (particles of 100 nm diameter). TiO₂ nanoparticles were provided from Degussa. The trade name was P25 (particle of 20 nm diameter). Dispersion of nanosized TiO₂ was carried out in distilled water under ultrasonication for 8 h. All SiO₂ and TiO₂ dispersed solutions were filtered using a 10- μm filter.

Four PPV precursor solutions were mixed with diameter 100 nm SiO₂/EG solutions in different weight ratios (1%, 2%, 4% and 8% in wt.%) The solutions were mixed under ultrasonication for 1 h and then spin-coated on the pre-cleaned glass substrates. The thermal conversion of the precursor into polymer was performed under vacuum at 300 °C for 3 h.

PPV/SiO₂ nanocomposites (20 nm, 1%, 2%, 4% and 8% in wt.%) and PPV/TiO₂ nanocomposites (20 nm, 1%, 2%,

4% and 8% in wt.%) were prepared by the similar procedure. The composition of all PPV nanocomposites was listed in Table 1.

UV-vis absorption spectra were obtained by using a CARY 5G spectrophotometer in the range of 300–800 nm in air and at room temperature. Infrared spectra were obtained by using a BRUKER IFS 28 spectrophotometer in the range of 400–4000 cm⁻¹. The PPV/nanoparticles films were directly mixed with dry KBr powder and then pressed into pellets. Raman spectra were obtained by using a BRUKER RFS 100 spectrophotometer in the range of 100–3500 cm⁻¹. Scanning electron microscopy (SEM) images were obtained by using a JEOL 6800 SEM apparatus.

Diodes were prepared by depositing the composite thin film onto indium tin oxide (ITO) substrates followed by thermal evaporation of a MgAg cathode of thickness 500 nm. Current-voltage characteristics of devices were recorded using a setup already described [16]. All the measurements were performed in vacuum and under ambient conditions.

3. Results and discussion

3.1. UV-vis spectra

Fig. 1 shows the UV-vis absorption spectra of a pristine PPV film and the nanocomposite samples. For the PPV/SiO₂ nanocomposites, the UV-vis absorption peaks were located in the range from 430 to 419 nm with SiO₂ particle diameter of 100 nm, and from 426 to 403 nm with SiO₂ particle diameter of 20 nm. The shift in energy became

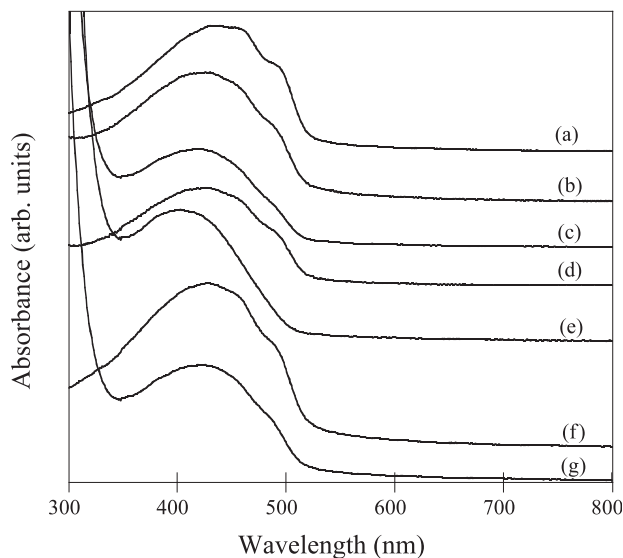


Fig. 1. UV-vis absorption spectra of PPV and nanocomposites: (a) PPV; (b) PPV/SiO₂-A (100 nm, 1%); (c) PPV/SiO₂-D (100 nm, 8%); (d) PPV/SiO₂-E (20 nm, 1%); (e) PPV/SiO₂-H (20 nm, 8%); (f) PPV/TiO₂-A (20 nm, 1%); (g) PPV/TiO₂-D (20 nm, 8%).

larger as the content of SiO₂ increased. This variation suggests that SiO₂ nanoparticles would reduce the conjugation lengths of PPV and the reduction becomes significantly important as the content of SiO₂ increases. Comparing samples having different nanoparticle sizes and a similar oxide concentration, we found that smaller nanoparticles induce larger blue-shift. It is possible that smaller nanoparticles would be easier to insert in polymer chains, producing a greater hindrance, i.e., reduce the conjugation chain lengths.

