UV-Induced Electrical and Optical Changes in *PVC* Blends

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Summary. 2-Chloro-polyaniline (2-Cl-*PANI*) in its non-conducting (emeraldine base, EB) form, prepared by a chemical route, was dissolved together with poly-(vinylchloride) (*PVC*) in *THF* for casting into thin (10–50 μm) films. Upon exposure to UV radiation, the electrical conductivity of these films increased by more than 4 orders of magnitude (from 10^{-6} to 10^{-2} S/cm). This is attributed to the dehydrochlorination of *PVC* by exposure to energetic photons and subsequent doping of 2-Cl-*PANI* (*i.e.* conversion to emeraldine salt, ES) by *in situ* created HCl. The doped films could be returned to their undoped form by exposure to NH_3 vapours. The UV-induced doping/NH_3 undoping cycles could be repeated several times. Various spectroscopic techniques were employed to follow the changes in the films upon exposure to UV radiation. The same photo-dehydrochlorination process has also been utilized for optical and/or lithographic purposes by preparing *PVC* blends containing methyl violet, and acid-base indicator dye. The photo-dehydrochlorination can be effectively sensitized by incorporating hydroquinone into the *PVC* blends containing methyl violet.

Keywords. Dehydrochlorination of *PVC*; Photochemistry; 2-Chloro-polyaniline; Optical litography; Photochemical sensitization.

Introduction

Exposure of poly-(vinylchloride), *PVC*, to high-energy radiation (γ-rays and UV), energetic particles (electrons, protons, heavy particles), and high temperatures causes extensive dehydrochlorination (loss of HCl) which limits its use for certain applications [1–5]. Therefore, substantial effort has been devoted to the development of additives preventing this process [1, 2]. An equal amount of effort has been devoted to understanding its mechanism; radicalic, ionic, and autocatalytic procedures have been discussed [6–9]. Photodegradation and photochemical modifications of *PVC* and the resulting polyenes have also been extensively studied for improving electrical conductivity of the films [10–12]. It has even been claimed that dehydrochlorinated *PVC* affords polyacetylene-like material [13]. By incorporation of electrically conducting polymers like polyaniline or polypyrrole into *PVC*, either by blending and/or by forming composites, mechanically stable and highly conducting films (in the range of 10^{-5}–1 S/cm) have been obtained [14–19].
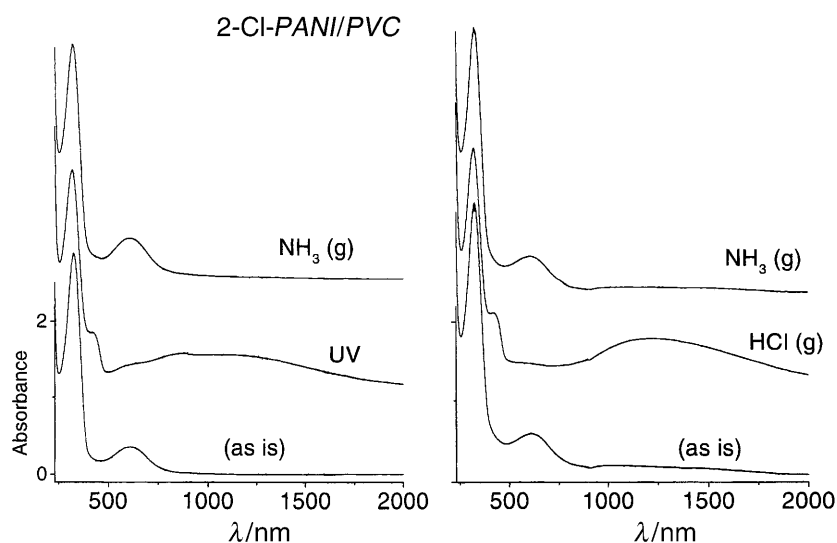
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During the last 4 years our work has concentrated on making use of this dehydrochlorination process by capturing the evolved HCl with *in situ* basic traps for improving the electrical and/or optical properties of *PVC* blends containing additives (a conducting polymer for electrical changes and a dye for optical changes) [20–22]. In this contribution, spectroscopic characterization of the electrical and optical changes of blended films as a result of UV exposure will be presented.

