Study of the effect of DMSO concentration on the thickness of the PSS insulating barrier in PEDOT:PSS thin films

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ABSTRACT

One of the most used secondary dopants in thin film processing of PEDOT:PSS is dimethyl sulfoxide (DMSO). In this work, we present results that explain, from the point of view of impedance spectroscopy, the mechanism of the increase in the conductivity observed on films based on PEDOT:PSS. The results obtained with this technique, combined with others such as AFM, and Raman and UV–vis–NIR spectroscopies, clearly show that there is a thinning of the insulating barrier of PSS surrounding conductive grains of PEDOT. It is shown that the thickness of the insulating barrier is related strongly and inversely with the onset frequency of AC conductivity. However, this is not the only existing effect, because for values beyond the optimal concentration of DMSO, we observe a decrease in the conductivity related with an increase of the separation of the PEDOT grains. The AC measurements and the AFM images also show the clear interplay between the increase of the PEDOT average grain size and the separation between them.

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1. Introduction

Currently, one of the most promising conductive polymers is poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonate), abbreviated as PEDOT:PSS. The reason for its technological and industrial importance lies in its ease of processing, high stability and transparency [1,2] compared with some other polymers, and so on. For these characteristics, it is considered as a promising material for replacing inorganic conductors on plastic electronics applications such as OLEDs, flexible photovoltaic devices, memories, and sensors. However, PEDOT:PSS thin films have a disadvantage: their low conductivity compared to indium-tin oxide (ITO) and other conductive polymers. Chemically, this problem has been addressed during the polymerization process [3], but from the point of view of physical synthesis, i.e., the combination of two or more components to form a connected whole without a change in chemical structure of these components, this issue has been partially resolved with the so-called secondary doping (i.e., increasing the conductivity by adding a variety of compounds in the aqueous dispersion of PEDOT:PSS) [4–17], UV radiation [18], films prepared under different drying conditions [19], etc., thus increasing the conductivity by several orders of magnitude. Despite the large number of publications related with the mechanism of conductivity enhancement caused by secondary doping, there is still controversy about the responsible mechanism of this enhancement and several explanations have been proposed [9–17] such as the secondary doping produces a conformational change of PEDOT chains in the films [12] or that their effect is to induce the segregation of the excess PSS [13–17].

In this paper, we present a study of the effects of dimethyl sulfoxide (DMSO) loading on the electrical and optical properties of PEDOT:PSS thin films. The films have been prepared under different baking temperatures, atmospheres and different concentrations of the secondary doping in order to study how the conductivity depends on these variables. We have found that the films baked in air, for a given doping concentration, showed the maximum conductivities, in contrast with previous reports [19]. These films have been characterized by using several techniques such as AFM, and Raman, UV–vis–NIR and impedance spectroscopies (IS). Our results show that the mechanism responsible for the increase in the conductivity is related with the partial phase separation of the excess PSS. Therefore the insulation of conducting PEDOT:PSS domains is reduced [13–17]. In addition, Nardes et al. [17] have shown that this enhancement in the conductivity is due to a transition from 3D variable range hopping (3D-VRH) to quasi-1D VRH.

As is well known, the impedance spectroscopy (IS) is a technique that allows to obtain information about the material under study

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through electrical models, which leads to acquire a complete picture of various physical phenomena occurring in the sample under different conditions. Thus, AC characterization enables to distinguishing individual contributions produced by different processes or elements present in the material, as grains, grain boundaries, sample–electrode interfaces, defects, charge transport, etc. [20]. Moreover, this technique has been used to characterize the mechanisms of charge transport in several conductor polymers such as polypyrrole [21–24] and PEDOT [10,25,26]. In the case of PEDOT, IS has been used to determine the limitations on the conduction of two kinds of PEDOT:PSS films made with two different aqueous dispersions, Baytron P and PH510 from HC Stark, which have very different average grain sizes, 40 nm and 100 nm, respectively [10]. The films with bigger PEDOT average grain sizes present better conductivities and their limitations on conduction arise from the intrinsic disorder in the PEDOT grains and not from the insulating PSS barriers. In this work, using IS, we have studied the effect of the secondary doping concentration on the thickness of the insulating PSS barrier and/or the degradation of the PEDOT:PSS thin films (Baytron P). In addition, we show that there are two determining factors in the conductivity enhancement, namely, the grain growth and an optimal average grain size in PEDOT. A great increase of the PEDOT average grain size has as consequence a longer separation between them. This is similar to that reported in organic solar cells, where it has been shown that an abrupt phase separation is, in general, unfavorable for high efficiency photovoltaic devices [27,28].

