

Spectroscopic Investigation of Onset and Enhancement of Electrical Conductivity in PVC/PANI Composites and Blends by γ -ray or UV Irradiation

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Electrical conductivity of blends and composites of poly(vinyl chloride) (PVC) with nonconducting polyaniline (PANI) increases when they are subjected to γ -rays or UV radiation. This is attributed to a radiation-induced dehydrochlorination (loss of HCl) of PVC, which in turn oxidizes (dopes) PANI within the PVC matrix causing the increase in electrical conductivity of these films. XPS, UV-vis-NIR and FTIR spectroscopic methods are used to characterize and verify this novel process. After the films are subjected to γ -rays (or UV radiation) the intensities in the XPS spectra of both $-N^{+}$ and Cl^{-} peaks increase, confirming the increase in charged species within the PVC matrix. Similar observations attributable to radiation-induced electrical conductivity are also observed in both the UV-vis-NIR and FTIR spectra. This radiation-induced conductivity can also be reversed to some extent by further exposing the films to NH_3 vapors, where the oxidized centers are partially reduced (undoped). Several UV/ NH_3 /UV cycles can be performed without much loss in conductivity- and/or conductivity-related spectroscopic features. The onset of the photoinduced conductivity both in PVC-only and PVC/PANI composite films is determined to be 300 nm (4.1 eV), which coincides with the first UV absorption band of PVC.

Introduction

Conducting organic polymers, prepared by both chemical and electrochemical routes, have been the focus of intense scientific activity for the past 10–15 years, and various very successful applications have been reported.¹ To improve the stability/functionality and/or range of applications of these materials, blending or making composites with other polymeric materials has also been successful.² Blending or forming composite of polyaniline, PANI, with poly(vinyl chloride), PVC, has been suggested for certain applications.³

PVC undergoes a high degree of dehydrochlorination (i.e., losing HCl), which limits its use for radiation processes such as sterilization, radiation-induced improvement, and/or stabilization.^{4,5} On the other hand electroactive polymers such as PANI lack the usual properties of common polymers (stability, processibility, etc.). Furthermore, electrical conductivity of the electroactive polymers increases when exposed to acids. Therefore, a synergism is expected to take place when a suitable prepared composite or blend of PVC/PANI is exposed to high-energy radiation like ^{60}Co γ -rays, UV light, or other energetic particles. The radiatively created HCl from the PVC is expected to be captured by the neighboring PANI moieties and become electrically conductive.

Attention has been recently devoted to investigate and understand the effects of ionizing radiation on conjugated polymers to either alter some particular polymer properties,⁶ or probe the changes in polymer properties,⁷ or to measure the radiation doses by following the changes in polymer properties.⁸ Our approach, the radiation-induced doping via an acid/base

chemistry within the PVC matrix, parallels these ideas but is totally different from the usual chemical and/or electrochemical methods of preparation of conducting polymers and is a novel method with unique and unforeseen possibilities.

Experimental Section

The composite films were prepared by dissolving aniline together with the commercially available PVC (Aldrich, high molecular weight) in THF (Aldrich) and cast into films by evaporation of the solvent. These films were later oxidized by $(NH_4)_2S_2O_8$ (Aldrich) in acidic (HCl or H_2SO_4) aqueous solutions according to the well-established methods.⁹ Subsequent reduction was achieved by treating the films with aqueous NH_4OH or NaOH. The blend films were prepared by first preparing the corresponding polyaniline either in conducting (acidic) or nonconducting (basic) forms and later dissolving it in THF together with PVC and casting the films after evaporation of the solvent. The resulting films with varying thickness between 10 and 50 μm were thoroughly washed and dried before analyses.

Electrical conductivities of the films were measured using a four-point probe which had a sensitivity of 10^{-6} S/cm or higher. Radiolysis or photolysis of the films was realized by subjecting them to either ^{60}Co γ -rays at varying doses (50–600 kGy) or a low-pressure Hg light source ($\lambda = 254$ nm, 4.9 eV) for varying duration. To reverse the radiation-induced changes, some of these films were further subjected to NH_3 vapors. Several UV/ NH_3 /UV exposure cycles were also conducted to check the reversibility of the process.

