

Preparation and characterization of transparent/conductive nano-composites films

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Abstract Polymer-embedding of nano-sized indium tin oxide ($\text{SnO} \cdot \text{In}_2\text{O}_3$, ITO) produces electrically conductive materials transparent to the visible light at filling factors higher than the percolation threshold. ITO powders are commercially available in an aggregated form and a disaggregation technique was required. Here, aggregated ITO nanoparticles were transformed to colloidal suspension by high-speed stirring. This finely dispersed ceramic suspension was stabilized by addition of poly(vinyl pyrrolidone) and the obtained colloidal system was cast on an optical-grade substrate (PET) to produce electrically conductive-transparent nanocomposite films. Preliminary mechanical and electrical characterization of these films showed good conductivity and interfacial properties.

Introduction

Nanocomposites are advanced materials obtained by combining two (or more) solid phases, one of which having at least one dimension in a nano-sized scale range (i.e.,

1–100 nm). Nanocomposites can be based on binary combinations of ceramics, metals and polymers, however polymer-based nanocomposites, that is systems made of a continuous polymeric matrix embedding nano-sized domains of another solid, are the most common systems. Depending on the required mechanical and/or physical characteristics, both high and low filling factors can be used, while filler shape and size can be controlled to achieve selected material characteristics. In macro-composites mechanical and physical characteristics can be approximately derived from those corresponding to the bulk phases of involved components linearly combined according to the mixture rule. In nanocomposite materials, owing to the very large interface extension, the properties are mainly determined by the type of interaction involved at interface. At high filling factors, the contribution from bulk phase properties may be even neglected in comparison with the interfacial term. For such a reason, nanocomposites are frequently termed ‘interfacial composites’.

With the exception of clay-polymer nanocomposites, which have been widely investigated [1] and today are at a commercial stage, the research activity on hybrid ceramic-polymer nanocomposites is still very limited [2, 3]. Nano-sized semiconductor ceramics, e.g., indium-tin oxides ($\text{SnO} \cdot \text{In}_2\text{O}_3$, ITO), antimony-doped tin oxides (ATO), etc., blended with thermoplastic polymers represent a new class of nanostructured material that can be exploited for a number of application in different technological fields (e.g., anti-reflection coating films, anti-glare, anti-static, electromagnetic shielding, etc.). Especially interesting is the possibility to produce optically transparent polymer-based films of a certain electrical conductivity. These materials may be processed by simple technologies already available for thermoplastic polymers (e.g., extrusion, injection moulding, etc.) that can be easily adapted for treatment of extended

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areas. However, to produce a transparent composite material the refractive index of matrix and filler phases should match exactly. Because polymers have a refractive index close to 1.5 while the refractive index of ITO is 1.9 in the visible spectral range, polymer/ITO blends result quite opaque. The only way to decrease opacity in polymer/ITO mixture is by reducing filler size to a nanometric range (i.e., less than 100 nm) which is quite lower than the visible light wavelength. In this case, scattering phenomena result significantly attenuated. Such transparency level can be enough for many technological applications if these nanocomposite materials are used in form of thin films as it is usually required for ITO electrodes.

In this paper, a method for the preparation of a hybrid ceramic-polymer (ITO-PVP) nanocomposite films starting from commercial nano-sized oxide powders is described. The preparation technique is based on commercial ITO powder classified as 'nano-sized'. However, this product is commercially available as a dry powder containing extended aggregates of nanoparticles. In order to achieve contact-free dispersion of ITO nanoparticles in PVP, a disaggregation process based on a high-speed stirring approach has been developed and used. This method is very general and it can be used also for disaggregating other types of commercial nano-sized ceramic powders.

Experimental part

Disaggregation process and ITO/PVP film preparation

The technique used to disaggregate commercial ITO powder (Aldrich, nano-size) was based on dispersing the ceramic aggregates into a low-viscosity liquid phase (e.g., ethanol) moving at high speed. In this fast-moving liquid, the aggregate periphery experiences the action of a high friction force (Stoke's law) which causes a progressive detachment of single particles from the aggregate (i.e., an erosive process). In addition, pressure gradients act on the aggregates causing their orientation, deformation, and breaking in smaller pieces. Collision of aggregates with moving surfaces also has a significant role in this breakup process. Previous studies have shown that shear flow is the most effective in disaggregation [4], consequently the involved apparatus (Miccia, Mod. D-8, Omogenizer, 0–35,000 r.p.m.) had a special design which enhanced the shear flow. Such a device allowed very fine disaggregation of starting ceramic powders for the special design of blades and the possibility to continuously process the suspension. The ceramic suspension was processed at 30 °C by using a thermostatic bath. In order to reduce cavitation phenomena, which limitate the use of high processing rate, a cylindrically shaped PET vessel with a neck perfectly adapted to

the stirrer probe was used, and to increase pressure in the stirring place, the probe was placed close to the vessel bottom. The powder was processed under inert atmosphere (nitrogen) to avoid variations of oxide stoichiometry which caused modification of electrical properties.