2. Experimental

The PEDOT:PSS (Baytron P V4071, HC Stark) blends were prepared with different concentrations by weight of dimethyl sulfoxide (DMSO, Sigma–Aldrich). The mixture of DMSO and PEDOT:PSS was adjusted, in a ratio by weight of 1:25, 1:15, 1:10, 1:5, 1:4, 1:3, 1:1, to give final solutions of 3.85%, 6.25%, 9.09%, 16.67%, 20%, 25%, 50% and 66.67% by weight of DMSO, respectively. The resulting solutions were stirred for 30 min at room temperature in sealed vials and filtered using nylon filters (1 μm). The thin films were deposited by spin coating technique on square substrates of Dow corning glass with length of 2.5 cm, which were previously cleaned in an ultrasonic bath with acetone, methanol and isopropyl alcohol by 20 min in each solvent, and finally the substrates were subjected to UV radiation. The spin-coated samples were baked for 15 min at 95 °C in air, N_2 atmosphere or vacuum (21 in Hg). The conductivities of the PEDOT:PSS films were obtained with four-point probe measurements, using a Keithley 2010 digital multimeter and a Keithley 238 Source Measure Unit, after the cooling of these samples. The conductivities obtained were confirmed with impedance spectroscopy results. The PEDOT:PSS pristine films showed conductivities of ~0.07 S/cm, which are similar to the specifications in the data sheet given by the supplier. To determine the film thickness, six measurements per sample were made with a profiler (Tencor Instruments, Inc.), distributed over the full sample to exclude local thickness variations. The transmittance spectra of the as-deposited films were measured at room conditions using an UV–vis–NIR Varian Cary 5E spectrophotometer. The impedance measurements were obtained using an impedance analyzer (Solartron impedance/gain phase analyzer 1260) with sinusoidal perturbation amplitude of 20 mV over a frequency range 10–3.2×10^7 Hz. Two gold electrodes were deposited on a sample of 1 cm × 1 cm by sputtering in coplanar geometry. The dimensions of electrodes were 1 mm × 8 mm and the spacing between them was 5 mm.
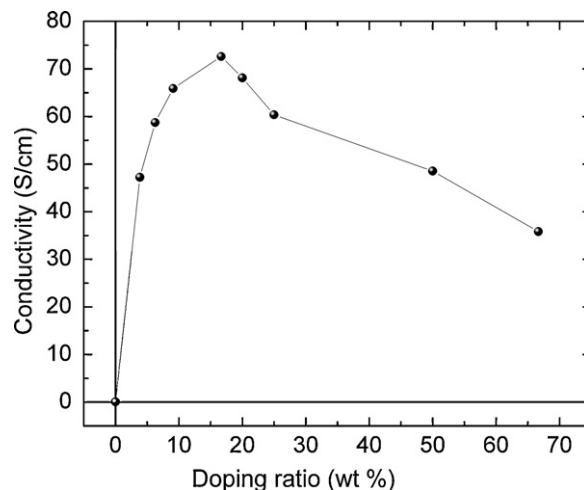
Fig. 1. Conductivity of thin films as a function of the amount of DMSO added in the aqueous dispersion of PEDOT:PSS. Thin films were baked in air. Note that the optimal concentration corresponds to one molecule of DMSO per three monomers by weight, approximately.