For the PPV/TiO₂ nanocomposites, the UV-vis absorption peaks were distributed in the range from 429 to 426 nm. The blue-shift was less important in this case. TiO₂ nanoparticles apparently have no effect on the conjugation of PPV. This result is in agreement with that obtained by Zhang et al. [17] who found the absorption of PPV in the nanocomposites was not perturbed by the presence of the TiO₂ nanoparticles, even when using a TiO₂ content of 50% in weight ratio. The UV absorption λ_{max} of all PPV nanocomposites was summarized in Table 1.

3.2. FT-IR spectra

Fig. 2 shows Fourier transform infrared (FT-IR) spectra of PPV and the nanocomposites. All spectra showed the bands at 3023 cm⁻¹ (C–H stretching of benzene rings), 1517 cm⁻¹ (C–C ring stretching), 962 cm⁻¹ (*trans*-vinylene C–H out-of-plane bending) and 836 cm⁻¹ (*p*-phenylene C–H out-of-plane bending). For PPV/SiO₂ nanocomposites, the band centered at 3450 cm⁻¹ corresponds to O–H stretching of Si–OH; the bands at 1107 and 794 cm⁻¹ were assigned to Si–O–Si asymmetric and symmetric vibrations, respectively [18].

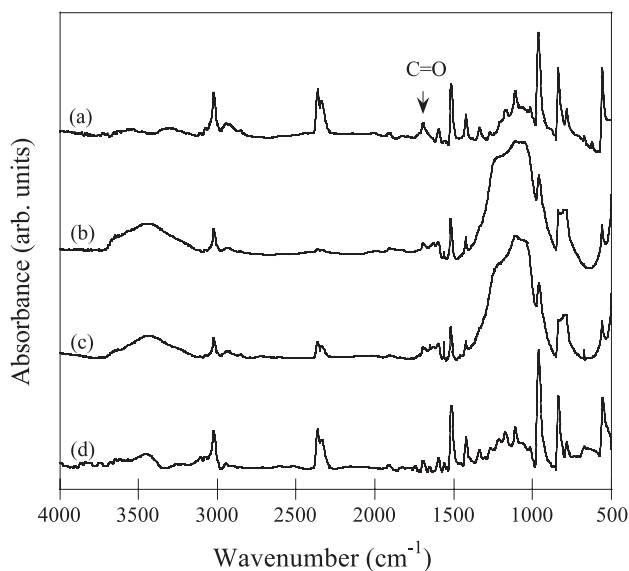


Fig. 2. FT-IR spectra of PPV and nanocomposites: (a) PPV; (b) PPV/SiO₂-B (100 nm, 2%); (c) PPV/SiO₂-F (20 nm, 2%); (d) PPV/TiO₂-B (20 nm, 2%).

For the PPV/TiO₂ nanocomposites, one additional band was found at 3445 cm⁻¹, which was assigned to O–H stretching of Ti–OH. Zhang et al. [17] claimed that they observed two additional bands at 1623 and 1105 cm⁻¹, which were assigned to the Ti–O and Ti–O–C stretching mode. They concluded that a Ti organic compound was formed and could result in the alignment structure of TiO₂ particles. We also found a small band at 1107 cm⁻¹, which can be assigned to the Ti–O–C stretching mode, but it is not obvious that an alignment of TiO₂ particles has occurred in the films. Besides, we notice that the band at 1693 cm⁻¹ was decreased. This band is related to the carbonyl group C=O formed during the thermal conversion [19]. The decrease in intensity of this band indicates that the presence of TiO₂ nanoparticles would prevent the oxidation of PPV chains and the composites would be more stable than the polymer. The spectra obtained in PPV/SiO₂ nanocomposites are similar to those of PPV/TiO₂ samples but the effect is smaller.

3.3. Raman spectra

Fig. 3 shows Raman spectra of PPV and some nanocomposites. According to Damlin et al. [20], the band at 1171 cm⁻¹ was assigned to mixtures of the C–C stretching and C–H in-plane-bending vibration. The two bands at 1327 and 1625 cm⁻¹ were from the C=O double bond vibrations, the first one corresponding to the benzene ring and the other being characteristic of the vinyl group stretching vibration. The two bands at 1547 and 1583 cm⁻¹ were assigned to the ring modes in the Wilson notation. The Raman spectra of PPV/SiO₂ nanocomposites were similar to the one of pure PPV film, with the exception of the triplet between 1500 and 1700 cm⁻¹. The intensity of the band at 1547 cm⁻¹ is weaker than the one at 1625 cm⁻¹. All the PPV nanocomposites with SiO₂ nanoparticles (100 and 20 nm) exhibit similar features in the Raman spectra.

