Radiation-induced conductivity control in polyaniline blends/composites

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Abstract

Polyaniline (PANI) blends with chlorine-containing polymers and copolymers and composites with HCl-releasing compounds were prepared to investigate their radiation response in terms of induced conductivities. Blends of non-conductive PANI with poly(vinyl chloride) (PVC), poly(vinylidene chloride-co-vinyl acetate), [P(VDC-co-VAc)], poly(vinylidene chloride-co-vinyl chloride), [P(VDC-co-VC)] were prepared in the form of as-cast films. A number of blends which are different in composition were exposed to gamma radiation and accelerated electrons to various doses, and the effects of irradiation type and composition of polymers on the conductivity of films were investigated by using conductivity measurements and UV–vis and FT-IR spectroscopy. The results clearly showed that ionizing radiation is an effective tool to induce and control conductivity in the blends of PANI-base with chlorine-carrying polymers as well as its composites prepared from HCl-releasing compounds such as chloral hydrate. The main mechanism behind this radiation-induced conductivity is in situ doping of PANI-base with HCl released from partner polymers and low molecular weight compounds by the effect of radiation.

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1. Introduction

Electrical properties of conductive polymers have been demonstrated to be changed over the full range from an insulator to a metallic conductor. Polyaniline (PANI) is one of the conductive polymers that received considerable attention in recent years for several important reasons: the monomer is inexpensive; the polymerization reaction can be easily controlled to give high yields; and PANI shows excellent thermal and chemical stabilities. Non-conductive PANI can be rendered conductive either by acid doping or oxidation. The emeraldine salt form of PANI can be easily obtained by HCl doping which imparts good environmental and thermal stability while enhancing relatively high conductivity. The concept of doping is of fundamental importance in understanding, evaluating and controlling of conductivity in conductive polymers. Reversible doping of conducting polymers can be accomplished either by chemical doping or electrochemical doping. During the doping process, an organic polymer with insulating properties is converted into a polymer approaching metallic conductivity. As described elegantly by Heeger (2002), reversible charge injection by ‘doping’ can be accomplished in a number of ways: (i) chemical doping by charge transfer; (ii) electrochemical doping; (iii) photodoping; (iv) charge injection at a metal–semiconducting polymer interface.

PANI holds a special position among all conducting polymers as shown by Salanneck and co-workers (1986) in the mid-1980s that it can be doped by two completely different processes: protonic acid doping and oxidative doping. Protonic acid doping of emeraldine-base units of PANI by 1 M HCl, for example, results in complete protonation of imine nitrogen atoms to give the fully protonated emeraldine hydrochloride salt (Chiang and MacDiarmid, 1986). By adjusting the HCl doping level as a function of pH of HCl doping solution a conductivity anywhere between the non-doped (10^{-10} S cm^{-1}) and fully doped (10 S cm^{-1}) form of the polymer can be easily obtained. Principle forms of
PANI-base are given in Fig. 1. Leucoemeraldine base corresponds to the fully reduced, whereas pernigraniline base to the fully oxidized forms of PANI.

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, as shown in Fig. 2. If the polymer is treated with a solution with pH greater than 4, the polymer becomes insulator (Chiang and MacDiarmid, 1986).

Poly(vinyl chloride) (PVC) is known to undergo extensive dehydrochlorination (resulting in mainly loss of HCl) when exposed to energetic radiations like gamma rays, accelerated electrons, etc. Therefore, onset and further enhancement of conductivity in the films prepared from PANI-base and PVC was observed when they were irradiated with ionizing radiation (Sevil et al., 1998). Since poly(vinylidene chloride) (PVDC) also undergoes a high degree of side chain degradation when exposed to ionizing radiation (resulting in extensive loss of HCl) as in the case of PVC, the main objective of this work has been the preparation of PANI/PVDC copolymer blends and improve their conductivities using gamma irradiation. For this purpose blends of poly(aniline-base) with PVC, poly(vinylidene chloride-co-vinyl acetate) [P(VDC-co-VAc)] and poly(vinylidene chloride-co-vinyl chloride) [P(VDC-co-VC)] were prepared and exposed to gamma rays (Bodugöz and Güven, 2005). Their physical and chemical properties were investigated by spectroscopic methods and dependence of conductivity on irradiation dose and changing composition of the components in the blends were analyzed systematically. Preliminary results regarding the use of a small molecular weight compound, namely, chloral hydrate as the source of HCl for inducing conductivity in PANI-base composite were also reported (Uzun et al., 2006).

2. Experimental

2.1. Materials

Aniline, vinylidene chloride and vinyl acetate monomers were obtained from BDH. Ammonium persulfate \([\text{NH}_4\text{C}_138\text{S}_2\text{O}_8]\) was used as initiator in this study and obtained from Carlo Erba Co. The aniline monomer was distilled twice before use. [P(VDC-co-VC)] (Aldrich) was used as purchased. The solvents N-methyl pyrrolidone (NMP),

![Fig. 1. Various oxidation states of polyaniline depicting the lowest oxidation state of PANI-LEB and the highest, PANI-PNB.](image1)

![Fig. 2. Protonic acid doping of emeraldine base yields the corresponding conductive salt form.](image2)
tetrahydrofuran (THF) and dimethyl formamide (DMF) were obtained from Aldrich and used without any purification.