3. Results and discussion

The effect of DMSO in the PEDOT:PSS thin films baked in an atmosphere of air was first studied by DC conductivity measurements at room conditions with the four-point probe technique. Fig. 1 shows these results to various concentrations of DMSO in the aqueous dispersion. We can observe that the conductivity increases rapidly as a function of DMSO concentration up to a maximum value, which corresponds to the optimal DMSO/PEDOT:PSS ratio of 1:5 by weight comparable to a concentration of around 17 wt% of DMSO, and then, decreases gradually. Note that other groups have observed this behavior [13,29]. Hereof has arisen some reports indicating that the mechanisms responsible of the increase in the conductivity are related with the increase of the grain average size of the PEDOT particle as well as the decrease of the PSS insulating barrier between PEDOT grains [13–17]. Note that at this concentration the conductivity increases by more than three orders of magnitude, i.e., from 0.07 S/cm to 73 S/cm for thin films with 0 wt% and ~17 wt% of DMSO, i.e., a ratio of DMSO to PEDOT:PSS of 0 and 1:5, respectively. On the other hand, after the optimal concentration a gradual decrease in the conductivity is observed. This latter is an evidence that when we increase the DMSO concentration there arises an additional mechanism, which is related with the obstruction of the electronic charge transport through the material. Therefore after the optimal loading, there are two mechanisms present in the films: one that increases and another that hinders the charge transport. However, the conductivities even at very high DMSO dopings are higher than the conductivity of the pristine PEDOT:PSS films. Finally, our reported conductivities are independent of the thickness of the films, with thicknesses ranging from 30 nm to 100 nm.

In order to study the effect on the conductivity by using different processing methods on PEDOT:PSS films, we have considered different baking temperatures and atmospheres. In this manner, the baking was realized in two additional situations: baking in an N_2 atmosphere and in vacuum for the most conductive film obtained previously. As is shown in Fig. 2, the conductivity of films with ~17 wt% of DMSO baked in atmosphere of air remains almost unchanged, with a little variation of 3 S/cm. In this way, we observe that the conductivity of the films does not depend on baking temperature. From our experiments under N_2 or vacuum atmosphere, we note that the conductivity of DMSO/PEDOT:PSS thin films decreases from 13% to 40% compared with those obtained
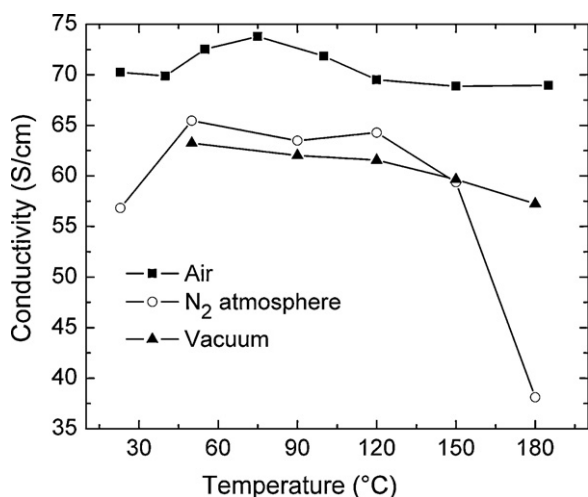
Fig. 2. Conductivity in of thin films as a function of baking temperature in different atmospheres, using 1:5 DMSO/PEDOT:PSS ratio by weight.

in air. Therefore, in this work we only focus to study the properties of films baked in air. Moreover, we observe that the air does not degrade the films with DMSO and, the conductivity is independent of the baking temperature, at least for room conditions, in contrast with previous reports [19]. These results suggest that oxygen plays a major role in increasing the conductivity via the high dipole moment of DMSO and that oxygen could be incorporated into the grain boundaries of PEDOT:PSS as defects, producing additional ways to charge transport, however, more studies are necessary.