To obtain further insight into the photolysis, a different batch of samples were exposed (for a predetermined period) to the

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selected monochromatic light source of the UV-vis-NIR spectrometer in the sample compartment, following a fast recording of the spectrum in the 300–750 nm range.

A Kratos ES 300 electron spectrometer with Mg K α X-rays at 1253.6 eV was used for recording the XPS spectra. The base pressure was kept below 5×10^{-9} Torr during recording. Due to degradation and discoloring of the films by the bombarding X-rays, low dosage (12 kV, 5 mA) and short recording times (1–5 s/point) were employed. FTIR, UV-vis-NIR, and FTIR spectra of the films were recorded using Bomem MB102 and Cary 5E spectrometers, respectively. Multiple preparation and/or measurements were performed to ensure reproducibility.

Results

Electrical conductivity of our PVC/PANI composite and blend films prepared in the nonconducting (basic) form increased by 3–4 orders of magnitude (from less than 10^{-6} S/cm to ca. 10^{-3} – 10^{-2} S/cm) when exposed to ^{60}Co γ -rays for a dose of 200 kGy or higher (due to the limitations of our conductivity measurements, we could not detect any changes in electrical conductivity of the films at lower doses). A similar increase is also obtained by exposure to 254 nm UV radiation. However, no electrical conductivity (within the limitations of measurements) could be detected in PVC-only films treated in the same way. The conductivity of the films prepared in the conducting (acidic) form was already on the order of 10^{-3} S/cm; as a result, an increase in conductivity after such an exposure was not detectable for these already conducting films. It is well-known that exposure to high-energy radiation creates charge carriers which may also cause increase in electrical conductivity; hence, the origin(s) of the increase in the electrical conductivity of our samples needed careful spectroscopic investigation. The films used for electrical measurements could not directly be used for IR and UV-vis-NIR spectroscopic investigations due to their extremely high absorbing capacities of the electromagnetic radiation. Hence the films used for these spectroscopic measurements were subjected to much lesser doses (ca. 50–100 kGy) than those used for electrical and/or XPS measurements. Nevertheless, several measurements were performed on samples exposed to doses between 50 and 400 kGy to ensure that those spectroscopic measurements were representative.

XPS Characterization. Information that can be derived and limitations of the XPS technique have been discussed and reviewed recently.^{10–13} Accordingly, although XPS is essentially a surface technique, some features can be correlated with bulk compositions as well.^{13,14} The relevant parts of the XPS spectra of PVC/PANI composite films in conducting (acidic) and nonconducting (basic) forms before and after exposure to the γ -rays are shown in Figure 1. In the spectrum (not shown here) of PVC only one Cl 2p spin-orbit doublet ($2p_{3/2}$ at 200 eV) and two C 1s and no N 1s peaks are observed, in agreement with the compiled reference XPS spectrum of PVC.¹⁵ The spectrum of the composite films in the conducting form contains one additional Cl 2p doublet at lower binding energy and three C 1s and two N 1s peaks. Assignment of the C 1s is not relevant to our findings and will not be discussed. The additional Cl 2p doublet can be assigned to chloride ion Cl^- ($2p_{3/2}$ at 199.5 eV) and two N 1s to neutral $-\text{N}-$ and oxidized $-\text{N}^+-$ moieties of the PANI component. The intensity of the $-\text{N}^+-$ peaks is closely related to the intensity of the Cl^- peaks, which are also related to the concentration of charge carriers giving rise to the electrical conductivity of these films.^{10–14} This point is also verified in the spectrum of the composite films in the nonconducting (basic) form, where intensities of both Cl^- peaks and $-\text{N}^+-$ are lowered. However,