To increase the stability of the as-prepared colloidal ITO suspensions a stabilizer was added to the systems. Poly (vinyl pyrrolidone) (PVP) showed excellent surfactant characteristics. Such polymer has been frequently used to stabilize colloidal suspensions of metals and ceramics. Here, a low molecular weight PVP was preferred (Aldrich, $M_w = 10,000 \text{ g mol}^{-1}$), since it allowed formation of only mononuclear ITO/PVP core/shell entities inside the suspension. The PVP molecules absorbed on the ceramic phase, preventing nanoparticle from re-aggregation during solvent removal. PVP was high soluble in alcoholic solvents and for the high affinity with ceramics it absorbed on the solid phase, coating uniformly the particles. High-speed stirring treatment cannot be done directly in presence of PVP, because of a fast polymer degradation process [5].

PVP is an amorphous polymer characterized by a low T_g value (about 60 °C), and therefore it is soft and has mechanical properties at room temperature inadequate for monolithic composite specimen preparation. However, high-quality nanocomposite films supported on special optical substrates can be based on these materials. In order to achieve good mechanical adhesion, the substrate surface required to have a certain surface porosity. Several transparent materials were test as substrate but the best results were obtained using commercial polyester (PET) films (the type used for slide printing). Alcoholic PVP/ITO suspensions were spin-coated on PET substrates in order to achieve films of uniform thickness, and dried in air at room temperature. The resulting thickness was ca. 500 μm . Then, dried films were baked in oven at moderate temperature (80 °C) to increase the dimensional stability of composite material.

Electrical and mechanical characterization

The measurements of current-voltage characteristics (IVCs) were made by using a four-probe technique. The sample is placed inside a cryostat, which is gradually immersed in the ^4He bath in order to have an accurate temperature control. Four Cu wires are connected to the sample for current biasing and measuring the voltage drop across it. Contacts have an *in-line* geometry, with the current leads placed outside. The copper wires are connected to the samples by using silver paste. The average spot diameter is $\leq 1 \text{ mm}$ and the distance between electrical contacts was of 5 mm. The leads pass through a series of filters to shield the sample from external electro-magnetic noise. The filter stage consists of RC low pass filters with a cutoff frequency of around

10 kHz, and they are placed at the same sample temperature. On the room temperature side, the leads pass through π -type feed-through filters with a cutoff of about 10 MHz before they are connected to the analog electronics. The voltage signal is provided by the NI-ATMIO16 ADC PCI card, and it is sent to the sample through a selectable high precision (0.1%) shunting resistor. The voltage across the sample is amplified by a factor of 100 by using a low noise instrumentation amplifier. The current is read across the precision resistor, and it is amplified by a factor $\times 10$. Both I and V outputs from amplifiers are read by analog single-ended inputs of the ADC card, and the IVC data are recorded on a connected personal computer.

Mechanical testing of nanocomposite material was done by micro-hardness measurements. A first set of tests was carried out by micro-hardness Vickers and Shore A. The Vickers microindentation tests were performed by a *Leica VMHT MOT*, using indentation loads of $1g_f$ and $5g_f$. Such indentation loads were used to have very low deep penetration that minimized the influence of substrate. The indentation time always was of 15 s. The nanocomposite film were supported on a PET overlap film. Shore-A hardness was performed by a durometer *Instron®-Shore S1*. Tests have been performed using always a static equipment support. In order to obtain good reproducibility of experimental results a mass of 1 kg centered on the axis of indentation was used as indicated by ASTM D-2240. In principle Shore-A hardness test is not suitable to thin polymeric films, but differently from Vickers test such set-up allowed to compare the influence on the results of two important testing parameters: time and temperature. The first series of tests were carried out at room temperature with a tip dwell time ranging from 1 s to 25 s. Tests were carried out at selected values of temperatures (25, 40, and 50 °C) with a fixed dwell time of 10 s.