Fig. 3 shows the transmittance spectra of the PEDOT films doped with different DMSO/PEDOT:PSS ratios. Despite the increase in the conductivity, the transparency of thin films is not affected adversely. We observed no bands or other extra features, besides the difference in transparency caused by changes in thickness of the films. From this, we can affirm that there is no change in the number of polaron and/or bipolarons present in the material, namely, that the mechanism producing the increase in conductivity is not due to the creation or modification in the number of charge carriers, but the increase in the mobility of these charge carriers, as has been suggested previously by other groups [30]. The next step in our study was to characterize the thin films for Raman spectroscopy (not shown) and, unlike those reported by other authors [12,18], we did not observe any change in the Raman spectra of thin
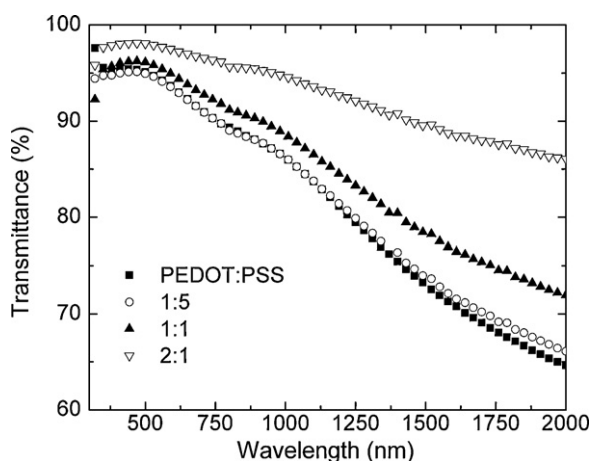

Fig. 3. Transmittance spectra of PEDOT:PSS films with different secondary doping ratios. Thin films were baked at 95 °C in an air atmosphere.

films even under several conditions, such as the addition of other secondary dopants (for example, ethylene glycol and dimethylformamide), UV radiation and different baking temperatures at several atmospheres. Then, we suggest that the mechanism that causes the increase in the conductivity, at least in our case, is not related with a conformational change in the polymer chain, from aromatic to quinoid structure, as has been previously suggested. Crispin et al. [13] and Gravalidis et al. [11] have also reached this same conclusion using techniques like X-ray diffraction and spectroscopic ellipsometry, respectively, for films treated with secondary dopants.

On the other hand, the morphology of thin films changes with increasing the amount of DMSO (Fig. 4). The morphology of these films becomes granular and, clearly, the topographic images show the formation of domains or grains that grow in size as a function of the DMSO concentration. These grains have been related with PEDOT rich nanoparticles by several authors [15,17]. In addition, the average roughness of the PEDOT:PSS films increases when we increase the secondary doping in the processing of the films. The increasing in the film roughness is an alternative way of verifying the growth of PEDOT rich grains [31]. Note that there are no regular domains, however our results of conductivity suggest the formation of favorable pathways in the films for all DMSO/PEDOT:PSS ratio studied in this work compared with the pristine PEDOT:PSS film. Relating the AFM images with the film conductivities shown in Fig. 1, it is observed that there is an optimal film morphology and, after this optimal DMSO doping (~17 wt% of DMSO), the conductivities begin to decrease. The increase of the conductivity up to the optimal DMSO loading is related with partial phase separation of the excess of the PSS and the increase of the PEDOT rich average grain size, which leads to the effective reduction of the PSS insulation barrier between the PEDOT grains [17]. Moreover, after the optimal DMSO loading, the continuous growth of the PEDOT grains as a function of the secondary doping has as consequence a longer average distance between the conductive grains and, therefore, a decreasing in the PEDOT conductivity.

Impedance spectroscopy is another technique very useful to correlate the film morphologies with the conductivity. This technique is able to distinguish different mechanisms in the material [20]. In Fig. 5 the conductivity as a function of frequency for the thin films with different contents of DMSO is shown. From figure we emphasize two features: first, that the conductivity obtained by IS is of the order of that obtained by the four-point probe technique, so we can rule out any effect associated with the contacts and, second, the existence of an inflexion point in the spectrum that depends directly on the conductivity and, therefore, on the amount of DMSO added to the PEDOT:PSS aqueous dispersion. The first feature is important because it allows us to consider as negligible interfacial effects or other effects (such as electrode polarization) associated with the contacts that could distort or mask the electrical properties of the material [32]. On the other hand, with respect to the second feature, we know that the high frequency dispersion is not caused by inhomogeneity in the thickness of the film, because by using PEDOT:PSS films with different thicknesses, IS curves were obtained with the onset frequency at the same value.

