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Electrical conductivity and spectroscopic characterization of Blends of poly(2-chloroaniline)/polyaniline P(2ClANI)/PANI copolymer with PVC exposed to gamma-rays

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HIGHLIGHTS

- P(2ClANI)/PANI copolymer nanoparticles have been synthesized.
- PVC/P(2ClANI)/PANI copolymer blend films showing radiochromic behavior were prepared.
- Three orders of magnitude increase in conductivity of composite films was obtained upon γ-irradiation of up to 200 kGy.

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ABSTRACT

Poly(2-chloroaniline)/polyaniline P(2ClANI)/PANI) random copolymer was synthesized in the form of nanoparticles by chemical routes. Incorporation of P(2ClANI) into PANI backbone significantly increased the solubility of copolymer in THF. Thin PVC/P(2ClANI)/PANI blend films were prepared by solvent casting and subsequently exposed to gamma-rays. Conductivity measurements on the irradiated blend films of PVC/P(2ClANI)/PANI showed that conductivity was increased from 10^{-8} S/cm to 10^{-5} S/cm when irradiated to radiation dose of up to 200 kGy. The increase in conductivity was also revealed by FTIR and UV–vis spectra.

1. Introduction

1.1. PANI

Polyaniline and other conducting polymers such as polythiophene and polypyrrole have shown great potential for applications due to their light weight, conductivity, mechanical flexibility and low cost.

Polyaniline is especially attractive because it is relatively inexpensive, has three distinct oxidation states with different colors and has an acid/base doping response. This latter property makes polyaniline an useful substance for acid/base chemical vapor sensors (Chiang and MacDiarmid, 1986). The different colors, charges and conformations of the multiple oxidation states also make the material promising for applications such as actuators, supercapacitors and electrochromics. They are suitable for manufacture of electrically conducting yarns, antistatic coatings, electromagnetic shielding, and flexible electrodes, (Skotheim et al., 1998).

PANI can be doped by protonation with a protonic acid or by charge transfer with an oxidation agent. Its electronic and optical properties can possibly be controlled reversibly by varying the doping level PANI. It has excellent environmental and thermal stability in the conducting form, but on the other hand it has inferior chemical properties like insolubility and difficulty in processibility. In order to overcome these unfavorable characteristics and to improve and widen its application possibilities blend and composite forms of PANI have been extensively studied. From the point of view of inducing conductivity blends of PANI with Poly(vinyl/chloride) (PVC) vinyl chloride/vinyl acetate copolymer (PVC-co-PvAc) and chlorinated poly(propylene) (PPCl) were tried and some blends were tested for their dosimetric responses under various irradiations conditions (Bodugöz et al., 2001, Sevil et al., 1998, 2000, 2003).

As it is known chlorinated polymers such as PVC or PPCl undergo a high degree of side chain degradation resulting mainly with extensive loss of HCl when exposed to ionizing radiation (Schnabel, 1985). When blends or composites of these polymers

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with non-conducting PANI are irradiated, released HCl can be captured by the neighboring PANI molecules thus enhancing electrical conductivity of the blend. Protonic acid doping of PANI has been achieved by a variety of methods, such as chemical, electrochemical, photochemical, etc. Through systematic studies carried out in the Laboratories of Radiation and Polymer Sciences of Hacettepe University, Ankara, Turkey it has been shown that ionizing radiation can be effectively used in initiating and enhancing the conductivity of PANI blended with HCl releasing polymers and substances (Güven, 2007, Bodugöz and Güven, 2005, 2011; Sevil et al., 1998, 2000, 2003). In these works radiation-induced doping of PANI in the presence of PVC, PVC/2-Cl-PANI, PPCl, and copolymers of VdCl,VCl with VAc has been studied and significant increases in conductivity with absorbed dose have been achieved.

1.2. PClANI/PANI copolymer

Polyaniline in its doped, conducting Emeraldine Salt (ES) form is not soluble or processable when compared to its undoped, non-conducting form Emeraldine Base (EB) which in fact shows a limited solubility in a few solvent. Although some derivatives of PANI emeraldine base are soluble in common organic solvents, but their conductivities are lower than PANI. For example, poly(2-chloroaniline) P(2ClANI) shows more than one order of magnitude solubility in THF when compared with PANI, both prepared by the same chemical procedures (Chiang and MacDiarmid, 1986 and Skotheim et al., 1998).