According to the literature reported previously [21], the change in the dominant triplet near 1600 cm⁻¹ can be related to the conjugation length of PPV: when the conjugation length is reduced, the band at 1625 cm⁻¹ grows stronger than the one at 1548 cm⁻¹. We found the same results when PPV was blended with SiO₂ nanoparticles. Hence, the change observed in the composite films suggests that the presence of SiO₂ nanoparticles reduce the conjugation length of PPV chains. This is compatible with the observations of UV-vis absorption spectra, which showed a large blue-shift of about 20 nm.

The Raman spectra of PPV/TiO₂ nanocomposites are similar to the one of the pristine PPV film whatever the concentration used. The intensity of the band at 1547 cm⁻¹ is stronger than the one at 1625 cm⁻¹. This suggests that the presence of TiO₂ nanoparticles in the polymer films would not reduce the conjugation length of PPV chains. This is also compatible with the UV-vis absorption spectra obtained in these films, which show that the shift is not significant.

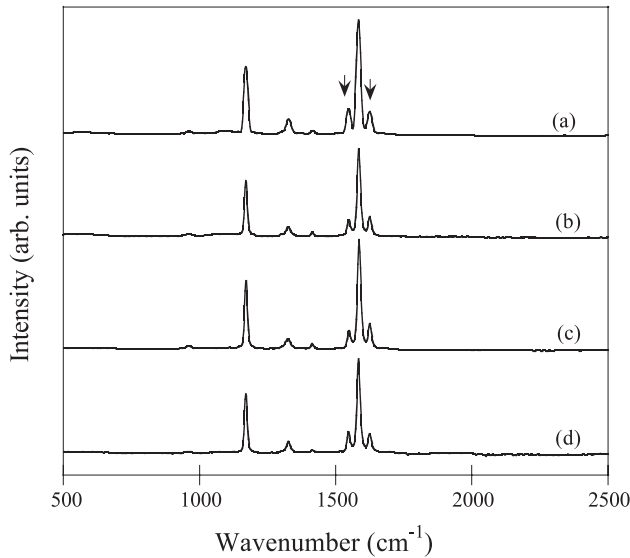


Fig. 3. Raman spectra of PPV and nanocomposites: (a) PPV; (b) PPV/SiO₂-B (100 nm, 2%); (c) PPV/SiO₂-F (20 nm, 2%); (d) PPV/TiO₂-B (20 nm, 2%).

We calculated the ratio of two peak heights (H_1 at 1548 cm^{-1} and H_2 at 1625 cm^{-1}), and we plot their ratio versus the concentration of the nanoparticles in Fig. 4. It can be seen that the peak ratio decreases as the concentration of SiO₂ nanoparticles increases. For samples containing TiO₂ nanoparticles, no noticeable variation of the peak ratio was observed with variation of concentration.

3.4. SEM observations

Fig. 5 shows the SEM images of some PPV nanocomposites. It can be seen that SiO₂ nanoparticles with diameter 100 nm form aggregated regions, while SiO₂ and TiO₂ nanoparticles with diameter 20 nm are dispersed more homogeneously. Zhang et al. [17] obtained similar images in

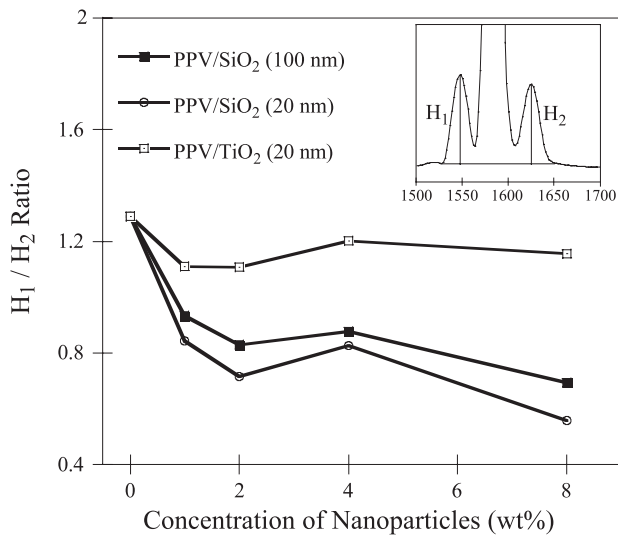


Fig. 4. Variation of the peak 1 (1548 cm^{-1})/peak 2 (1625 cm^{-1}) ratio as a function of the nanoparticle concentration.