PVC/PANI(basic)+Radiation

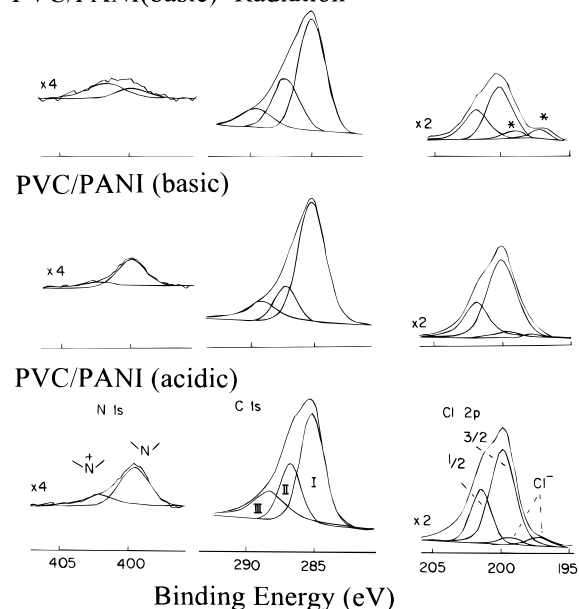


Figure 1. Part of the XPS spectra of PVC/PANI composite films in conducting (acidic) and nonconducting (basic) forms. The figure also contains the spectrum of the nonconducting form after subjected to ^{60}Co γ -rays.

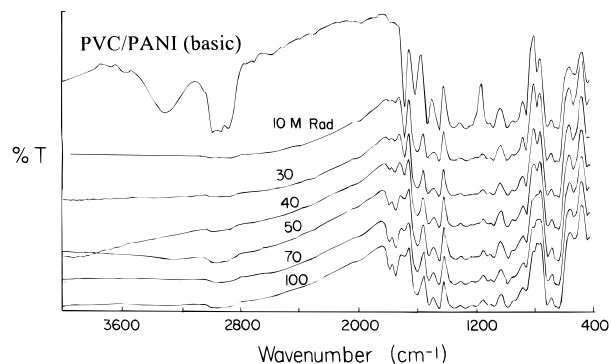


Figure 2. FTIR spectra of nonconducting (basic) PVC/PANI composite film before and after subjected to indicated doses of ^{60}Co γ -rays.

when the same nonconducting film is exposed to γ -rays, the intensity of both the Cl^- and $-\text{N}^+-$ peaks increases. Since these films do not contain ample charge carriers beforehand, it is clear that the HCl created in situ, as a result of the radiolysis, is captured by undoped, neutral PANI moieties to affect formation of new charged PANI^+Cl^- moieties, hence the electrical conductivity. Similar spectra are obtained for blend films and by exposing the films to the 254 nm UV radiation.

FTIR Characterization. In Figure 2, we display the spectrum of the nonconducting (basic) form of the composite film and after exposure to several doses of ^{60}Co γ -rays in air. Three important features are noteworthy. (i) Carbonyl bands around 1700 – 1800 cm^{-1} appear and gain more intensity with dosage. (ii) The free carrier absorption broad band starting around 1600 cm^{-1} is a clear indication of increase in electrical conductivity. (iii) There are several characteristic changes in the 1640 – 400 cm^{-1} region, some of which can be identified with structural changes associated with electrical conductivity.^{16–23} Appearance of carbonyl bands can be prevented by performing the γ -ray exposure in a vacuum, but other features indicating the increase in electrical conductivity remain.

UV-Vis-NIR Characterization. In Figure 3, we display the UV-vis-NIR spectra of the similar approximately 15 μm

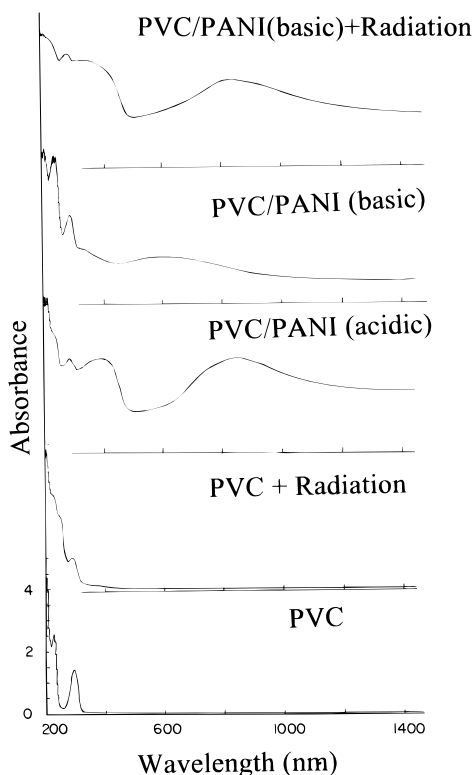


Figure 3. UV-vis-NIR spectra of films of 15 μm thick PVC, conducting (acidic) PVC/PANI composite, and nonconducting (basic) PVC/PANI before and after subjecting to ^{60}Co γ -rays.

