Radiation-Induced Conductance in The Blends of Poly(Aniline-Base) With Poly(Vinyl Chloride) and Poly[(Vinylidene Chloride)-*co*-(Vinyl Acetate)]

*H. Bodugoz**[1], *U. A. Sevil*[2], *O. Güven*[1]

[1]Department of Chemistry, Hacettepe University, Beytepe, 06532, Ankara, Turkey
[2]Ankara Nuclear Research and Training Center, Saray, 06105, Ankara, Turkey

Bodugoz@eti.cc.hun.edu.tr

Summary: In this study blends of Poly(Aniline-Base)/Poly(Vinylidene Chloride) co-(Vinyl Acetate) were exposed to radiation to increase the conductance of Poly(Aniline-Base). Aniline was polymerized by following the procedure of Focke's chemical oxidation method and Poly (vinyl acetate / poly (vinylidene chloride),(PVAc/PVnCl), copolymer was synthesized by solution polymerization Various Poly(Aniline-Base)/Poly(Vinylidene Chloride) co-(Vinyl Acetate) films were prepared which were then exposed to gamma rays. The change in the structure was investigated by FT-IR and UV-visible spectorphotometer.

INTRODUCTION

Conducting polymers have attracted considerable scientific and technical interest in recent years. Polyphenylene, polypyrrole, polythiophene and polyaniline have been applied in the development of batteries, electronic devices, displays, sensors, functional electrodes.

Most of the organic polymers are insulators. Some polymers with conjugated π - electron backbones become electrically conducting, however if they are treated with strong oxidizing or reducing agents. The process that induces an insulator to conductor transformation in such polymers is called as "doping". A significant portion of the conducting polymer studies has been devoted to the case of polyaniline (Macdiarmid et al.,1989).

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Polyaniline (PANi) has three different oxidation states which are called leucomeraldine, pernigranilene and emeraldine. Only emeraldine polymer exhibits conductivity. If emeraldine base polymer is treated with acidic solution (either organic or inorganic protonic acids) with pH lower than 4, it is converted to emeraldine salt form which is the conducting form of the emeraldine polymer If the polymer is treated with a solution with a pH greater than 4, the polymer becomes insulator. Their further utilization is expected to be increased with developments in the preparation of composite structures containing conductive polymers. Poly(vinyl chloride) (PVC), is known to undergo extensive dehydrochlorination when exposed to energetic radiations like gamma rays, accelerated electrons, etc. Similar effect has been observed for poly(vinyl acetate) (PVAc), when it is irradiated with ionizing radiations causing the release of acetic acid. The electrical conductivity of poly(aniline-base)is known to increase when exposed to strong acids like HCl. Therefore onset and further enhancement of conductivity in the films prepared from PANI-B and PVC and PANI-B and PVAc are expected when they are irradiated with ionizing radiations (Sevil, Güven and Süzer,1998). Various PANI-B/PVC composite films were prepared using chemically prepared PANI-B (Toshima et al. 1995) which were then exposed to gamma rays. Similar films were also prepared from PANI/PVAc-PVnCl mixtures to see the effect of later copolymer structure.

EXPERIMENTAL PART

MATERIALS

All monomers, oxidants and solvents used in this study were obtained from Carlo Erba Co. Vinylidene chloride and vinyl acetate monomers were obtained from BDH. The aniline monomer was distilled twice before use. The solvents tetrahydrofurane (THF) and dimetyl formamide (DMF) were used without any purification.

METHOD

Synthesis of Polyaniline

Polyaniline was synthesized following the procedure of Focke'S (1987) chemical oxidation method. Aniline monomer was dissolved in 1 M hydrochloric acid (HCl), and ammonium persulphate oxidant was added as initiator after dissolving in 1M HCl. Green precipitate was filtered and washed several times with HCl until became colorless. The polymer, polyaniline obtained from this method is conductive polyaniline and called as emeraldine-salt (PANI-salt).

Synthesis of Poly (vinyl acetate) / poly (vinylidene chloride) (PVAc/PVnCl) copolymer

Poly (vinyl acetate / poly (vinylidene chloride),(PVAc/PVnCl), copolymer was synthesized by solution polymerization of respective monomers at 50 ^{0}C AIBN was used as initiator and polymerization was carried out at nitrogen atmosphere.

Synthesis of Poly(aniline)/Poly(vinyl chloride) and Poly(aniline)/Poly(vinylidene chloride) Blends

It is not possible to synthesize PANI/PVC and PANI/PVnCl by using conductive PANI-salt. Because PANI- salt is insoluble in THF and DMF. So it must be first converted into soluble PANI-base.

