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ARTICLE

Comparative Study of the Conductivity Percolation Behaviour of Nanocomposite Thin Layers Made of Nanoparticulate ITO and Carbon Nanotubes Colloids

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Abstract: The electrical conductivity behaviour of two transparent conducting nanocomposite thin films made of nanoparticulate indium tin oxide (ITO) and carbon multiwall nanotubes (MWNTs) colloids deposited on a polycarbonate substrate was studied. The carbon MWNTs films exhibit a low critical threshold (0.083 vol. %) compared with that of the ITO films (0.19 vol. %). The surface morphology of the films shows stronger aggregation of the carbon MWNTs above the critical threshold. The elctrical conductivity obtained for the ITO films is 526 Sm^{-1}, which is larger than that obtained for the carbon MWNTs films (65 Sm^{-1}). The optical properties of ITO films show higher transmission in the visible range with a smaller transmission window than that of the carbon MWNTs. Both coatings show similar mechanical properties against abrasion with a very good adhesion on the plastic substrate.

Keywords: Colloid; Electrical conductivity; Thin films; ITO nanoparticles; Carbon nanotubes.
PACS: 81.20.FW

Introduction

The electric conducting percolation behaviour in nanocomposite systems composed of mixtures of conducting and insulating species have gained an increasing interest due to their applications in thin film technology, e.g. for electromagnetic shielding, antistatic purposes and corrosion protection [1-5]. The electrical properties of such systems depend on the dispersion of the conducting fillers, their size and aggregate structure formed in the host insulating matrix [6-8]. These systems have poor electrical conductivity below a certain volume fraction of the conducting filler defined as the critical threshold, where there are no contacts between adjacent filler particles. Above the critical threshold, agglomerates are grown to reach a size which makes it possible for them to touch each other resulting in a formation of a conductive network within the insulating phase. To understand the network formation, there are many so-called percolation models. A review on various models was given by Lux [9] and Clerc *et al.* [10].

Coating plastic substrates of functional layers is the aim of many researchers. In most applications, the layers must possess a combination of mechanical, electrical and optical properties as well. For example, low electrical conductivity (~ 10^{-4} Sm^{-1}) to dissipate static charge build up is necessary besides high electrical transparency and good mechanical durability. However, because of their poor thermal stability, the deposition techniques available to coat such substrates are therefore limited. So, the route to get transparent conductive coatings on plastics is to use composites that can be fully treated at relatively low temperatures (T < 200 °C). The most used materials are conductive fillers

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dispersed in an inorganic-organic matrix. Among the most important conducting materials, there are n-type oxide semiconductors (TCO) such as indium tin oxide (ITO) and fluorine or antimony doped tin dioxide (FTO, ATO) [8]. In_2O_3:Sn (ITO) has attracted the highest attention for its high conductivity though the relatively high price often limits its use. Conjugated polymers, such as polyaniline and polypyrrole, are among the best conducting polymers which are widely used as transparent conducting films [11, 12]. Carbon nanotubes are very interesting materials which drive remarkable scientific researches including chemistry, electronic transport, mechanical and field emission properties. The use of carbon nanotubes to impart electrical conductivity while maintaining high optical transparency is nowadays possible [13-15]. They have potential applications as catalyst supports, as cathodes in field emission displays and as electrodes [16]. The unique quality of this form of carbon is simple in that the individual particles possess the attributes of high electrical conductivity and high aspect ratio combined with a unique capability of forming ropes of individual particles. The combination of all these properties allows the formation of conductive networks through the materials with tunable electrical resistivity and good transparency.

In this work, a comparative study between tin doped indium oxide (ITO) nanoparticles and carbon multiwall nanotubes as conductive fillers dispersed in an inorganic-organic matrix and deposited on a plastic substrate at low temperature was conducted. The optical and mechanical properties of both systems are also given.