Results and Discussion

Electrical changes: 2-Cl-PANI/PVC blends

Polyaniline (*PANI*) in its doped, conducting form (emeraldine salt, ES) is not soluble or processable, in contrast to its undoped, non-conducting form (emaraldine base, EB). Furthermore, 2-chloro-polyaniline (2-Cl-*PANI*) is by more than one order of magnitude better soluble in *THF* as compared with *PANI*. Doping is very important for tailoring the electronic properties of the resulting product. The conventional methods of doping involve harsh acid treatment either by wet and/or vapour techniques, and alternative routes are highly desirable. Our procedure uses of the dehydrochlorination of PVC to affect the doping. Figure 1 shows the UV/Vis-NIR spectra of the 2-Cl-*PANI/PVC* composite film after 15 minutes of UV exposure with 5 minutes of further exposure to NH_3 vapour. In the same figure, the results of direct acid and NH_3 treatment are also given. The freshly prepared blue film has an absorption band centred around 600 nm and a strong transition around 300 nm (similar to *PANI*) which is indicative of the undoped form of the polymer (EB). The 600 nm band shifts to longer wavelengths upon exposure to UV, and the films become green, indicative of the doped salt form (ES) [24, 25]. Exposure to

Fig. 1. UV/Vis-NIR spectra of a 2-Cl-*PANI/PVC* blend film before and after exposure to UV radiation for 15 min and after further exposing them to NH_3 vapours for 5 min; spectra of the film before and after acid and subsequent NH_3 vapour exposure are also given
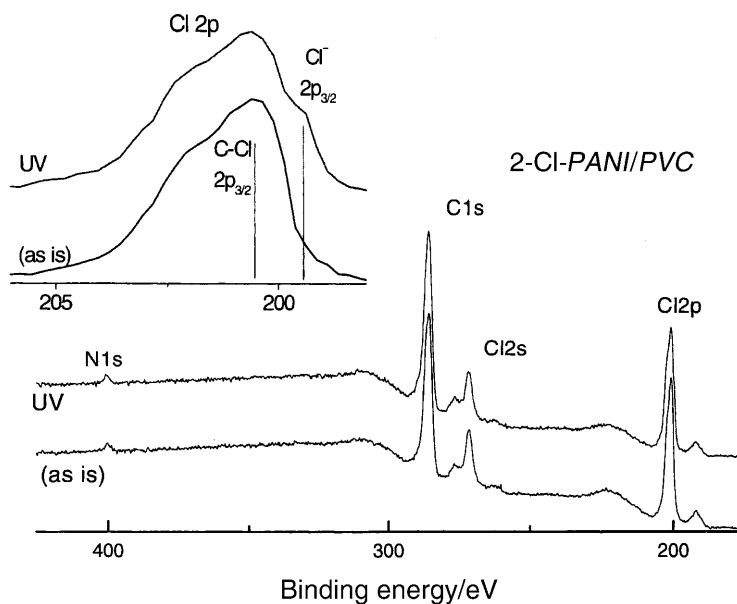
Fig. 2. XPS spectra of 2-Cl-*PANI*/*PVC* composite films before and after UV exposure

