

Doping of 2-Cl-PANI/PVC films by exposure to UV, γ -rays and e-beams

U.A. Sevil^a, O. Güven^b, Ö. Birer^c, Ş. Süzer^{c,*}

^a Ankara Nuclear Research and Training Centre, Beşevler, Ankara 0600, Turkey

^b Department of Chemistry, Hacettepe University, Ankara 06532, Turkey

^c Department of Chemistry, Faculty of Science, Bilkent University, Ankara 06533, Turkey

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Abstract

2-Chloro-polyaniline (2-Cl-PANI) is chemically prepared in its non-conducting (Emeraldine Base, EB) form and dissolved together with polyvinylchloride (PVC) in THF for casting into thin (10–50 μm) composite films. The electrical conductivity of these films increases by more than four orders of magnitude (from 10^{-6} to 10^{-2} S/cm) when they are exposed to UV, γ -rays and e-beams. This is attributed to the dehydrochlorination (loss of HCl) of PVC by exposure to energetic particles and subsequent doping of the 2-Cl-PANI (i.e., conversion to Emeraldine Salt, ES) by the in-situ-created HCl. The doped films can also be returned to their undoped form by further exposure to NH_3 vapours. The UV (or other particles)-induced doping/ NH_3 undoping cycles can be repeated several times until almost total dehydrochlorination of the PVC matrix. UV–Vis–NIR, Fourier transform infrared (FTIR) and X-ray photoelectron spectroscopic (XPS) techniques are employed to follow the changes in the composite films upon doping by exposure to these energetic particles. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Polyaniline (PANI), in its doped, conducting form (Emeraldine Salt, ES) is not soluble or processable when compared to its undoped, non-conducting form (Emeraldine Base, EB). Furthermore, some derivatives of PANI emeraldine base are highly soluble in common organic solvents. For example, 2-chloro-polyaniline (2-Cl-PANI) has more than one order of magnitude solubility in THF when compared with PANI, both prepared by the well-known chemical routes [1,2]. Doping, however, is very important for tailoring the electronic properties of the resulting product. The conventional method of doping involves some harsh acid treatment either by wet and/or vapour techniques and alternative routes are highly desirable. In a previous work, we demonstrated that the electrical conductivity of PANI/PVC composite films can be drastically increased by exposure to γ -rays or UV radiation as a result of dehydrochlorination (loss of HCl) of

polyvinylchloride (PVC) and subsequent doping of the PANI by the in-situ-created HCl [3]. Dehydrochlorination of PVC is an unwanted process and has been well-studied especially under UV exposure [4–6]. In our case, however, we make use of this undesired property of PVC. Similar strategy was earlier followed by Ogun [7,8] in his laminated polypyrrole/PVC films where photodehydrochlorination and doping with I_2 or FeCl_3 were employed; by Wan [9] in preparing transparent and conducting PANI/PVC coatings; by Ouyand and Chan [10] in preparing polypyrrole/PVC; and by Laska [11] PANI/PVC conducting films. In another recent study, it was reported that exposure to X-rays of the PANI in composite Langmuir–Blodgett films affected the electronic properties in a way similar to acid doping [12]. In the present study, 2-Cl-PANI/PVC composite films were exposed to various energetic particles and the changes were followed by spectroscopic techniques.

2. Experimental

The 2-Cl-PANI was prepared chemically by polymerising the freshly distilled monomer in a very strong acidic