Experimental

Two coating sols were prepared to be deposited onto a polycarbonate (PC) substrate. The first one is alcoholic colloid based on crystalline ITO nanoparticles having an average crystallite size of 25 nm (cubic In_2O_3 cubic structure). ITO paste of 75 vol. % solid content was added to a Glycidoxypropyltrimethoxysilane (GPTS) under hydrolysis. The obtained sol was diluted with 1-Propanol in an ultrasonic bath. The loading ratio of ITO nanoparticles to the GPTS matrix was adjusted between 0.05 and 0.9 vol. %.

The second coating sol was an aqueous suspension containing carbon MWNTs from Nanocyl S.A as conducting filler with a solid content up to 10 mg / ml. The suspension was dispersed using a dispersion agent called hexaadecyl trimethyl ammonium chloride (HDTAC, Fluka, 98%) in doubly distilled water by mixing them under stirring in an ultrasonic bath, then supplied to a microfluidizer and pumped under 1700 bar pressure for 10 min. The obtained suspension was then added to the GPTS under hydrolysis to provide a range of carbon MWNTs loading from 0.05 to 0.6 volume fraction.

Both sols were filtered and then deposited on 3 mm thick PC substrates using the spin coating techniques with a spinning speed of 2000 rpm. The wet layers were dried for 10 min at 40 °C and then heated in an oven for 30 min at a temperature of 130°C.

The electrical properties of the films were characterized by measuring the sheet resistance (R) using a contactless non-destructive system from Lehighton Electronics, Inc. The electrical resistivity (ρ) of the films was determined by $\rho = R \times t$, where t is the thickness of the films, measured with a Tencor P-10 surface profilometer. The electrical conductivity (σ) is the reciprocal of ρ.

For the analysis of the surface morphology, a White Light Interferometer (WLI) from Zygo New View 500 and SEM (JEOL 6400) were used.

Concerning optical characteristics, a CARY 5E UV-VIS-NIR spectrophotometer (Varian) was used to measure the transmission of the coatings, using air as reference.

Finally, the mechanical properties as adhesion and mechanical durability of the films were tested following standard procedures [17-19].

Results and Discussion

The electrical conductivity behaviour of coatings deposited on PC substrates using spin coating method and heated at 130 °C for 30 min as a function of the loading ratio of the conducting fillers is shown for ITO nanoparticulate films (Fig. 1) and for carbon MWNTs films (Fig. 2). The maximum available loading ratio of carbon MWNTs was 0.6, as it was difficult to disperse more fillers in the colloid, because of the strong aggregation forming an unstable sol. In both layers, low electrical conductivity is observed at a small loading ratio which increases sharply at a certain loading ratio. However, it is observed that for carbon MWNTs films (Fig. 2) the increase of conductivity is sharper. At a higher loading ratio, the electrical conductivity increases smoothly and reaches a maximum value of (526 Sm^{-1}) for ITO nanoparticulate films and (65 Sm^{-1}) for carbon MWNTs films. This can be explained as a result of the higher content of the conductive filler which is avaliable in the ITO based film.

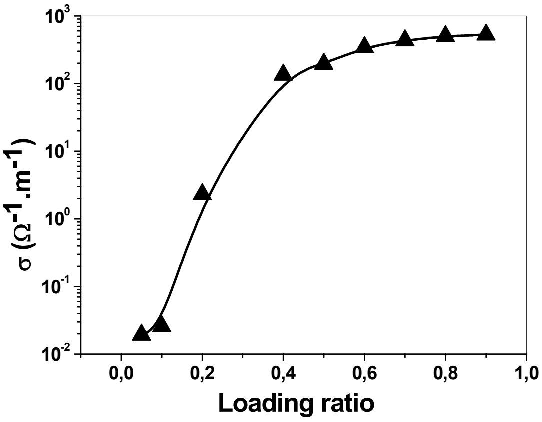


FIG. 1. The electrical conductivity of ITO based coatigs onto a PC substrate as a function of the loading ratio of the ITO nanoparticles.