In regard to the second point, it is important to recall that the total measured electrical conductivity can be described as the sum of two contributions associated, a DC conductivity $\sigma(0)$ (or σ_{DC}) and an AC conductivity $A\omega^s$ as
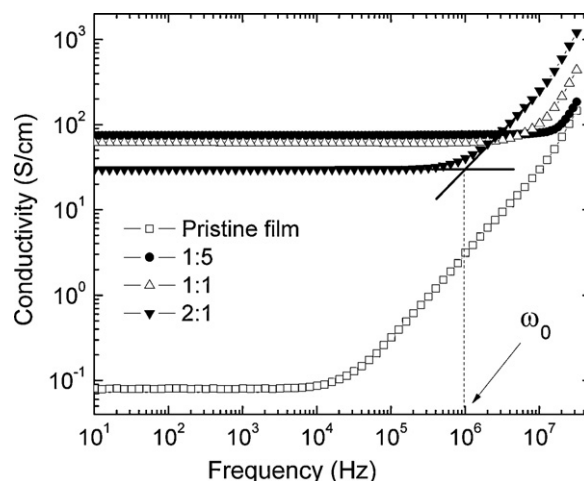
$$\sigma(\omega) = \sigma(0) + A\omega^s, \tag{1}$$

where A is a constant and $s < 1$. The fact that the conductivity can be described by Eq. (1) is one of the most important features in disordered materials and it has been derived from different hopping models to explain the AC response in these materials. As is well known, for materials where the charge transport is due to hopping,
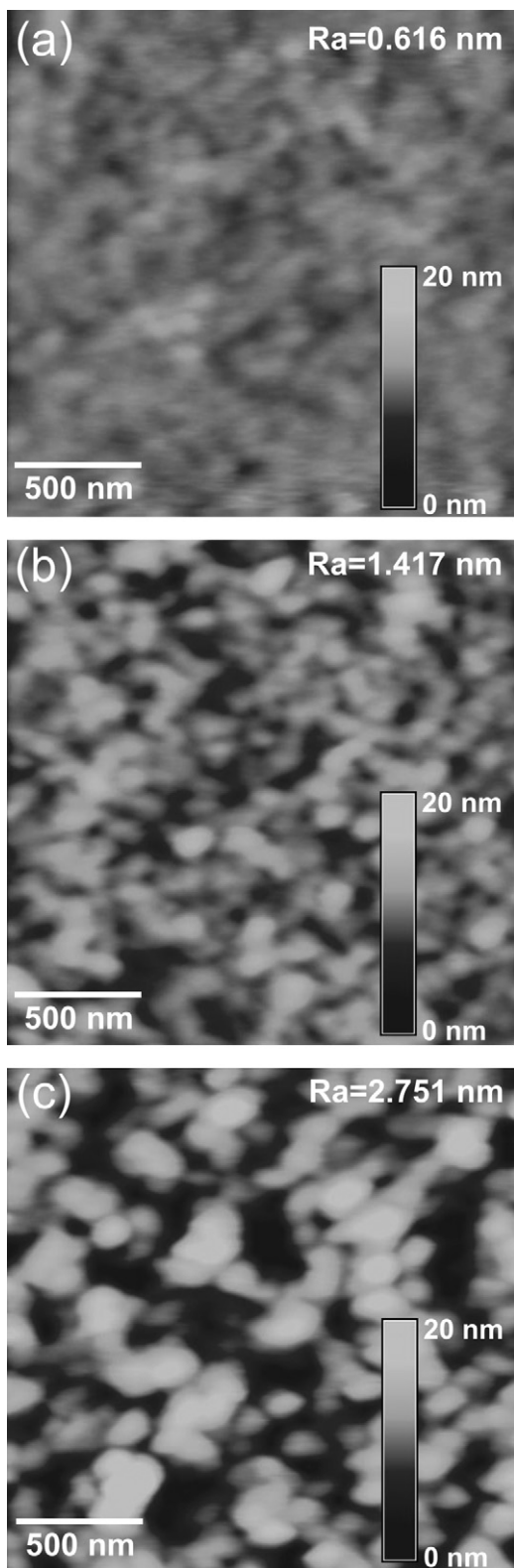
Fig. 4. Topographic images and roughnesses obtained by AFM for thin films at different DMSO/PEDOT:PSS ratios by weight. (a) 0 (PEDOT:PSS), (b) 1:5 and (c) 1:1. The images show the increase of the average grain size of particles as well as the roughness of the films with the DMSO loading in the aqueous dispersion of PEDOT:PSS.