ammonia vapour reconstitutes the EB form. The electrical conductivity of the films 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 reach values of 10^{-2} S/cm. We attribute this UV-induced doping mainly to dehyrochlorination of *PVC* as has also been claimed for *PANI*/*PVC* films [20–22]. Our argument is further supported by other spectroscopic findings. Figure 2 shows the XPS spectra of 2-Cl-*PANI*/*PVC* films before and after exposure to UV. In addition to the strong Cl $2p_{3/2}$
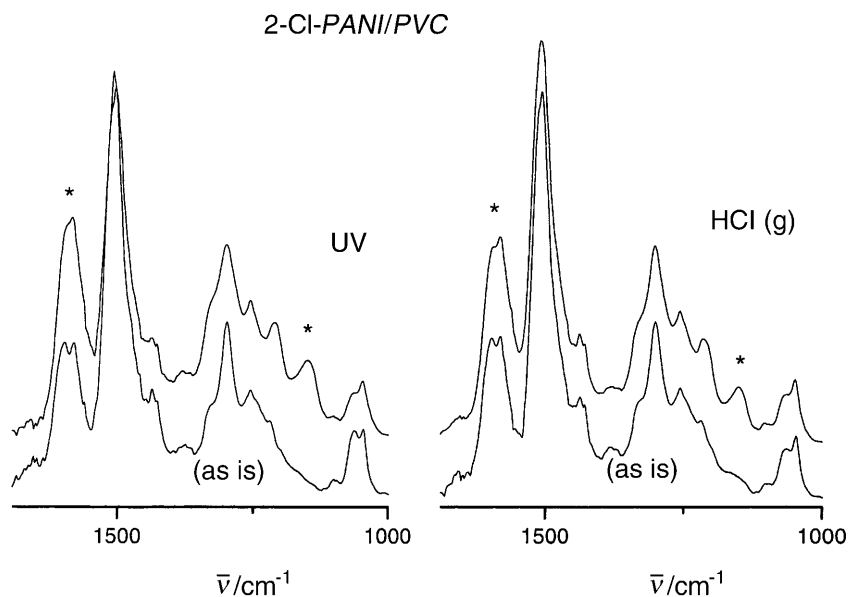
Fig. 3. FTIR spectra of 2-Cl-*PANI*/*PVC* composite films before and after UV exposure
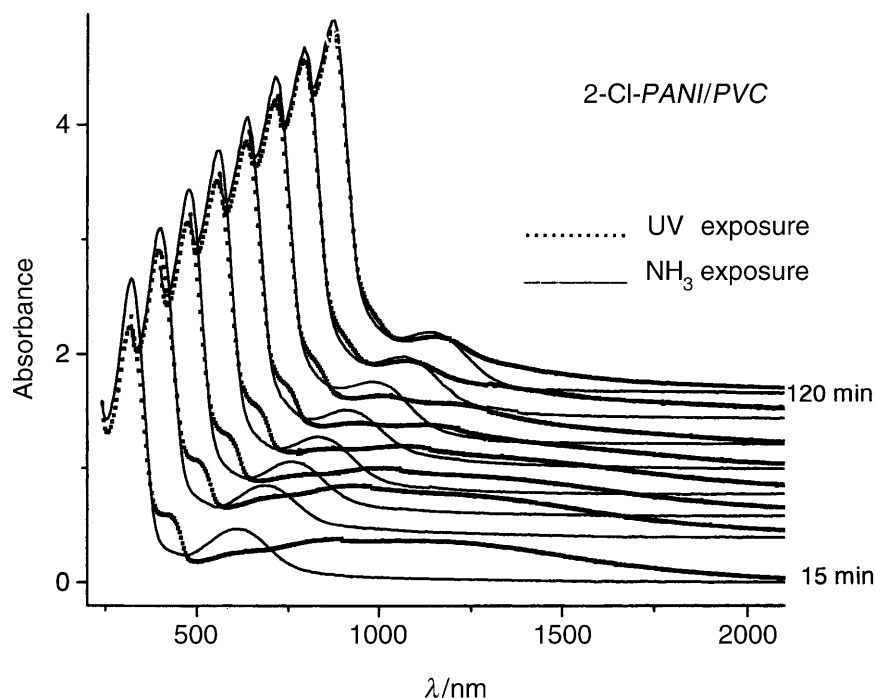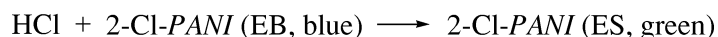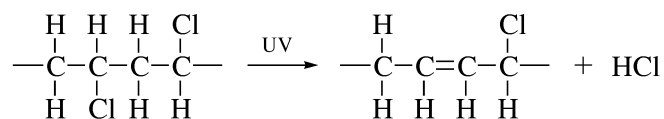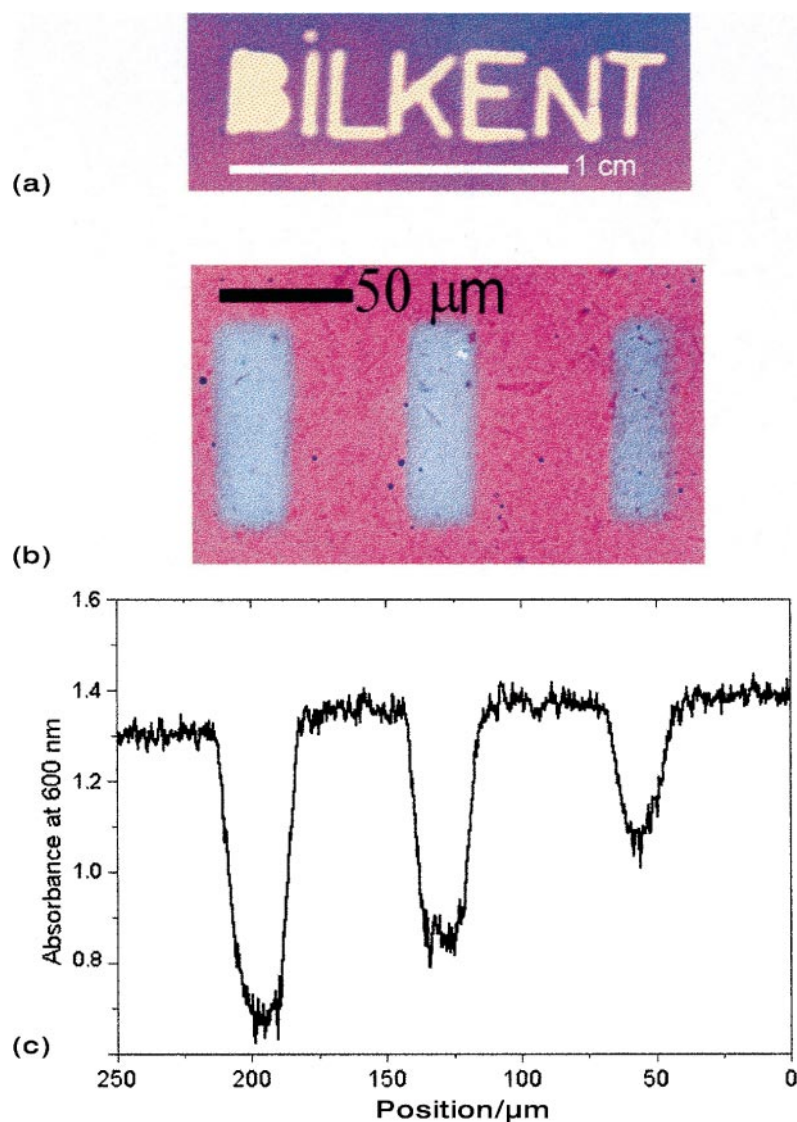
Fig. 4. UV/Vis-NIR spectra of 2-Cl-*PANI*/*PVC* composite films exposed to UV/NH$_3$ cycles