Results and discussion

The SEM-micrograph given in Fig. 1a shows the microstructure of the starting ITO product (Aldrich, nano-size ITO). As visible, the starting material is a largely aggregated dry powder. Because the aggregation process is accomplished at room temperature, atomic diffusivity is low and nanoparticles are not sintered together, but they are just aggregated according to a coagulation process. Particle surface contamination by a large amount of electrolytes and stabilizer molecules has probably a role in preventing sintering. As a consequence, it is possible to completely separate nanoparticles by applying a relatively mild mechanical action to the aggregate powder, in the form of dispersion in a liquid medium. Complete disaggregation of micronic ITO nanoparticle aggregates has

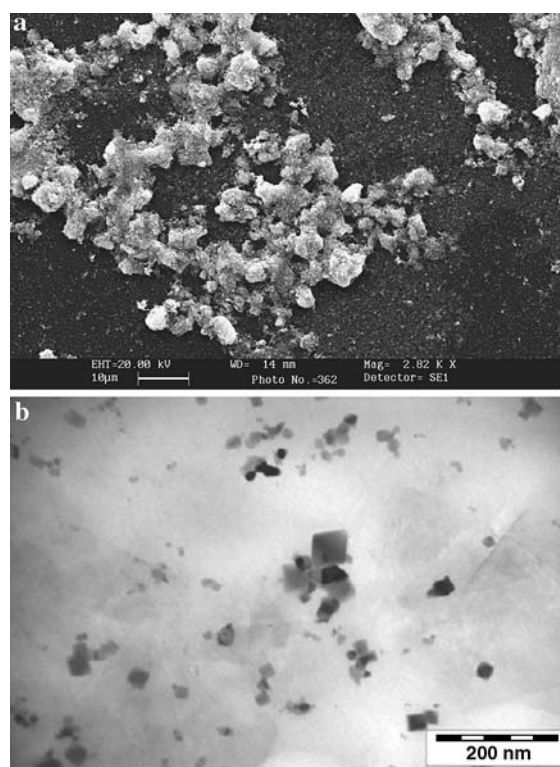


Fig. 1 SEM-micrographs of ITO powder in the as-received commercial form (a), and after the defragmentation treatment (b)

been accomplished by applying high-speed stirring to ITO powder dispersions (see Fig. 1b). Such an approach was described in literature for polymeric microparticle separation [4, 6–11], but it has been found to work also with ceramic aggregates.

The ITO powder disaggregation was performed in a polar medium (alcohol) characterized by a strong affinity with the hydrophilic ceramic surface. Ethyl alcohol resulted really adequate as suspending medium for the low viscosity value ($\eta = 1.2 \times 10^{-3} \text{ Ns/m}^2$, a 25 °C), that allowed to achieve high stirring rates. A little amount of surface agent was added to this system in order to improve dispersion of starting ceramic phase and to increase the stability of colloidal suspensions. Several surfactants were tested: AOT, lauryl sulphate, silanol (generated in situ by partial acid hydrolysis of tetra-methoxy-silane). The starting suspension was opaque and unstable (in fact, sedimentation resulted in a few minutes), but after adequate homogenization treatments (e.g., 5 h at 10,000 r.p.m.) a stable iridescent colloidal system resulted. Suspension stability and transparency significantly improved, with increasing of processing time, but the surfactant presence was not strictly necessary and a complete re-dispersion of ceramic aggregates was observed also by stirring dispersions of ITO powder in pure-ethanol medium. Since oxides are partially hydrated at surface, alcoholic molecules stably bonded particle surface by hydrogen bridge formation. Probably,

alcoholic molecules may behave just like mild steric stabilizers. However, colloidal suspensions resulting from breakup treatments in absence of surfactants were much less stable and required to be used in as-prepared form.

To increase stability of the as-prepared colloidal ITO suspensions a stabilizer was added. Poly(vinyl pyrrolidone) (PVP) showed excellent surfactant characteristics. Such polymer has been frequently used as stabilizer for colloidal suspensions of metals and ceramics. The PVP molecules absorbed on the ceramic surface, preventing nanoparticle from re-aggregation both in the dispersing medium and during solvent removal. PVP was high soluble in alcoholic solvents and for the high affinity with ceramics it absorbs on the solid phase, coating uniformly each particles and producing stable colloidal systems.

When colloidal suspensions were dried by ethanol evaporation, uniform ITO/PVP nanocomposite samples resulted. As visible in Fig. 2, these ITO/PVP nanocomposite films were high transparent in the visible spectral region. PVP is classified as optical plastic owing to the great transparency and refractive index close to the glass value (1.5). For such reason, this thermoplastic polymer has been used in the optoelectronic field for preparing ceramic-polymer composites for waveguide application [12, 13]. Therefore, high transparent film were obtained by PVP-embedding of nano-sized ITO powders which at filling factors above the percolation threshold resulted electrically conductive.