* Corresponding author. Tel.: +90-312-266-4946; fax: +90-312-266-4579; e-mail: bilchem@fen.bilkent.edu.tr

solution using $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as the oxidiser/initiator [1,2]. A stronger acidic medium (5–6 M HCl) was needed to obtain 2-Cl-PANI, whereas only 1 M HCl was necessary for PANI [13]. Subsequent reduction was achieved by treating the dried powder with NaOH or NH_4OH . The polymer was later dissolved together with PVC in THF which was also freshly distilled prior to use. The solubility of the 2-Cl-PANI(EB) in THF is much higher compared to PANI(EB) due most probably to the increased polarity and/or prevention of the parasitic polymer growth from the *ortho*-position [2]. The 2-Cl PANI/PVC composite films were prepared by codissolving the polymers in distilled THF and casting the solution into thin films on quartz (for UV–Vis–NIR) and NaCl windows (for IR) by evaporating the solvent under saturated THF atmosphere. The films obtained were about 10–50 μm thick and uniform enough to obtain reproducible spectra. Similar films were also used for X-ray photoelectron spectroscopy (XPS) measurements.

XPS measurements were carried out on a Kratos ES300 electron spectrometer using Mg K α x-rays. UV–Vis–NIR characterisation was carried out with a Varian Cary 5E spectrophotometer and a Bomem MB102 spectrometer was used for Fourier transform infrared (FTIR) measurements. UV irradiation was achieved with a low-pressure Hg light source (UVP R-52G model, $\lambda = 254$ nm, 4.9 eV) and for the γ -ray exposure, a ^{60}Co source with varying doses (50–600 kGy) was used. The e-beam exposures were carried out with 7 MeV electrons (0–500 kGy) at the University of Maryland linear accelerator at a dose rate of 0.3 Gy/s.

3. Results and discussion

Fig. 1 displays the UV–Vis–NIR spectra of the 2-Cl-PANI/PVC composite film after 15 and 30 min of UV exposure together with 5 min of further exposure to NH_3 vapours. As-prepared composite blue film has an absorption band centred around 600 nm as well as the strong transition around 300 nm (similar to PANI) which is indicative of undoped form of the polymer (EB). The 600-nm band shifts to longer wavelengths upon exposure to UV (as well as γ -rays and e-beams) and the films become green, indicative of the doped salt form (ES) [2,14,15]. Exposure to ammonia vapours brings the ES films back to its EB form. Electrical conductivity of the films also follows the optical pattern; undoped EB composite films have conductivities in the range of 10^{-6} S/cm but the conductivity of the doped ES films can go up to 10^{-2} S/cm. We have not been able to observe any significant electrical or optical change of the 2-Cl-PANI-only powders upon exposure to the energetic particles or UV as opposed to the observations reported for the PANI–Langmuir–Blodgett films [12] and hence attribute this energetic particle-induced doping mainly to dehydrochlorination of PVC as was also claimed for PANI/PVC films [3]. Our argument is further supported by other spectroscopic findings. Fig. 2 shows the XPS spectra of 2-Cl-PANI/PVC films before and after exposure to γ -rays at a dose of 200 kGy. In addition to the strong Cl $2p_{3/2}$ peaks at 200.5 eV, which is assigned to chlorine bonded to carbon, a shoulder at 199.5 eV develops after exposure to energetic particles which is not observed in 2-Cl-PANI-only

