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Optical properties of biocompatible polyaniline nano-composites ☆

C. Dispenza [a,b,*], M. Leone [c], C.Lo. Presti [a], F. Librizzi [c], G. Spadaro [a,b], V. Vetri [c]

[a] *Dipartimento di Ingegneria Chimica dei Processi e dei Materiali, Università degli Studi di Palermo, Viale delle Scienze, 90128 Palermo, Italy*
[b] *Centro Interdipartimentale di Ricerca sui Materiali Compositi, Università degli Studi di Palermo, Viale delle Scienze, 90128 Palermo, Italy*
[c] *Dipartimento di Scienze Fisiche ed Astronomiche, Istituto Nazionale per la Fisica della Materia, Via Archirafi, 90100 Palermo, Italy*

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Abstract

Polyaniline (PANI) is an electro-active polymer of great interest thanks to its outstanding physical and chemical properties which make it suitable for various applications in optics, bioelectronics, biosensors, diagnostics and therapeutic devices. Unfortunately, PANI is infusible and insoluble in most common solvents and, thus, very difficult to process. In the attempt of improving processability, yet preserving its interesting properties, PANI has been synthesized in the form of particles and dispersed into a hydrogel matrix. The synthesis of PANI–hydrogel composites proceeds via γ-irradiation of PANI dispersions as obtained by 'in situ' polymerization of aniline in the presence of water-soluble, polymeric stabilizers. The chosen stabilizers are able to undergo to chemical cross-linking when exposed to ionizing radiations, so forming the highly hydrophilic network that entrap PANI particles. The presence of a hydrogel matrix induces biocompatibility to the final composite material which, in a typical bottom-up approach, may become suitable for the development of biocompatible, optoelectronic devices. Some morphological and optical features of these novel soft, functional nano-composites are here presented.

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1. Introduction

Organic conjugated polymers have shown great promise in the field of optoelectronics, demonstrating applications over a wide range of technologies including light detection, electrochromic displays, light emitting diodes, optical switching and optical computing. Specifically, the ability for many polymeric materials to undergo coupled alterations in optoelectronic properties, due to chemical and electrical perturbations of their redox state lend to them unique advantages within the field of functional materials [1].

Polyaniline, among the other organic conjugated polymers, owns its popularity to the high conductivity in the doped state (up to 1 S/cm), its excellent environmental and thermal stability as well as the electrochemical stability [2]. The transition between the most reduced form (leucoemeraldine), which is insulating, to the half-oxidized, semi-conductive form (emeraldine base), or to the fully oxidized insulating form (pernigraniline base), causes also a strong color change (in transmission) between colorless to blue or to violet, respectively. The emeraldine base form can be easily doped by means of protic acid treatments to obtain protonated emeraldine, which is green in color and electrically conductive. However, the intractability of PANI has limited its application, especially in its pure,

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* Corresponding author. Address: Dipartimento di Ingegneria Chimica dei Processi e dei Materiali, Università degli Studi di Palermo, Viale delle Scienze, 90128 Palermo, Italy.

E-mail address: dispenza@dicpm.unipa.it (C. Dispenza).

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inherently conductive form. Processing difficulties can seriously restrict devices manufacture and function.

Apart from electrochromics and optoelectronic device components, also chemical and biological sensors may benefit from the interesting properties of PANI. The function of a sensor is to provide information on the physical, chemical or biological environment through an electrical response, which is function of the environmental property to be measured. Biosensors, in particular, contain biological entities such as enzymes, antibodies, bacteria, etc. as recognition agents, and in some cases they can couple diagnostic functions with therapeutic technologies (such as in 'smart' drug delivery systems) [3,4].

An integration of the sensoring function with an optical effect, intrinsically generated by the material, can be achieved by PANI-based materials. But, especially for biomedical application, the quality of the sensor–human interface has to be carefully considered, being biocompatibility, tolerance toward biofouling, chemical and physical stability obvious requirements. These results can be achieved following two different manufacturing approaches: either by coating the sensing device with a suitable biocompatible material or by applying a typical composite material concept, i.e. by producing a composite material where the sensing material is dispersed in a biocompatible support matrix. The great advantage of the latter approach is the possibility of device miniaturization.