It is known that ceramic powders embedded in PVP matrices achieve dimensional stability after thermal annealing in oven at moderately high temperatures [14, 15] and a similar consolidation treatment has been done by exposing the material to laser beam. Consolidation was attributed to an increase in the PVP molecular weight owing to the presence of residual hydrogen peroxide

catalyst in the polymer [12]. Significant consolidation was observed also after thermal annealing of ITO/PVP nanocomposite films. In this case, the dry films were baked in oven at 80 °C for a few hours. Consolidation was obtained under these mild thermal conditions probably because of the larger extension of interface involved in nanocomposites. However, also chemical cross-linking phenomena may be involved in the consolidation process. In this case, a chemical reaction caused conversion of thermoplastic PVP matrix into a three-dimensional network, as suggested by the experimentally observed lower hydrophilicity and solubility in water and ethyl alcohol of resulting nanocomposite films.

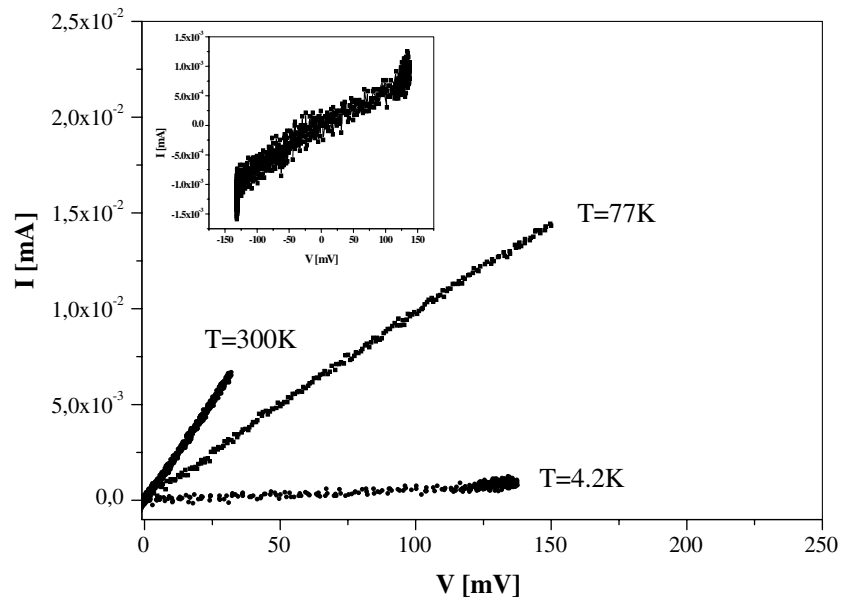
As shown in Fig. 3, the IVCs of ITO/PVP nanocomposite films, characterized by filling factors higher than 60% by weight, was recorded at different temperatures. The resistance of the sample is almost 4.6 K Ω at room temperature, and it increases of a factor 38 at the liquid helium according to the semiconductive nature of ceramic phase. In particular, the nano-composite material shows to be still conducting at the cryogenic temperatures, and its behavior in terms of IVCs is quite ohmic. As shown in the inset of Fig. 3, the experimental data show a slight deviation from the linearity at $T = 4.2$ K, as expected from the semiconductive nature of ITO. At higher voltage values the material does not show any deviations from the linear behaviour. The absence of hopping and tunnelling conduction mechanism at high applied voltages can be probably related to the high filling factor used in the composite preparation. According to the geometrical configuration of electrical contacts reported in the previous section, the electrical resistivity resulted to be 27, 86, and 1,000 Ωcm at temperatures of 300, 77, and 4.2 K, respectively. Such values are only slightly larger than similar results reported in the literature for ITO-based films (10^{-1} Ωcm), even if these measurements were performed after an heavy material baking [16].

In order to evaluate the effect of ceramic nanophase addition on the film mechanical properties, hardness tests have been done. The average values obtained by micro indentation tests on ITO-PVP and pure PVP films are reported in Fig. 4. Vickers hardness values were almost not dependent on the load, to evidence the negligible influence of substrate adopted. The insertion of ceramic particles in polymeric matrix produced an increase in the Vickers hardness of about 50%. The measured values of Vickers hardness, indentation depths, and related standard deviation on 30 measurements are reported in Table 1. A first set of shore hardness tests was carried out at room temperature with selected values of the indentator dwell time in the range 1 s to 25 s. The experimental results for the two different type of materials are shown in Fig. 5. The hardness decrease with increasing of dwell time was related to