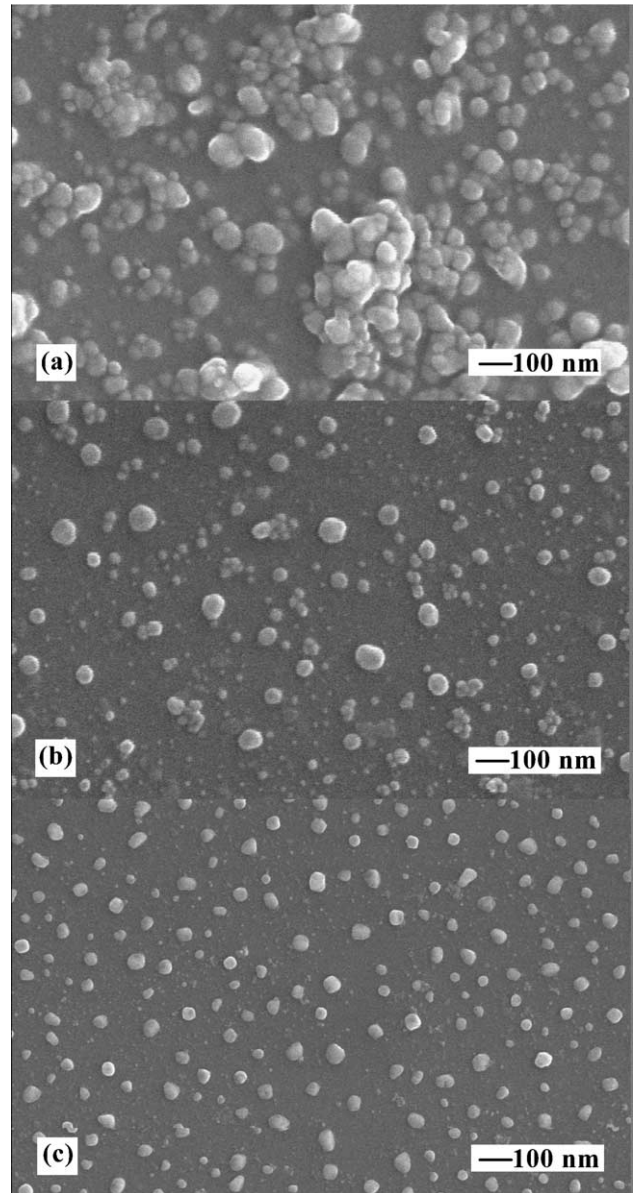


Fig. 5. SEM images of: (a) PPV/SiO₂-B (100 nm, 2%); (b) PPV/SiO₂-F (20 nm, 2%); (c) PPV/TiO₂-B (100 nm, 2%).

their composite films. They also found that TiO₂ nanoparticles would aggregate to form large packed regions of about 200 nm within the samples containing 40% TiO₂ nanoparticles.

3.5. Electrical characteristics of ITO–PPV composite–MgAg devices

Fig. 6 shows the current density versus the applied field for devices with different concentrations of PPV/SiO₂ and PPV/TiO₂ composites. In devices using PPV/SiO₂, we observe different behavior patterns, depending on the particle sizes. For small size particles, the conductivity of the composite decreases with the increasing concentration, while for larger size, it increases with the concentration.

