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Interfaced conducting polymers

J. Stejskal[a,*], P. Bober[a], M. Trchová[a], D. Nuzhnyy[b], V. Bovtun[b], M. Savinov[b], J. Petzelt[b], J. Prokeš[c]

[a] Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague 6, Czech Republic
[b] Institute of Physics, Academy of Sciences of the Czech Republic, 182 21 Prague 8, Czech Republic
[c] Charles University, Faculty of Mathematics and Physics, 180 00 Prague 8, Czech Republic

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ABSTRACT

The materials composed of pairs of conducting polymers, polyaniline, polypyrrole and non-conducting poly(*p*-phenylenediamine), were prepared by the coating of one polymer with the other. The course of polymerizations and morphology of the resulting composites have been recorded and the products were characterized by FTIR and Raman spectroscopies, DC and broad-band AC conductivity and permittivity measurements. The interfacial interaction between conducting polymers does not introduce any new effects concerning the conductivity. On the other hand, using composites where the conducting polymer is embedded in non-conducting polymer matrix allows for the control of structure at nanoscale and for the design of materials with new conductivity properties. This is illustrated by coating the conducting polymers with the poly(*p*-phenylenediamine) which has the conductivity by eight orders of magnitude lower, which yields composites with an intermediate conductivity, by three orders of magnitude lower than that of the conducting polymers.

1. Introduction

Polyaniline (PANI) and polypyrrole (PPy) are probably the most studied conducting polymers. They are closely related to each other and both are prepared by the chemical oxidation of respective monomers or by their electropolymerization. They were usually investigated separately, and only several comparative reports on both polymers have been published [1–7].

The copolymerization of aniline and pyrrole may be regarded as a route to combine both polymers [8–16]. The molecular structure of copolymers, however, is complex. Monomer reactivity ratios widely differ [10] and, consequently, the copolymers are chemically heterogeneous by definition [17], *i.e.* they are composed of chains differing in the participation of aniline and pyrrole constitutional units. The copolymerization leads to the reduction in the conductivity due to the decrease in chain conjugation and, consequently, most copolymers are non-conducting [8]. They may be useful, however, in applications that do not require high conductivity [11,12].

There is probably a little interest in the simple blending of both polymers. The polymerization of one polymer, however, on the top of the other is a challenge. This approach is based on the principle that virtually any object immersed in the reaction mixture used for the preparation of conducting polymers becomes coated with a thin film of this polymer. If one conducting polymer is used as a substrate for the coating with another one, such approach affords good interfacial contact between both polymers, because the chains of the second polymer grow on the chains of the first one. The depositions of PANI onto PPy nanotubes [18–22], PPy microspheres [23] or electropolymerized PPy films [24] may serve as examples. PANI coating led to enhance the microwave absorption [23], or improved the barrier properties and thus enabled a better corrosion protection of copper [24].

The reverse process, the deposition of PPy on PANI nanofibres [25], PANI-coated steel wire [26], PANI-coated carbon fibers [27], PANI suspension [28], PANI-coated carbon nanotubes [29] or electropolymerized PANI films [30–33] has also been reported. The composites had improved properties in corrosion protection [33], when applied in supercapacitors [18,21,34], in analytical sciences [19,20,26], in monitoring temperature [32] or in sensing of alcohol [6]. PPy/PANI coaxial nanoarrays were used in flexible supercapacitors.

* Corresponding author.
E-mail address: stejskal@imc.cas.cz (J. Stejskal).

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The combination of both conducting polymers has recently been tested in the coating of cotton textile, which has subsequently been used as electrodes in the monitoring of carnivorous plant response to mechanical stimulation [35]. Cotton was coated with one polymer, PANI or PPy, and then alternatively with the second. The sensing function was similar in single or double-coated textile, but the conductivity of the latter type was improved, due to the higher content of the conducting component. The combination of PANI with another conducting polymer, poly(3,4-dioxythiophene), has also been recently reported [36]. The composites had improved thermoelectric properties.

The present study concentrates on classical globular forms of conducting polymers, *i.e.* on powders. Another polymer, poly(*p*-phenylenediamine) (PPDA), has also been included in the present study. This polymer is closely related to PANI, but its conductivity is lower by about eight orders of magnitude [37]. One of the polymers was used as a template, which was coated by the second polymer. The former polymer can thus be regarded as filler and the latter as a matrix. All combinations of the three polymers have been prepared. The presence of PANI or PPDA accelerates the oxidation of aniline and may affect the morphology of resulting materials and, subsequently, their electrical properties [38]. The course of the oxidations has also been recorded.