Fig. 2 High transparent-conductive ITO/PVP nanocomposite film

Fig. 3 Current-voltage characteristics of the ITO based nanocomposite at different temperatures



the viscoelastic nature of polymeric component visible either in the pure polymer and nanocomposite. At the same dwell time, the filled film has a hardness value greater than non-filled film, as already evidenced in Vickers micro indentation tests. The obtained values of hardness are strongly influenced by substrate and can be used just for comparison purposes. To a dwell time of 20s the PVP film showed a loss of hardness while the nanocomposite film showed scarce time-dependence. Further tests were performed at 25, 40, and 50 °C, with a fixed dwell time of 10s. Results obtained, either on PVP film and PVP-ITO film, are presented in Fig. 6. In this case the experimental evidence is that increasing the temperature, hardness reduces with a similar trend between 25 °C and 40 °C. Ranging from 40 °C to 50 °C the reduction was higher for PVP than for PVP-ITO material. This behavior confirmed that ITO

Table 1 Average Vickers hardness (HV_m), standard deviation and average depth of marks (h_m) on a PVP film filled with ITO and deposited on a PVA substrate

	1g _f	5g _f
HV_m^2 (Kg/mm)	4.5	4.4
Standard Dev.	0.2	0.1
h_m	3.0 μm	6.7 μm

filling of PVP decreased the viscoelastic response with temperature.

Conclusions

The obtained ITO/PVP nanocomposite films are electrically conductive and transparent in the visible spectral

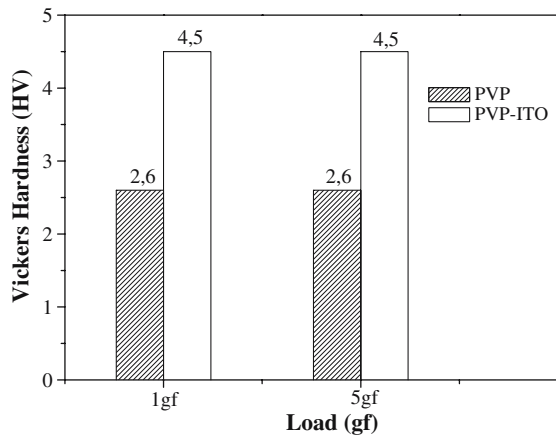


Fig. 4 Vickers hardness of PVP film and PVP-ITO film with indentation loads of 1g_f and 5g_f. Films are deposited on a polymeric substrate of PMMA

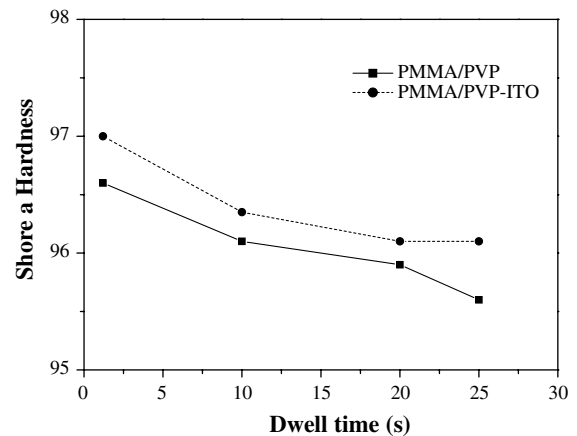


Fig. 5 Shore-A hardness of PVP and PVP-ITO films, with different dwell time and deposited on a PMMA substrate. Error is calculated using *t*-Student, with confidence interval of 90%

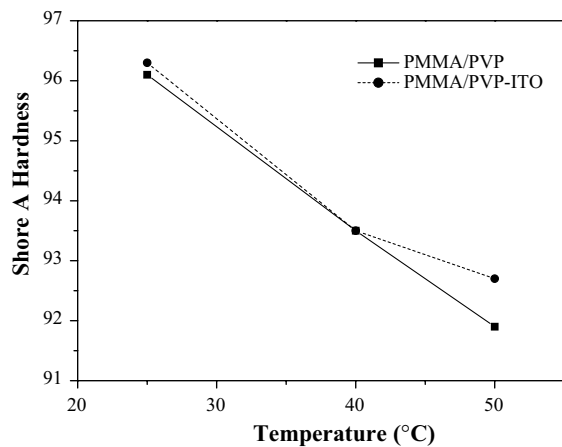


Fig. 6 Variation of Shore-A hardness in relation to temperature, with constant dwell time. The samples examined are PVP and PVP-ITO films on substrate of PMMA. Error is calculated using *t*-Student, with confidence interval 90%

region and consequently they can be potentially useful for a number of technological applications. In addition, these films showed mechanical properties higher than pure PVP because of the ceramic reinforcement presence and good polymer-ceramic interface adhesion.

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