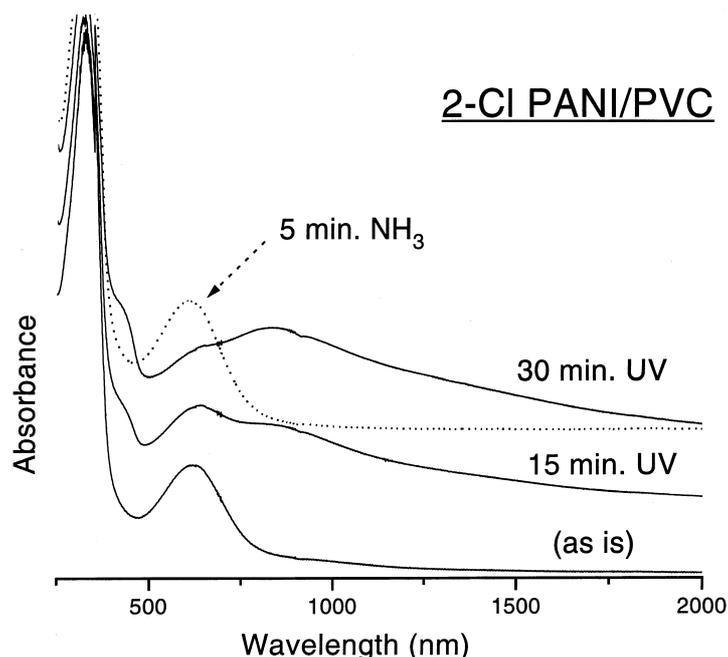


Fig. 1. UV–Vis–NIR spectra of 2-Cl-PANI/PVC composite films before and after 15 and 30 min exposure to UV and after further exposing them to 5 min of NH_3 vapours.

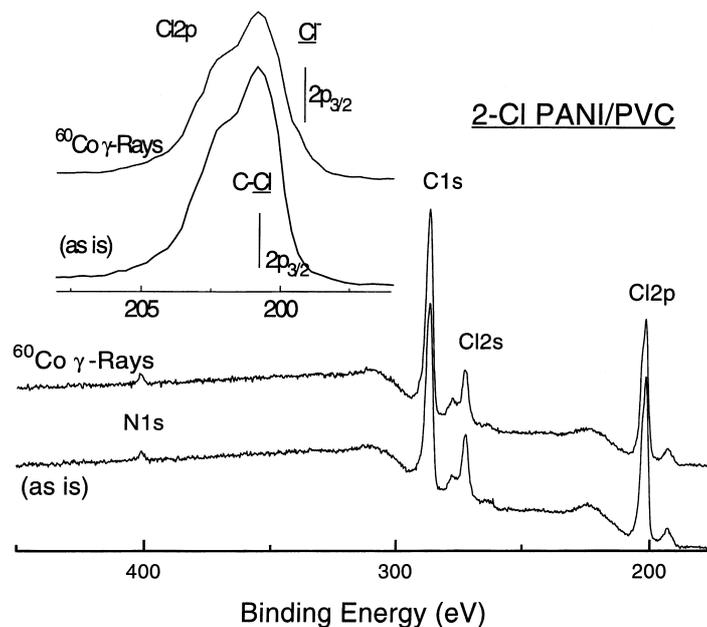


Fig. 2. XPS spectra of 2-Cl-PANI/PVC composite films before and after 200 kGy ⁶⁰Co γ -rays exposure.

films. This shoulder is assigned to chloride ion Cl⁻ and strongly supports the dehydrochlorination of the PVC as

the reason for doping of the EB films [3,16,17]. In Fig. 3, FTIR spectra of the 2-Cl-PANI/PVC films are shown as a