Fig. 5. Frequency dependent AC conductivity for some of the thin films baked at 95 °C in air. The onset frequency ω_0 is obtained by the intersection of two straight lines, as is shown in the plot for thin film with a DMSO/PEDOT:PSS ratio of 2:1 by weight. Note that the onset frequency is proportional to the DC conductivity.

the conductivity at low frequencies is determined by overcoming the highest energy barriers between pair of localized states in the film for the formation of a percolation path. As is mentioned above, the onset of AC conductivity is proportional to the DC conductivity and this useful parameter characterizes the way in which are connected different conductive grains [33]. Furthermore, in disordered systems the correlation length ξ, which is associated with the distance between localized sites, can be associated inversely to the onset frequency (ω_0) [34]. Thus, we can conclude that the optimal concentration of DMSO produces smaller correlation length and shorter connections between PEDOT chains in the thin film. All this is evident from Fig. 5, because when we increase the amount of DMSO the conductivity and the onset frequency ω_0 also increase up to a value very close to the operating limit of the impedance analyzer (3.2×10^7 Hz). When DMSO is added beyond the optimal concentration, the position of inflexion point decreases, in similar way to the DC conductivity measured (see Fig. 1). With our results of impedance spectroscopy and AFM, we observe that the conductive grains continue to grow whereas the separation distances between them also increase, so that the second mechanism becomes dominant. In other words, the separation between the grains increases hindering the charge transport across insulating barriers. Finally, our results are in agreement with the available literature, i.e., the formation of a three dimensional network [35,36], bigger aggregates [17,36,37], conductive pathways and reorientation (but not a conformational change) of the PEDOT:PSS chains. These conductive pathways are formed by reducing the correlation length between conductive grains and are observed with impedance spectroscopy. Clearly, we can argue that the conductivity is highest when the frequency hopping is a maximum. This indicates that the system transports charge more efficiently and in less time when the DMSO forms favorable connections between PEDOT:PSS grains.

To compare the curves shown in Fig. 5, in Fig. 6 we plot their master curves, which are obtained by normalizing the total conductivity to their DC conductivity vs. ω/ω_0. Note that ω_0 is the frequency value where the conductivity begins to depend on the frequency. For our case, this frequency ω_0 was calculated using a method proposed previously [38], where ω_0 is obtained using the intersection point of two straight lines, one corresponding to DC conductivity and other related with AC conductivity (as we show in Fig. 5). However, it is possible to use another method [34]. As can be clearly observed, the curves corresponding to films with lower conductivities tend to the universality that applies to disordered materials ($s = 0.9$) whereas the films with higher conductivities do not fulfill this condition, giving an exponent $s > 1$. These last results are far from the universality because the obtained onset frequency is close to the operating limit of the equipment (3.2×10^7 Hz) and,
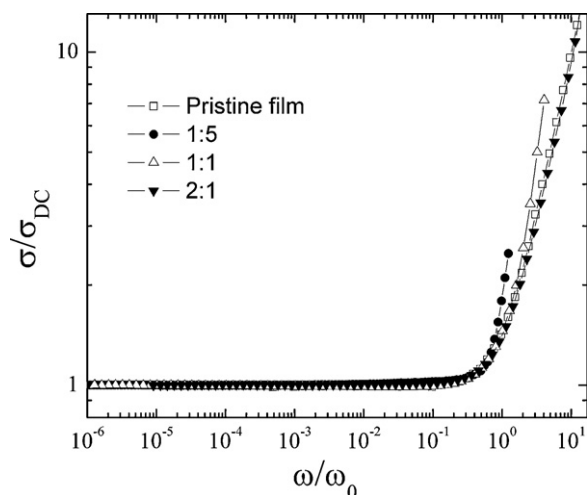
Fig. 6. Scaled conductivity (σ/σ_{DC}) vs. scaled frequency (ω/ω_0) for DMSO/PEDOT:PSS thin films baked at 95 °C in air.

in this region ($>1 \times 10^7$ Hz), the measurement error is $\geq 10\%$ [39]. Moreover, in the impedance complex plane, we observe the formation of one single semicircle for majority of measurements, except for the thin films with very high conductivity, which present distortions at all frequencies but especially to high frequencies. However, this does not change the fact that ω_0 can be directly related with the DC conductivity on the films and this with the amount of DMSO added.