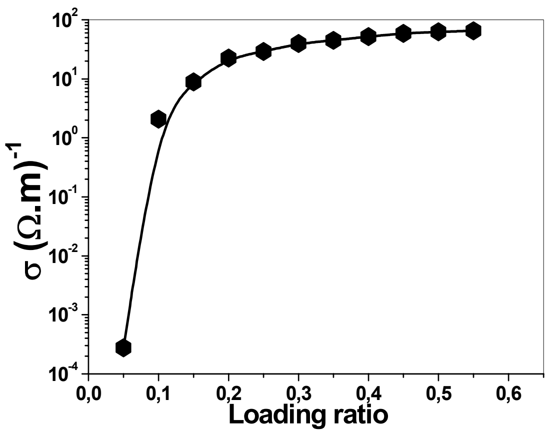


FIG. 2. The electrical conductivity of carbon MWNTs based coatings onto a PC substrate as a function of the loading ratio of the carbon MWNTs.

The electrical conductivity of the nanocomposite coatings was described by the classical percolation model, as

$$\sigma = \sigma_0 \, (V - V_c)^s$$

where σ is the direct electrical conductivity, σ_0 is the proportionality constant which represents the intrinsic electrical conductivity of the conductive filler, V is the conductive filler volume fraction, V_c is the percolation threshold at which the conductivity of the composite starts to increase sharply and s is the critical conductivity exponent.

To check if the composite conductivity follows the previous power law, a log-log plot of the electrical conductivity σ and V-V_c is drawn as shown in Figs. 3 and 4. Fig. 3 shows that the data for ITO nanoparticulate films would fit very well the power law. The threshold percolation loading ratio (V_c) which gives the best linear fit is 0.19. The s value is determined as the slope of the least square fit line which is found to be 1.3. Compared with the system of the carbon MWNTs, a well fit of the experimental data is found, however with much lower percolation threshold of 0.083. The high aggregation of carbon nanotubes and their ability of forming ropes due to the van der Waal forces may explain the lower percolation threshold of the nanotubes system compared with that of the nanoparticulate system. It is observed that the nature of the conducting filler and the microstructure have a strong influence on the percolation threshold. The s value is found to be 1.2, which is close to the value found for the ITO nanoparticulate system. The exponent s measures the power of the conductivity increase above V_c.

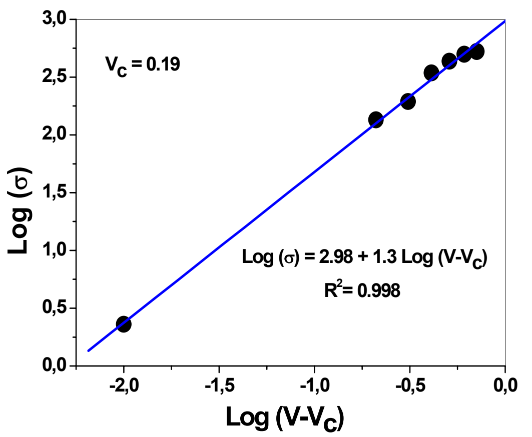


FIG. 3. Log-log graph of the conductivity and V-V_c for ITO based layers.