2. Experimental part

2.1. Synthesis of conducting polymers

PANI was prepared by the oxidation of 0.2 M aniline hydrochloride with 0.25 M ammonium peroxydisulfate in aqueous medium [39]. The precipitate was collected on filter, rinsed with 0.2 M hydrochloric acid, with acetone, and dried in air, then over silica gel at room temperature.

PPy was similarly prepared by the oxidation of 0.2 M pyrrole with 0.5 M iron(III) chloride, and the PPDA by the oxidation of 0.2 M *p*-phenylenediamine dihydrochloride with 0.25 M ammonium peroxydisulfate [37,40] in water, and the oxidation products were treated as above.

2.2. Coating of conducting polymers

Individual polymers were used as templates for the coating with the same or another polymer. Freshly prepared 50 mL reaction mixture used for the preparation of PANI or PPDA or 100 mL that for PPy was poured over 1 g of template polymer. In this way, about 1 g of polymer was produced over 1 g of the template polymer.

2.3. Characterization

The powders were compressed at 70 kN by a manual hydraulic press to the pellets of 13 mm in diameter and 1 mm thick. The room temperature conductivity was determined by a four-point method in the van der Pauw arrangement using a Keithley 220 Programmable Current Source, a Keithley 2010 Multimeter as a voltmeter, and a Keithley 705 Scanner equipped with a Keithley 7052 matrix card.

A Thermo Nicolet NEXUS 870 FTIR Spectrometer with a DTGS TEC detector recorded Fourier-transform infrared (FTIR) spectra of the samples dispersed in potassium bromide pellets. A Renishaw InVia Reflex Raman microspectrometer was used to collect the spectra excited with a HeNe laser (633 nm) focused with a research-grade Leica DM LM microscope on the sample. A Peltier-cooled CCD detector (576 × 384 pixels) registered the dispersed light which was analyzed with a spectrograph using a holographic grating of 1800 lines mm^{-1}.

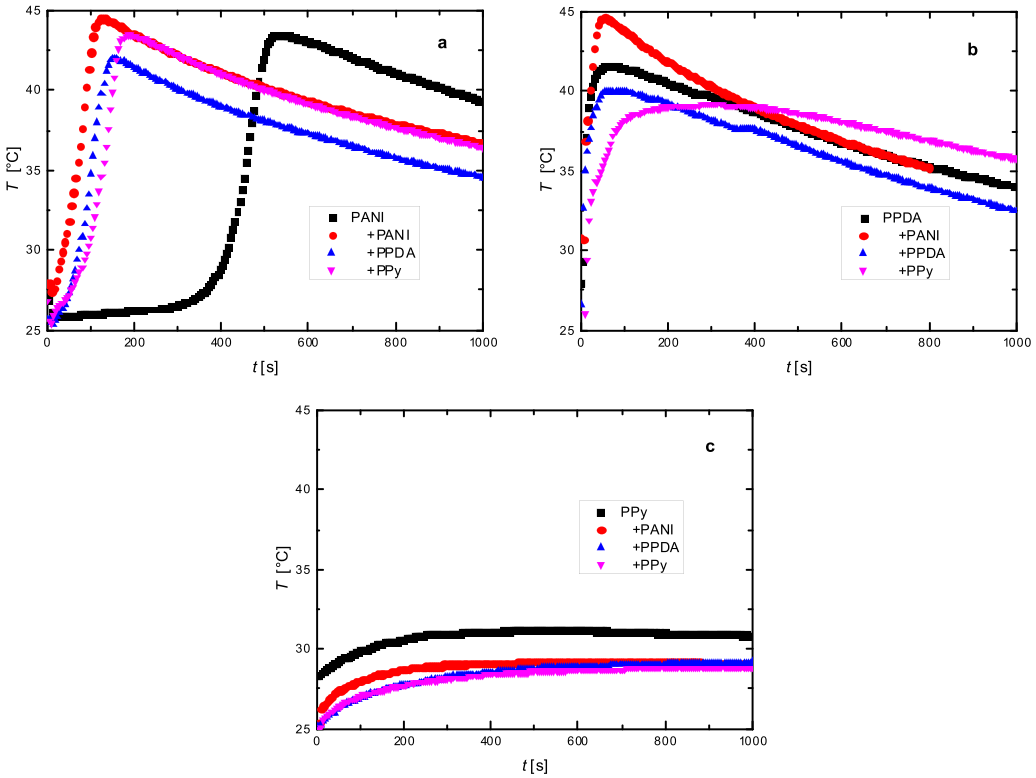

Fig. 1. Temperature profile during the oxidation of (a) aniline, (b) *p*-phenylenediamine and (c) pyrrole in the absence (squares) and in the presence of respective polymers: PANI (circles), PPDA (up-triangles) and PPy (down-triangles).