Low solubility of PANI (EB) makes it difficult to find a co-solvent to be used in the preparation of blend films of chlorinated polymers. Even for apparently soluble binary polymer systems homogeneous dispersion of PANI chains in the other polymer matrix always presents a problem. Knowing that P(2ClANI) is more soluble than PANI though less conductive, we prepared random copolymers of these two. Thus we wanted to benefit from the existence of P(2ClANI) for the enhancement of solubility of the copolymer at the same time take advantage of PANI for better conductivity.

The aim of the present work has therefore been to synthesize copolymers of aniline with 2-chloroaniline and prepare its blends with PVC to investigate the change in conductivity of the PVC/copolymer blends when exposed to gamma-rays.

2. Experimental

2.1. Synthesis of P(2ClANI)/PANI copolymer

The P(2ClANI)/PANI random copolymer was prepared chemically using $(NH_4)_2S_2O_8$ as the oxidizer/initiator in aqueous 5 M HCl at 0–5 °C using freshly distilled monomers (Chiang and MacDiarmid, 1986; Skotheim et al., 1998). The copolymer was synthesized from a molar feed composition of 1:2 of aniline, 2-chloroaniline respectively. Subsequent reduction was achieved by treating the dried powder with NaOH or $(NH)_4OH$. Dried copolymer particles were of nanosize.

2.2. Preparation of the blend films

The copolymer in non-conductive form was dissolved together with PVC (Aldrich) powder in THF at room temperature in 1:1 weight ratio. The blend films were obtained by solvent casting of homogeneous solutions. The resulting films with thicknesses varying between 10 and 50 μm were thoroughly washed with alcohol and distilled water and dried before further use.

2.3. Irradiation of the blend films

The P(2ClANI)-co-PANI/PVC blend films were irradiated with gamma rays at room temperature. The irradiations were carried out in Issledovatelj self protected type ^{60}Co gamma irradiator at a dose rate of 0.18 kGy/h. The dose rate was measured using Fricke dosimetry.

2.4. Measurement of conductivity

The resistance of unirradiated and gamma irradiated blend films were measured by using four probe technique (Keithley 2100 I-V four probe Instrument).

2.5. Spectroscopic measurements

FTIR and UV–vis spectra of pristine and treated films were recorded with a Nicolet 520 and Varian Cary 5E spectrometers respectively.

2.6. SEM images

The morphologies of nanosized P(2ClANI)/PANI copolymer particles and PVC/P(2ClANI-co-PANI) composite films were examined using a 6360 LV, JOEL model scanning electron microscope directly from the powder and films.

3. Results and discussion

3.1. SEM images of the P(2ClAN)/PANI copolymer particles and PVC blend film

Fig. 1 is the SEM image of P(2ClANI)/PANI copolymer particles. Fig. 2 is the SEM image of PVC/P(2ClANI)/PANI blend film. As can be seen from Fig. 1 size of the P(2ClANI)/PANI copolymer particles are around 65 nm. The film obtained from the PVC/P(2ClANI)/PANI blend has a very smooth surface. Such smooth surface structure could not be obtained when we prepared PANI only based composite films in our earlier studies (Sevil et al., 1998). Incorporation P(2ClANI) moieties into the PANI structure not only enhanced the solubility of the copolymer but also improved the surface of the blend films obtained from their mixtures with PVC. The ease of solubility of copolymer particles may also be due to the very fine, nanosize particles obtained after drying of the synthesized copolymers.

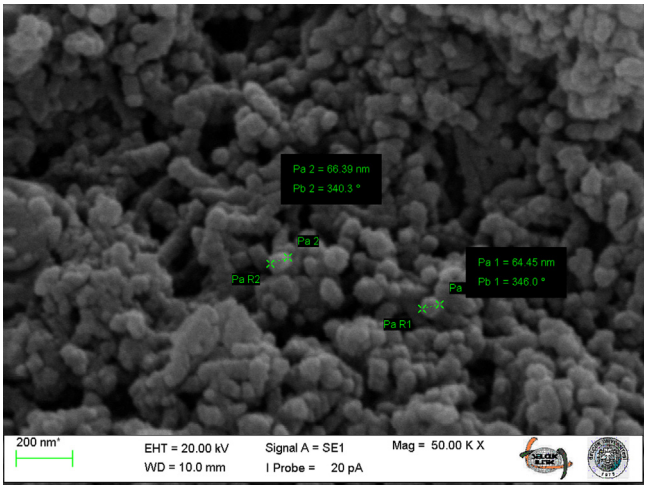

Fig. 1. SEM image of the P(2ClANI)/PANI copolymer nanoparticles.