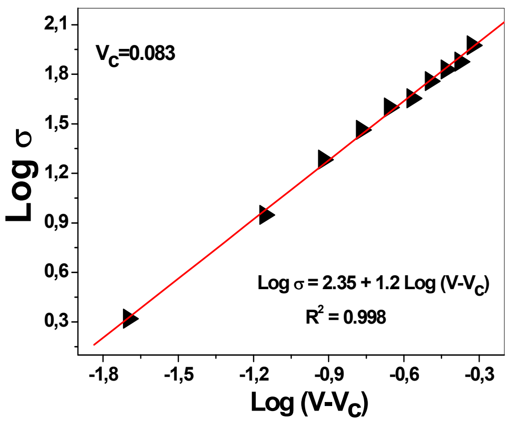
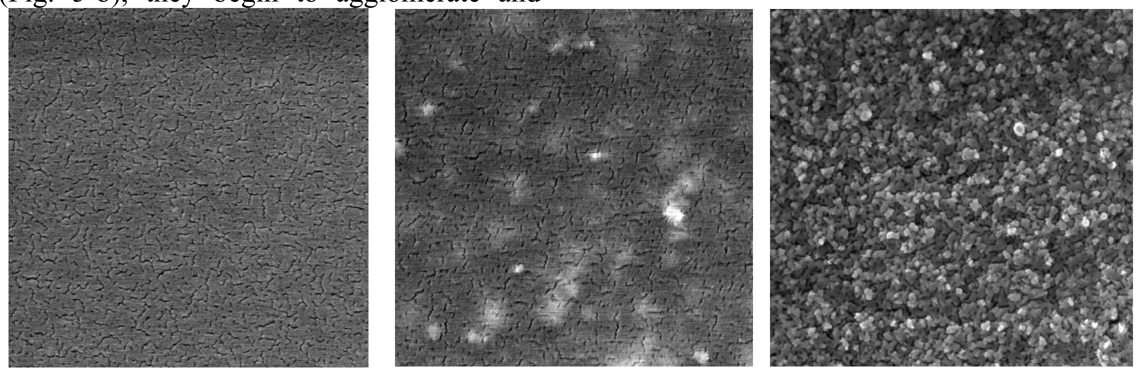


FIG. 4. Log-log graph fort the conductivity and V-V_c for MWNTs layers.

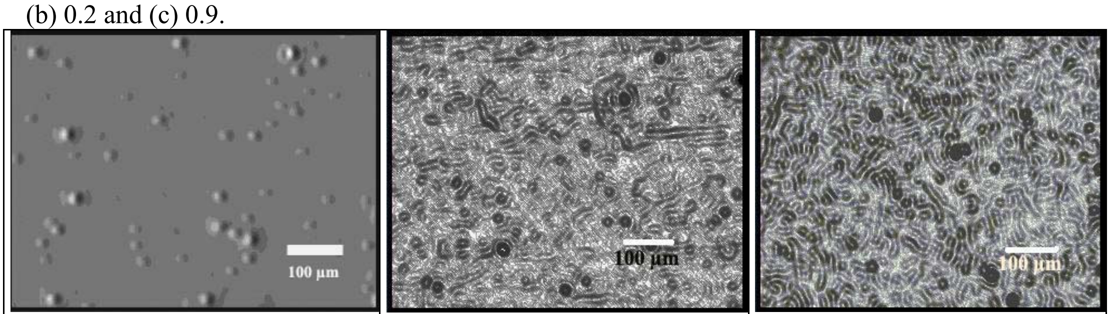
The explanation for such behaviour is attributed to the contact between the adjacent conductive fillers. Fig. 5 shows SEM micrograph of surface morphology of the ITO nanocomposite layers deposited on a PC substrate with different loading ratios. In the region of $V_c < 0.19$ (Fig. 5-a), a tiny segregated cluster is observed, as there are no contacts between the nanoparticles which are distributed separately within the host insulating matrix. By rising the nanoparticles concentration above the threshold percolation (Fig. 5-b), they begin to agglomerate and touch each other forming a conductive network leading to a remarkable increase of the electrical conductivity of the coating. By further increment of the concentration of the ITO nanoparticles (Fig. 5-c), an observable morphology of the ITO network is shown which also results in an increase of the electrical conductivity of the film.