The main objective of the present work is to incorporate PANI nanoparticles into a soft, wet and biocompatible matrix, such as a polymeric hydrogel, yet preserving all the important optical features of PANI. The choice of hydrogels as support material also resides on the high permeability of these media by gases and liquids and on the optical transparency to visible light. The inherent hydrogel flexibility should also allow the formation of supramolecular structures in the dry state due to self-assembly of PANI particles [5]. The conductive hydrogel matrix can also work as a template for subsequent electrochemical reactions (such as electrochemical polymerization of a second electrochromic polymer).

Synthesis of PANI–hydrogel composites proceeded via 'in situ' polymerization of aniline in the presence of steric stabilizers, namely poly-vinyl-pyrrolidone (PVP) or poly-vinyl-alcohol (PVA), followed by γ-irradiation of the so obtained PANI dispersions, in order to induce chemical cross-linking to either PVP or PVA. The preparation of hydrogels by radiation cross-linking is a very simple and, therefore, very attractive process and it has been subject of intensive research over the years. Hydrogels can be obtained by radiation techniques in several ways, including irradiation of pure polymers, monomers or solution of polymers and/or monomers in bulk, solution or emulsion. Advantages and disadvantages of each approach, as well as the mechanism of reactions leading to gel formation are discussed in the literature [6,7]. Poly-vinyl-pyrrolidone and poly-vinyl-alcohol are among the polymers used for the preparation of hydrogels via high energy irradiation, especially for wound dressing and tissue engineering applications [8,9]. For the purpose of the present investigation, irradiation conditions, such as irradiation dose and polymer concentration in water, have been selected in order to obtain macroscopic gelification of the whole sample. The absence of residual aniline, in both dispersions with PVP and with PVA, has been assessed by HPLC and GC and the water content of both composite hydrogels has been measured gravimetrically (approx 96% wt for both). Results of the electrical characterization of both dispersions and hydrogel composites, via cyclic voltammetry and impedance spectroscopy, as well as the characterization of the swelling behavior of the pure PVP and PANI/PVP hydrogels, are elsewhere reported [10]. Pure PVA and PANI/PVA hydrogels behave similarly as far as swelling behavior and electrical properties are concerned (unpublished results), whereas PANI/PVA nano-composites show very distinctive features with respect to the PANI/PVP analogs in terms of morphology and optical properties. In particular, here we discuss some experimental evidences from scanning electron microscopy (SEM) and atomic force microscopy (AFM) analysis, carried out on both films obtained from the dispersions and hydrogels upon freeze drying, and preliminary results of the optical characterization of these novel soft composites.

2. Experimental

PANI aqueous dispersions have been obtained by chemical oxidation of an acid solution of aniline using ammonium persulfate as redox initiator and either PVP (Mw = 160 000) or PVA (Mw = 47 000, degree of hydrolysis 88) as steric stabilizer. Details of the synthetic procedure are reported elesewhere [10].

During synthesis the conversion of aniline with reaction time was monitored by both high performance liquid chromatography (HPLC) and gas chromatography (GC) and both techniques confirm that aniline is no longer present after the first 15 min of reaction time for the synthesis carried out in the presence of PVP, and after 30 min when in the presence of PVA. Before irradiation, dispersions were diluted 10-fold with the steric stabilizer/water solution (at 4% wt), already used to prevent macroscopic precipitation of PANI during polymerization, so that stabilizer weight concentration was kept constant. Hydrogel composites were obtained by ^{60}Co γ-irradiation of the diluted dispersions of synthesized PANI. Irradiation was performed in glass vials under nitrogen at a dose rate of 2 kGy/h and a total absorbed dose of 40 kGy. During irradiation, temperature was maintained at 10 °C.

The original pH of the diluted dispersions and hydrogels was equal to 1.6 ± 0.1; pH of dispersions was brought to 4 ± 0.1, 7 ± 0.1 and 9 ± 0.1 by adding aqueous 1 M NaOH, while pH of hydrogels was brought to the above reported three values by equilibrating them in three different phosphate buffers until constant weight of the swollen hydrogel was attained.