In the sythesis of PANI-base, 1 gram PANI-salt was poured into 400 mL 0.5M ammonium hydroxide solution. After mixing for three hours, the solution was filtered and the polymer was dried under dynamic vacuum. Upon treatment with 0.5 M NH_4OH solution, substituted polyanilines become sligtly soluble in THF and completely soluble in DMF. After dissolving PVC and PVAc/PVnCl in DMF separately, these solutions were mixed with PANI-base solutions. Homogeneous solutions of these polymers transferred into petri dishes to obtain smooth films. Polymer films were dried under vacuum to remove solvent. Polymer films were irradiated in ^{60}Co-gamma source at room temperature to various doses.

CHARACTERIZATION

Nicolet 520 model FT-IR spectrometer used for the spectroscopic analysis of films. UV-vis spectrophotometer was also used for the characterization.

RESULTS AND DISCUSSION

PVC undergoes a high degree of dehydroclorination when exposed to gamma rays. We thus expect that this released HCl would be trapped by the nonconducting PANI emeraldine base present in the blends and becomes converted to its conducting salt form (Figure 1). From the FT-IR data (Figure 2) we have determined that the intenstiy of the peaks in 1200-800 cm^{-1} region was changed upon exposure to radiation. The peaks at 1315, 1140 and 810 are related with the change in the electrical conductivity of the material (Sevil and Güven, 1998) and their intensities increased with radiation dose. The band at 1723 cm^{-1} was due to the C=O groups.

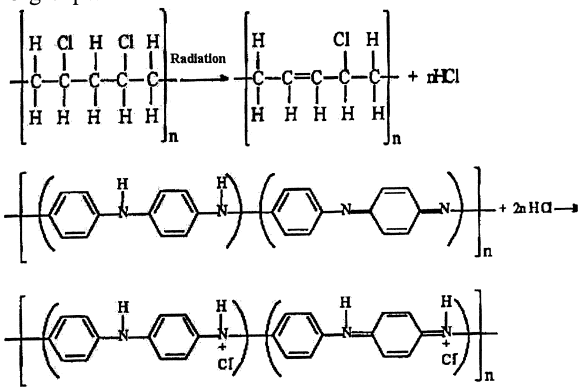

Figure 1: Radiation induced conductivity mechanism of PANI/PVC.

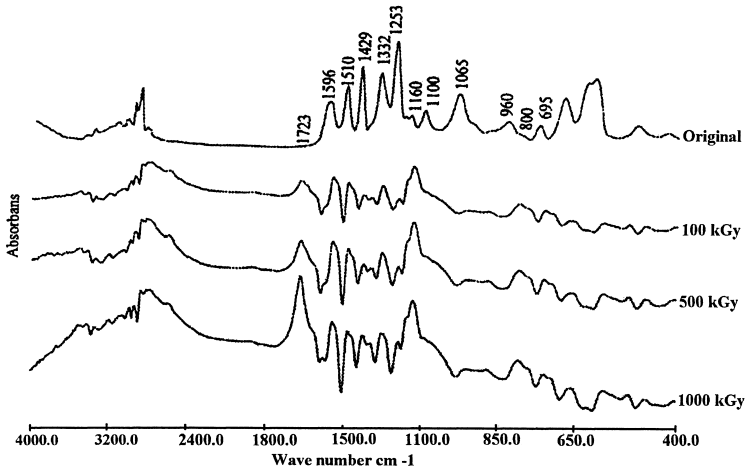

Figure 2: Ft-IR spectra of PANI/PVC blends at different dose.

There are also features which change with radiation dose in the UV-vis spectra (Figure 3). Nonconducting blends have strong absorption bands in all regions and especially a broad band around 600 nm. After these films are exposed to gamma irradiation, absorption of the characteristic peaks of the nonconducting form decrease with increased radiation dose and a new band around 800 nm arises and grows stronger with irradiation dose. To investigate the effect of weak acid group on the conductivity of PANI, PVAc blends were prepared but the results were not AS good as in the case of PVC. By considering the strong effect of HCl , we decided to increase the radiation induced HCl emission by using PVnCl. For this purpose we synthesized PVAc/PVnCl copolymers in 1/1 mole ratio. PVAc content in the copolymer provided us to prepare smooth films. PVAc/PVnCl- PANI blends thus prepared were irradiated at 100 kGy and 500 kGy doses. Figure 4 shows the FT-IR spectra of these films. Figure 5 shows the Uv-vis spectra of 500 kGy irradiated films. Similar effect as in the case of PVC can be seen in this figures. The increase in band intensity at 1140cm $^{-1}$ is related with the increase in conductivity. The is increase is more noteworthy in 500 kGy irradiated films.