films used for XPS analysis. PVC has three strong absorption bands in the UV region around 300 nm. The greenish conducting PVC/PANI films have absorption bands in all regions and especially a broad band starting from 600 nm extending to the NIR region which is usually associated with electrical conductivity.^{16–25} For the bluish nonconducting PVC/PANI composite films this absorption is weaker and is strongly blue-shifted. After exposure to the ^{60}Co γ -rays the absorption spectrum of this nonconducting film matches that of the conducting counterpart, as evidenced by its spectrum.

Similar changes can also be affected by 254 nm UV exposure, as shown in Figure 4. In the same figure we also show that the spectral (and the corresponding electrical conductivity) changes can be reversed by further exposure of these films to NH_3 vapor. Several UV- NH_3 -UV cycles can also be realized, as demonstrated in the same figure. Similar spectra are also obtained by exposing to HCl vapors instead of radiation.

Photolysis. To get further insight into the mechanism and determine the onset of the photolysis, we exposed the films to monochromatic light with varying energies starting from NIR (800 nm) going down into the UV region. In Figure 5 we display the part of the absorption spectra of PVC-only and the nonconducting PVC/PANI films after exposure to 30 min of light with the corresponding energy within the sample compartment of our spectrometer. As can be seen from the figure, both PVC and the composite film undergo a drastic change only after exposure to light at 300 nm (4.1 eV). The change in PVC is a simple UV degradation,^{4,5} whereas the change in the composite is exactly what was observed by either the ^{60}Co γ -radiolysis or UV photolysis.

Discussion and Conclusions

Our spectroscopic analyses and photolysis investigation all confirm that the radiation-induced dehydrochlorination of PVC

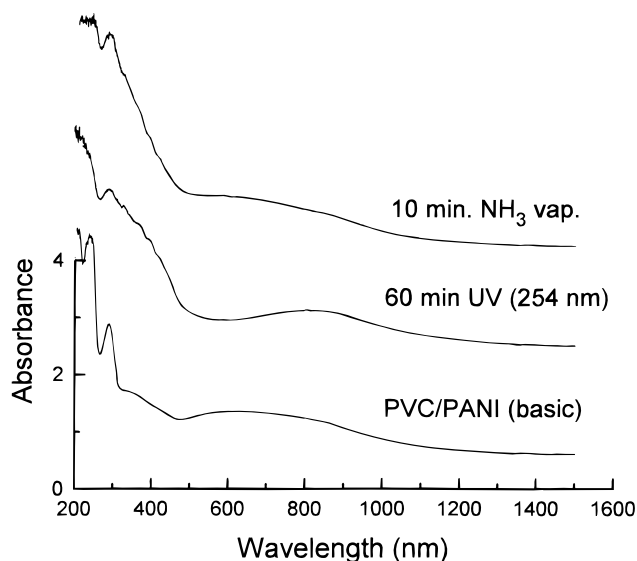
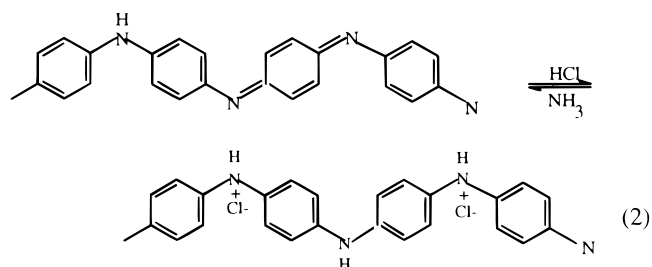
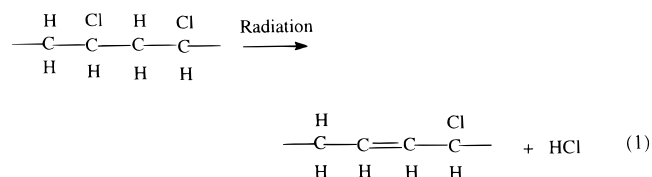
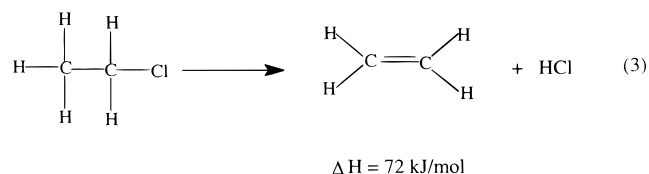