peak at 200.5 eV which is assigned to chlorine bonded to carbon, a shoulder at 199.5 eV develops after exposure to UV which is not observed in 2-Cl-*PANI* films without addition of PVC. This shoulder is assigned to Cl$^-$ and supports the dehydrochlorination of *PVC* as the reason for doping of the EB films [26]. In Fig. 3, FTIR spectra of 2-Cl-*PANI*/*PVC* films are shown before and after UV or acid exposure. Here again increased absorbance of the bands around 1600 and 1160 cm^{-1} is indicative of doping [24–28]. Figure 4 gives the UV/Vis-NIR spectra of a film after several UV/NH$_3$ cycles. The UV-doping process eventually dies off as more and more HCl is removed from the *PVC* matrix. The overall process can be described as follows:

$$\text{—CH}_2\text{—CHCl—CH}_2\text{—CHCl—} \xrightarrow{UV} \text{—CH}_2\text{—CH=CH—CHCl—} + \text{HCl}$$

HCl + 2-Cl-*PANI* (EB, blue) $\longrightarrow$ 2-Cl-*PANI* (ES, green)

Optical changes: methyl violet/PVC blends

The *PVC* matrix itself is slightly acidic, probably due to ever-existing HCl during preparation of the powder. Therefore, different indicators/dyes were tried since some were UV-sensitive and others had an unsuitable range for their colour changes [29]. Methyl violet which changes its colour around *pH* = 1 was found to be most
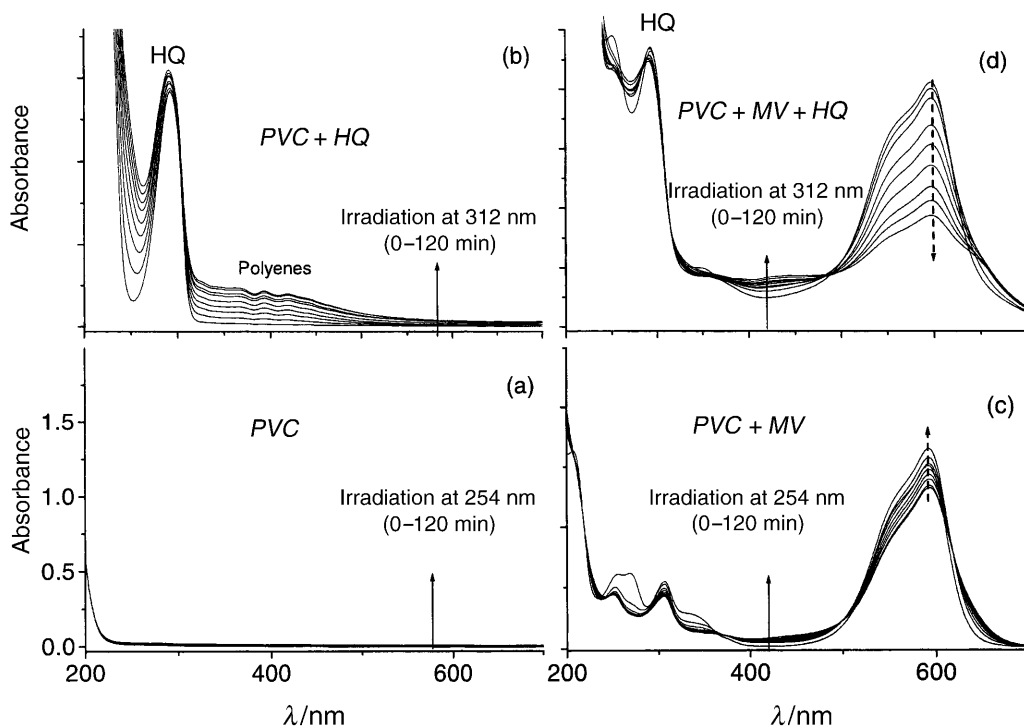
Fig. 5. (a) Photograph of a macroscale lithographic example of a *PVC* film containing methyl violet (10:1 by weight); (b) photograph of a microscale lithographic example of a *PVC* film containing methyl violet (10:1 by weight); (c) lateral absorbance changes of the microscale pattern at 600 nm along the *x*-axis