Fig. 6 shows WLI images for the surface of carbon MWNTs composite coatings with different loading ratios. Fig. 6-a shows a WLI surface image for a coating containing only 0.05 volume fraction of carbon MWNTs loading. It appears as an isolated cluster, which is different from the 0.15 volume fraction shown in Fig. 6-b, where an interconnected network of the nanotubes encapsulating within the insulating matrix appears on the surface. This interconnection explains the drastic increase of the electrical conductivity. Fig. 6-c shows the same image for 0.4 volume fraction, where a more homogeneous network of nanotubes was formed enhancing the electrical conductivity of the coatings.



(a) (b) (c)

FIG. 5. The SEM surface morphology of GPTS_ITO layers with different ITO loading ratios: (a) 0.05, (b) 0.2 and (c) 0.9.



(a) (b) (c)

FIG. 6. WLI of the surface of GPTS_MWNTs layers for: (a) 0.05, (b) 0.15 and (c) 0.4 carbon MWNTs loading ratio.

Optical Properties

The transmission in the UV-VIS-NIR for the ITO based coatings and the carbon MWNTs on PC substrates was characterized as shown in Fig.7. Both coatings have a high transmission in the visible range; however that of ITO based layers shows higher transmission with smaller transmission window. Furthermore, the ITO layer exhibits a sharp decrease in transmision around $\lambda = 1300$ nm showing almost no transmission in the NIR range. The main effect of this behaviour is due to the high absorption peak related to the presence of free carriers. It is also observed that both coatings exhibit high absorption in the UV region.

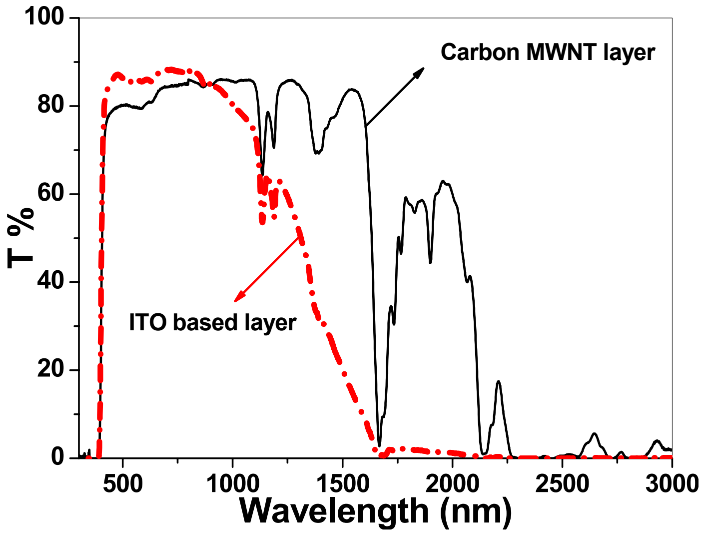


FIG. 7. The optical transmission in the UV-VIS-NIR range for ITO based layer and carbon MWNTs layer onto a PC substrate.

Mechanical Properties

The mechanical stability of the coatings is also an important factor to be taken into consideration. Both films gave excellent adhesion on polycarbonate substrates when tested with the tape test procedure (DIN 58196-K2). The resistance against abrasion was excellent according to the rubber test (DIN58196-G10). The hardness measured using the pencil test (ASTM D 3363–92a) ranged between 1H and 2H depending on the GPTS concentration with respect to the conducting fillers.

Conclusion

Nanocomposite thin films were deposited onto polymeric substrates using two coating colloids made of conductive ITO nanoparticles and carbon MWNTs. The electrical conductivity of both nanocomposite films exhibit a classical percolation law with a critical threshold of 0.083 for carbon MWNTs and 0.19 for ITO nanoparticles. The maximum obtained electrical conductivity for ITO films is 526 $\Omega^{-1}.m^{-1}$, which is larger than that obtained for the carbon MWNTs films (65 $\Omega^{-1}.m^{-1}$). The ITO films show higher transmission than that of carbon MWNTs ones. Both types of films exhibit good mechanical durability against abrasion and scratch.

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