On the other hand, it is well known that the conductivity of a material can be described by using the complex conductivity, $\sigma^*(\omega) = \sigma(\omega) + i\sigma''(\omega)$, or by the complex permittivity, $\varepsilon^*(\omega) = \varepsilon(\omega) - i\varepsilon''(\omega)$, which are related by the Kramers–Kronig relations in the following way:

$$\varepsilon(\omega) - \varepsilon_\infty = \frac{\sigma''(\omega)}{(\varepsilon_0 \omega)} \qquad \varepsilon''(\omega) = \frac{\sigma(\omega)}{(\varepsilon_0 \omega)}. \tag{2}$$

Both components of permittivity are shown in Fig. 7. From figure, we observe that there is a strong dispersion at low frequencies whereas it decreases when the frequency is increasing. This dispersion is higher for films with an optimum amount of DMSO and it is related to the conductivity of the films. This dispersion is not due to the existence of electrode polarization since, as has been shown by Hwang et al. [32], the effect of the electrodes can be excluded
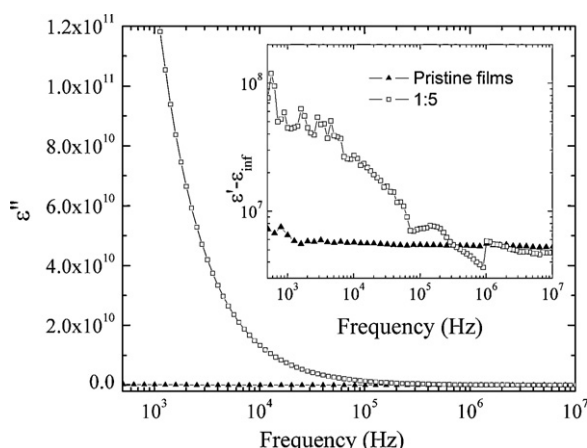
by comparison between the results of DC measurements and low-frequency AC measurements. Similar behaviors to those reported in Fig. 7, have been reported in the literature [40,41]. From these works, we conclude that the low-frequency dispersion, which is greater when the conductivity is higher, is related with an increase in both order and grain size of PEDOT domains in the films. It means that the higher value of imaginary part of permittivity at low frequency, for optimal concentration of DMSO in the thin films, is related with the enhancement of mobility of charge carriers.

4. Conclusion

Impedance spectroscopy has been used for studying the effect of the DMSO concentration in the PEDOT:PSS films. In this paper we present results using this powerful technique to explain the mechanism that enhances the conductivity, caused by the DMSO added in the aqueous dispersion of PEDOT:PSS. Our results clearly show that DMSO decreases the insulating barrier thickness of PSS between conducting grains up to an optimal value, as is observed by the increase of the onset frequency of AC conductivity in the impedance spectra. Moreover there exists another effect beyond the DMSO optimal concentration, not explained in adequate way in the literature, which is responsible of the decreasing of both, the conductivity and the onset frequency. This effect is caused by the increase in the separation between conducting grains when the grains increase its average size. In other words, there is an interplay between the size of conducting domains and the insulating barriers. All these effects are clearly observable in the AFM images, where we observe how the domains grow whereas the insulating barriers change in thickness. Moreover, we have shown that, in our case, there is not a conformational change in the PEDOT:PSS chains, but an enhancement in the mobility of charge carrier due to both the thinning of the PSS insulating barrier and the increase of the PEDOT conductive grains.

Fig. 7. Variation of imaginary part of permittivity with frequency for different PEDOT:PSS thin films at several DMSO concentrations by weight. In the inset we show the frequency-dependent dielectric constants for both films. Region with less noise is shown.

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