suitable [29]. Upon exposure to UV radiation it is possible to create macroscale (Fig. 5a) and microscale (Fig. 5b) optical writing which has been stable for more than one year at room temperature. The stability of the optical modification obviously must be related to the correct combination of the dye and the preparation conditions. Figure 5c shows the same microscale pattern in terms of absorbance change at 600 nm along the *x*-axis and in the middle of the print of Fig. 5a. Since the pattern was imprinted *via* the shadow projection method, the pattern lacks fidelity to some extent (blurring and spots). We believe this mainly to result from artefacts of our lithographic tools rather than from the photochemical process which can be

improved using different techniques or masking procedures. Again the reason of the optical changes stems from the dehydrochlorination of *PVC*.

Sensitization of photodehydrochlorination: methyl violet/PVC/hydroquinone blends

It has been long recognized that impurities in *PVC* have adverse photo-chemical effects [1–5]. In Fig. 6 the spectroscopic changes as a result of different UV wavelength and irradiation duration are shown. Although pure *PVC* does not exhibit any appreciable changes when exposed to either 254 or 312 nm radiation for 120 minutes, a blend containing 10% (w/w) hydroquinone undergoes extensive dehydrochlorination as well as polyene formation when exposed to 312 nm UV radiation which corresponds to the maximum of hydroquinone absorption. At the same time, methyl violet is extensively converted to its basic form in the blend containing additional hydroquinone as is further proven by the optical writing displayed in Fig. 7. Dramatic sensitization by hydroquinone is thus clearly demonstrated. The process must obviously involve an efficient energy transfer from the photo-excited hydroquinone to *PVC*. Further studies are needed to elucidate the detailed mechanism of the process.

Fig. 6. UV/Vis-NIR spectra recorded every 15 min for 2 h: (a) thin film of *PVC* exposed to 254 nm radiation; (b) *PVC* blend film containing hydroquinone (*PVC : HQ* = 10 : 1) exposed to 312 nm radiation; (c) *PVC* blend film containing methyl violet (*PVC : MV* = 10 : 1) exposed to 254 nm radiation; (d) *PVC* blend film containing methyl violet and hydroquinone (*PVC:MV:HQ = 10:1:1*) exposed to 312 nm radiation

Fig. 7. Photographs of a macroscale lithographic example of a *PVC* film containing methyl violet (lower field) and methyl violet and hydroquinone (upper field)

Experimental

2-Chloro-polyaniline in its non-conducting form (emeraldine base) was prepared according to a known procedure [23, 24]. The blended films were prepared by dissolving *PVC* and the basic components, 2-chloro-polyaniline or methyl violet, in various weight ratios in freshly distilled tetrahydrofuran (*THF*) and casting the solution into $10–50\,\mu m$ thick films by evaporation of the solvent under a saturated *THF* atmosphere at room temperature. Photolysis of the films was realized by subjecting them to UV-irradiation at 254 or 312 nm. FTIR spectra were recorded using a Bomem 102 spectrometer, and a Cary 5E spectrometer was used in the UV/Vis-NIR range. XPS spectra were obtained using a Kratos ES300 electron spectrometer. The large scale pattern was imprinted by irradiating the film through a $200\,\mu$ steel mask with the UV source. The script 'BILKENT' was cut in the steel mask with an industrial CO_2 laser, and it was placed on top of the sample. For the microscale lithographic study, a Zeiss UMSP 80 microscope spectrometer equipped with a 75-Watt Xe source was used. The sample was placed on a scanning *xy*-stage with sub-micron resolution. The microscale pattern was imprinted by irradiation of the film through a quartz mask with a previously printed pattern. The mask was placed after the monochromator, and the shadow of the mask was projected on the sample. After irradiation at 300 nm, the lateral absorbance change of the pattern at 600 nm was recorded, and the photograph of the pattern was taken with 40-fold magnification.

Acknowledgements

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