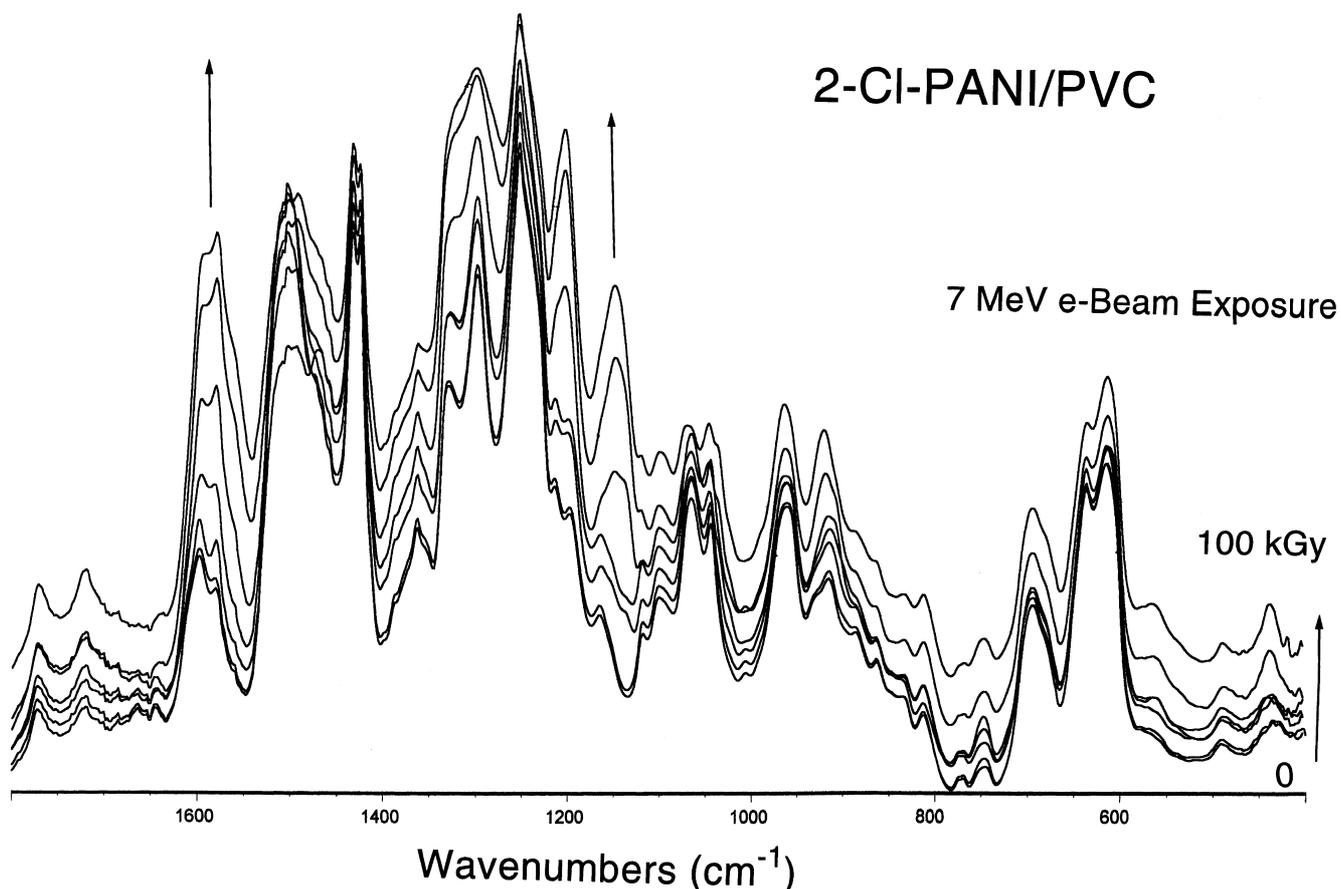


Fig. 3. FTIR spectra of 2-Cl-PANI/PVC composite films before and after exposure to 7 MeV e-beams.