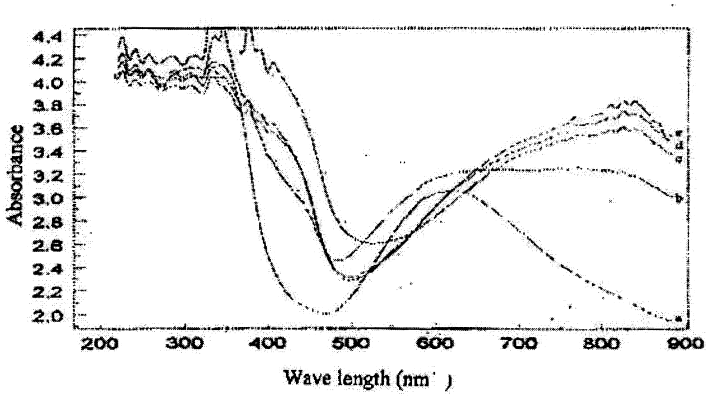

Figure 3: UV-vis spectra of PANI/PVC blends at different dose a) Original, b)100 kGy c)200 kGy, d) 500 kGy e)1000 kGy.

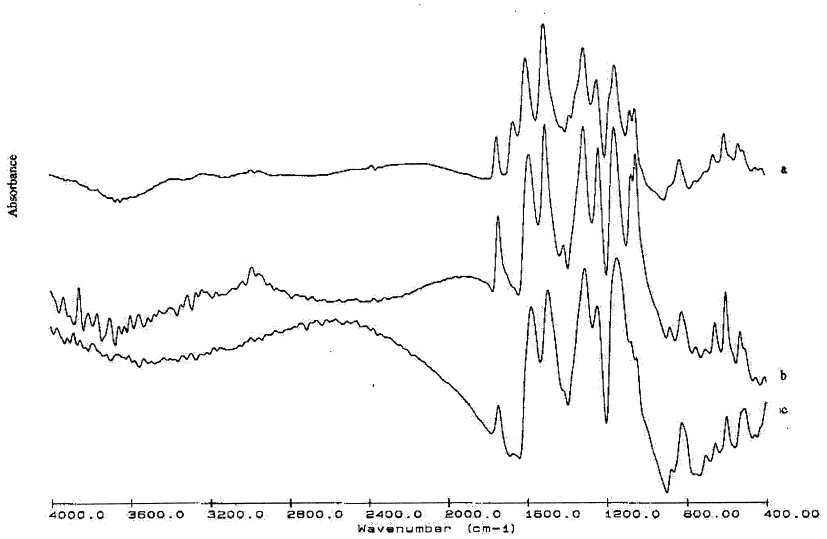

Figure 4 Ft-IR spectra of PVnCl/PVAc-PANI blends a)original b) 100 kGy irradiated c) 500 kGy.

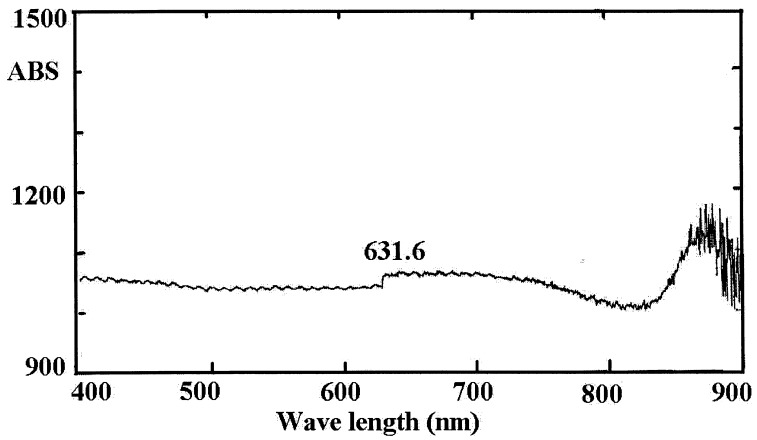

Figure 5: UV-vis spectra of 500kGy irradiated PVnCl/PVAc-PANI.

CONCLUSION

By irradiating PVC- PANI and PVAc/PVnCl-PANI blends with gamma rays, radiation induced conductivity was observed. HCl gas which is the major radiolys product of pvc and PVAc/PVnCl caused the nonconductive PANI base to become conductive. Further experiments are planned to increase the conductivity of PANI-base. In the related previous studies (U. Sevil and O .Guven), conductivity studies using four probe method on the irradiated films indicated that conductivity of the films increased with increasing dose. Pristine films showed a conductivity of 10-8 S/cm in average. Irradiation of blend films to several hundred kGy caused an increase in conductivity up to 10-2 S/cm .

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