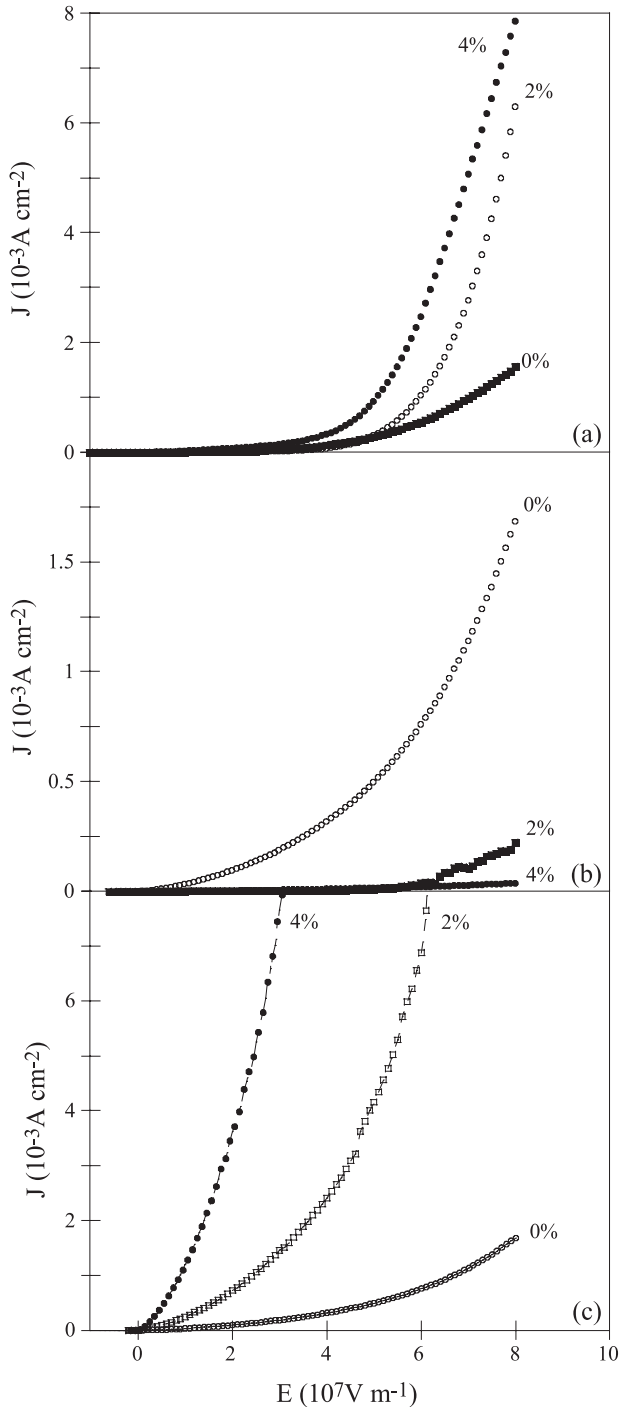


Fig. 6. Current density vs. applied field in diodes with different nanoparticle concentrations: (a) ITO-PPV/SiO₂ (100 nm)-MgAg; (b) ITO-PPV/SiO₂ (20 nm)-MgAg; (c) ITO-PPV/TiO₂ (20 nm)-MgAg.

This observation is partially in agreement with the results previously reported [12,22] on similar systems. In fact, following the results reported in Ref. [12], the current intensity in diodes using PPV/SiO₂ composites was lower than that obtained in PPV with an identical diode structure. The oxide particle size was about 5 nm in the work of Ho and Friend [12] while it was not mentioned in the work of

Chang and Whang [22]. The change in the electrical properties of the polymer was interpreted as a consequence of the disorder introduced by the nanoparticles that in turn hinders the carrier transport, leading to a decrease in the carrier (hole) mobility. It should be noticed that in these composites, optical measurements indicated a reduction of the conjugation length, which became more important with the increasing concentration of nanoparticles. We did obtain very similar results in composites using small diameter particles (20 nm) both in optical and electrical experiments. However, with larger particles (100 nm), the behavior of the composite films is different. Despite a decrease in the conjugation length (less important than that observed in composites using small size particles), the current intensity was found to increase with the concentration. This behavior was already observed in different PPV derivatives containing SiO₂ nanoparticles [12,23]. The size of the particles used in these works was 30–80 nm [12] and 7 nm [23]. In the work of Carter et al. [11], the enhancement of the conductivity observed in composites was explained by the change in the morphology of the film. Indeed, they argued that the rough interface caused by the presence of the particles would enhance the contact surface between the electrode and the active layer and increase the carrier injection. Given the size of the nanoparticles and the thickness of the films (110 nm), this would be likely to occur. Conversely, the particle size used in the work of Blom et al. [23] was much smaller and such an explanation would not hold when considering the thickness of the samples (200 nm). By calculating the effective thickness L_{eff} of the space charge width, presumed to develop in such devices, the authors found that this thickness could be reduced by half in the studied composite films. Besides this effect, the mobility of the charge carriers was found to be practically unchanged in composites. Therefore, modifications of the morphology of the polymer induced by the particles would be the main factor for causing the increase of its conductivity. The results we obtained in samples using 100-nm particles would be in agreement with these works.