2-Cl-PANI/PVC

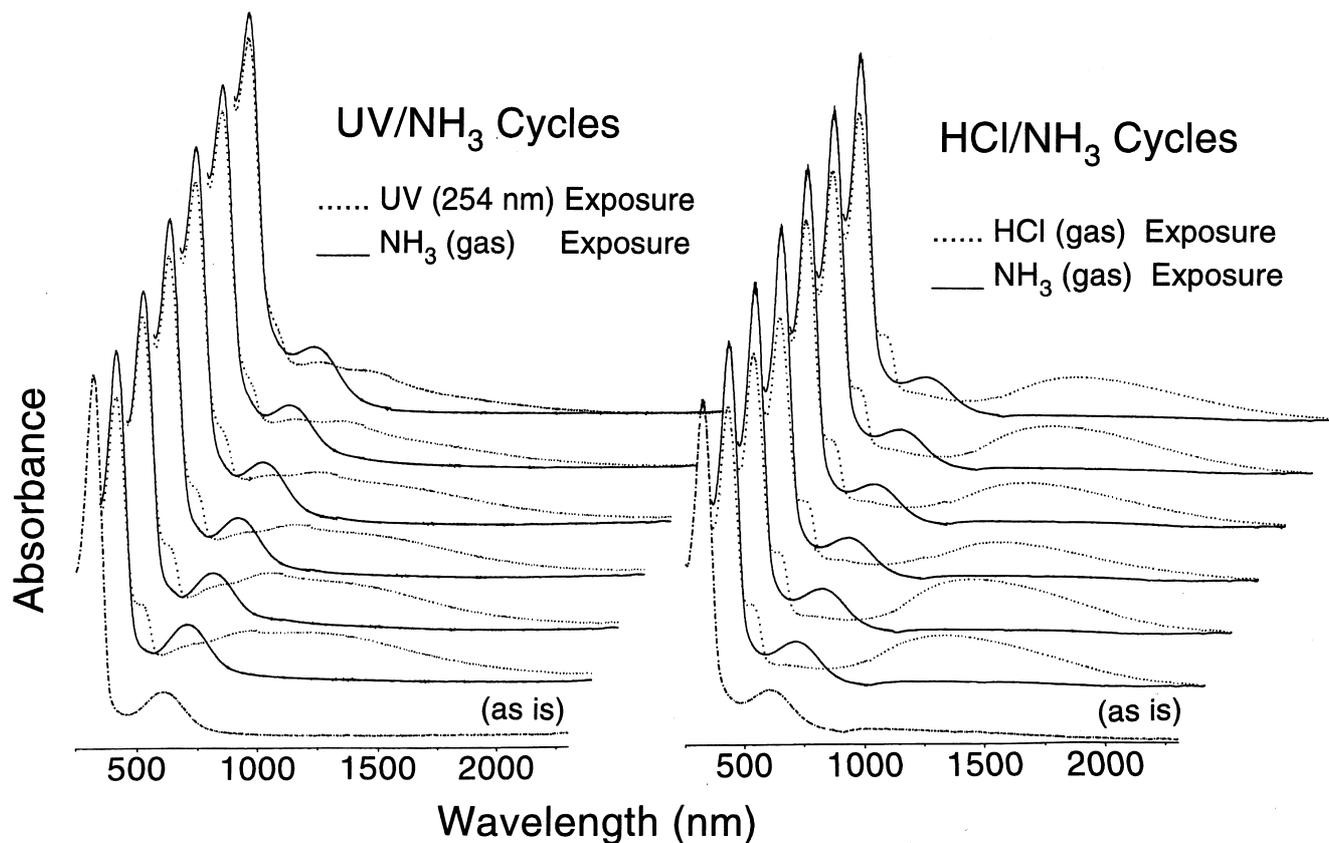
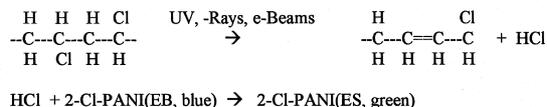


Fig. 4. UV-Vis-NIR spectra of the 2-Cl-PANI/PVC composite films exposed to UV/NH₃ and HCl/NH₃ cycles.

function of e-beams exposure. Here again, increased absorbance of the bands around 1600 and 1160 cm⁻¹ is indicative of doping [2,3,14,18,19]. The overall process can be described as follows:



It is also possible to dope the EB films by direct exposure to HCl vapours. Fig. 4 shows the UV/NH₃ and the HCl/NH₃ cycles. The UV doping process eventually dies off as more and more HCl are removed from the PVC matrix.

4. Conclusions

As a continuation of our previous work on PANI/PVC composite films, we demonstrated that exposure to energetic particles induces doping which can also be reversed to a certain degree. Since the conducting polymer is embedded into the PVC matrix, the measured electrical con-

ductivities are low (in the range of 10⁻³–10⁻² S/cm) for both energetic particle or UV and gaseous HCl-exposed films compared to the conductivities of usual conducting polymers. However, this completely solvent-free novel process can still be useful in several applications like dosimetry, radiation monitoring or on/off devices under irradiation environment, etc.

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