Figure 4. Spectra showing the effect of the UV/ NH_3 /UV cycles.

is the reason for the induced electrical conductivity of the polyaniline moieties within the PVC matrix, which can be described as



The photolysis onset for this process is 300 nm, corresponding to 4.1 eV, and is too high for a possible molecular HCl elimination mechanism, which can be estimated from the enthalpy of the following gas-phase reaction:²⁶



The other possibility is the mechanism for Cl atom abstraction with the subsequent attack on the neighboring H, leading to HCl elimination. The energy required for this second process can be estimated from the C-Cl bond energy, which is 330 kJ/mol, or 3.4 eV, and is much closer to our spectroscopic onset and obviously coincides with the strong absorption band of the PVC matrix.

In our process, since the conducting medium (PANI) must be imbedded in the PVC matrix, very high conductivities on the order of 10^1 – 10^3 S/cm, typical for conventional conducting polymers, cannot be reached, which naturally limits its applications. However, on/off devices under irradiation environments,

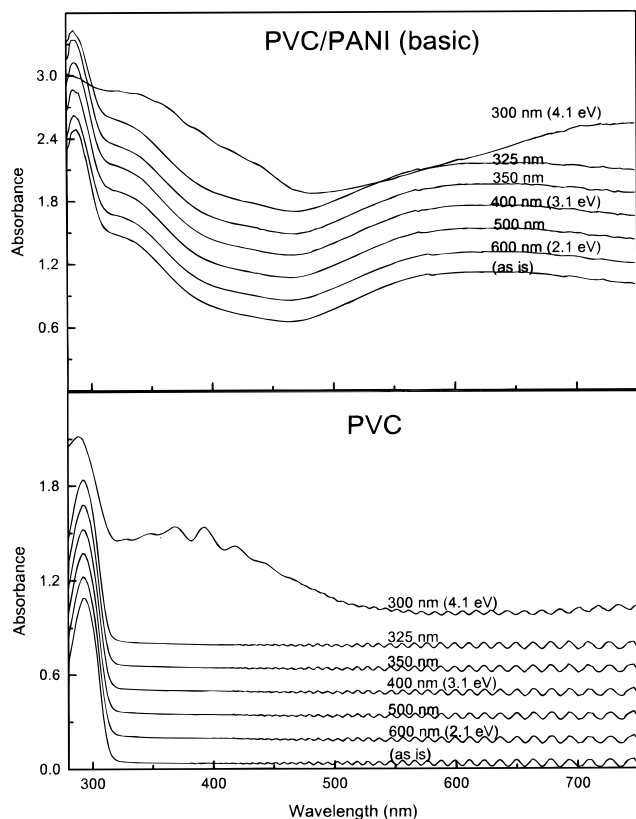


Figure 5. UV-vis spectra of (i) (lower part) 15 μm thick PVC film before and after subjecting to 30 min radiation with the indicated energy in the sample compartment of the spectrometer; (ii) (upper part) 15 μm thick nonconducting PVC/PANI composite film with the same treatment as PVC.

radiographic imaging/lithography, dosimetry, and/or radiation monitoring are among some possible applications using this novel process since the acid-base (or the oxidation-reduction) chemistry is accomplished within the PVC matrix rather than using the usual wet chemical and/or electrochemical methods.

Although most of the spectra refer to composite films, comparable changes in both electrical and spectral features have also been obtained for blend films. Differences between the two and limitations of this radiation-induced electrical conductivity need further studies.

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