Turning to the PPV/TiO₂ composites, the fact that the PPV conjugation length was not changed by incorporation of the particles suggests that the transport of carriers along the polymer chain would not be affected by the oxide. In addition, using identical particle size, we obtained an increase of the conductivity in the case of TiO₂ and a decrease in the case of SiO₂. This difference suggests that the change in the morphology of the polymer film at the interface is not the only factor in the enhancement of the current. We note that previous studies in polymer/TiO₂ composites reported contradictory results on the conductivity of these materials. For instance, polyaniline/TiO₂ (80–100 nm) composites show a decrease of the conductivity due to the reduction of the chain length [24]. In contrast, composites made with poly(phenylimino 1,4-phenylene 1,2-ethenylene 2,5-dioctyloxy 1,4-phenylene 1,2-

ethylenylene-1,4-phenylene) and TiO₂ (10–20 nm) exhibit an increase in conductivity with the oxide concentrations [25]. This behavior was supposed to be induced by the formation of a conducting pathway formed by a percolative network of nanoparticles. This process may be possible in PPV/TiO₂ composites but cannot explain the behavior of PPV/SiO₂ systems. Therefore, the nature of the oxide should be considered in the modification of the conductivity of PPV films upon incorporation of the nanoparticles. Study of optical properties of PPV/oxide composites has shown that the nature of the particles modifies the luminescence of the composites by the change in the polarization component of the carrier and exciton energy in the vicinity of the particles [26]. This effect is supposed to be due to the dielectric permittivity of the inclusion. Such a change in the contact region between the particles and the polymer may also influence the charge carrier movement from the polymer to the particles, resulting in a change of the overall conductivity of the composite. In fact, the added particles probably contain Lewis acid groups on their surface (OH groups), which would promote surface conducting pathway by interactions with the polymer chains [27]. Comparing the Lewis acidities of TiO₂ and SiO₂, it is expected that the charge carrier transport would be more favorable in PPV–TiO₂ composites than in PPV–SiO₂ ones as proved for ionic transport in nanocomposite polymer electrolytes [27]. This facility combined possibly with the formation of conducting pathway by the nanoparticles could explain the increase of the conductivity of the PPV–TiO₂ composites with increasing TiO₂. In contrast, the transport being lower at the polymer/SiO₂ interface, increasing the particle concentration would result in a decrease of the conductivity because of the increase of the nonconducting pathway. During the preparation of the (precursor + nanocomposite particles) solutions, we observed that the TiO₂ particles tend to settle quickly, while those of SiO₂ of similar size take a longer time. This can be explained by the difference in density of the materials (4.2 for TiO₂ and 2.6 for SiO₂). When the films were deposited, TiO₂ particles would be more accumulated near the ITO layer than SiO₂ particles, enhancing the surface contact and favoring the charge injection from the anode. However, a further study using different dielectric particles is needed to fully understand the role of the surface interactions between the polymer and the inclusions in the change of their conductivity.

4. Conclusion

In this work, we have investigated composites made by incorporation of SiO₂ and TiO₂ nanoparticles into PPV. Using different optical techniques, we have observed that SiO₂ nanoparticles reduce the conjugation lengths of the polymer, the reduction being more significant with increasing concentration or decreasing particle size. The incorporation of TiO₂ nanoparticles in PPV did not significantly

affect the structure of the polymer, and in contrast, seems to stabilize it by reducing the formation of carbonyl groups. The conductivity of the composites was also measured and showed different variation tendencies depending on the nature and the size of the particles used. Several factors can influence the charge injection into the polymer and their movements inside the composites: morphology of the contact between the film and the electrode, dielectric and chemical properties of the particles, and the rupture of the polymer chain length. The use of different kinds of dielectric materials of various sizes and the use of other polymer host matrices would be necessary to fully understand the role of the nanoparticles in these composites.

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