2.2. Methods

PANI was synthesized by following the procedure of Focke’s chemical oxidation method (Focke et al., 1987). The PANI obtained by this method is conductive PANI and is called as emeraldine-salt (PANI-salt). Vinylidene chloride and vinyl acetate mixtures were irradiated in a $^{60}$Co gamma cell to various doses in air to obtain copolymers with varying compositions. For solution casting of PANI/PVC and PANI/P(VDC-co-VAC) films, PANI-base and PVC and PVDC copolymers were pairwise dissolved in NMP/THF. Homogeneous solutions of these polymer mixtures were transferred into petri dishes to obtain smooth films. Film samples were prepared in different mol ratios on repeating unit basis of respective PANI and partner polymers. The same procedure was followed to cast PANI/[P(VDC-co-VC)] and PANI/PVC films. Conductivities of pure PANI and PANI blends were measured by using standard four-probe method under DC current. A Keithley 2410 source meter was used as voltage and current source. Measured current values were plotted against voltage values and resistivity of samples was calculated from the slope of the $I-V$ plots.

2.3. Spectroscopic measurements

A Nicolet 520 model FT-IR spectrometer was used to obtain spectra between 4000 and 400 cm$^{-1}$. For each spectrum 32 scans were collected and a nominal 4 cm$^{-1}$ resolution was used. For the investigation of non-irradiated and irradiated pure PANI-salt and PANI-base, PANI samples were mixed with spectroscopic grade KBr (Aldrich), ground and pelletized. For the investigation of PANI blends, thin films were prepared. To obtain good FT-IR spectra of the blends very thin films were required. For this purpose new films were prepared with a thickness of $\frac{1}{4}$ of those prepared for conductivity measurements.

3. Results and discussion

The measurement of radiation-induced conductivity in polymers has been developed as a technique to study the influence of radiation on the electrical behavior of insulating polymeric layers used in radiation environments. Electrical conductivity of organic polymers can be significantly increased during the time that the material is exposed to a radiation flux due to the formation of transient conductive species (electrons, holes). These species also known as charge carriers rapidly recombine once the irradiation is stopped with the result that the conductivity quickly decreases to near the initial value. The absorption of relatively high doses, however, may cause permanent changes in the conductivity.

Despite vast number of papers published on conductive polymers and especially on PANI, only a few articles have been concerned with ionizing radiation effects on conductive polymers. Güven et al. (1986) attempted to investigate the effect of gamma rays on the conductivity of polypyrrole and found that a maximum in conductivity was observed at a dose of 2 kGy-irradiated polypyrrole (Güven et al., 1986; Ercan et al., 1995). Wolszczak and co-workers (1995) reported some results on radiation effects on conducting polymers such as PANI, polypyrrole and polythiophene. Their research program was directed toward a better understanding of the effect of gamma and electron beam irradiation on these conductive polymers by investigating structural properties controlling the electronic conductivity after and during irradiation. They observed an increase in conductivity after irradiation of insulating PANI form (even under air atmosphere). Malmonge and Mattoso (1997) reported that PANI-base irradiated under humid atmosphere developed significant radiation-induced conductivity whereas conductivity, of the salt form was found to decrease with irradiation substantiated by conductivity, ESR and UV–vis spectroscopy measurements. Radiation-induced conductivity in various oxidation states of PANI was investigated by De Azevedo et al. (1999) and the results were interpreted as an oxidative effect of polymer surface combined with the radiolysis of adsorbed water molecules. Their results indicate that the film resistance of emeraldine base and leucoemeraldine salts decreases exponentially for the dose range of 0–250 Gy upon exposure to gamma rays, while for emeraldine salt the resistance slightly decreases for low doses and increase linearly for high doses. The influence of 2.5 MeV electron irradiation on the conduction behavior of HCl and camphor sulfonic acid-doped PANI films in the high current regime was studied by a Xu et al. (2000). No significant changes were reported either on the conductivities or on the maximum current densities for samples irradiated at room temperature up to 300 kGy. Both of these properties were observed to decrease when the irradiation was carried out at high temperatures, $\sim$95°C.

Güven and his group (1986) have been studying extensively on radiation-induced conductivity in conducting polymers and blends. They published the effect of ionizing radiation on polypyrrole (Güven et al., 1986; Ercan et al., 1995). They also demonstrated that the electrical conductivity of PANI/PVC blend films can be significantly increased by exposure to gamma rays or UV radiation as a result of dehydrochlorination of PVC and subsequent doping of the PANI by the in situ-created HCl (Sevil et al., 1998). They prepared several PANI/PVC blend films using conventional chemical routes then exposed these blends to gamma rays. Their conductivity measurements indicated that conductivities of the irradiated films of PANI/PVC blends were increased with the increasing radiation dose by more than 6 orders of magnitude from $10^{-8}$ to $10^{-2}$ S cm$^{-1}$. 
In another work of this group (Sevil et al., 2003; Bodugöz et al., 1998) PANI samples blended with PVC and chlorinated poly(propylene) (PPC1) were irradiated to different doses and high-frequency conductivities were measured. The gamma and electron irradiation of the PPC1/PANI and PVC/PANI blends resulted in significant decrease in the resistance of the blends investigated. They showed that conductivities of these blends increased with increasing dose in the dose range of 5–150 kGy. According to their preliminary investigations the short-term stability of the blends after irradiation seemed to be satisfactory for potential dosimetry applications.

Radiation-induced conductivity of the PANI/PVC and PANI/PVDC copolymer blends involves the removal of HCl from PVC and PVDC chains as radiolysis products and subsequent addition onto PANI structure. Fig. 3 shows this mechanism. The doped state appears to consist of poly(semiquinone radical cation) which gives rise to polaronic conduction band yielding increase in the conductivity (Bodugöz and Güven, 2005).

After exposure to radiation, color of the blends turns to green from dark blue which is also the case for conventional acid-doping process. From this point of view, the same approach can be used for the radiation-induced conductivity mechanism, but it should be noted that the control of irradiation conditions is much more complex than the conventional method of doping because of the side reactions and by-products of irradiation. PVC is known to undergo extensive dehydrochlorination (resulting in mainly loss of HCl) when exposed to energetic radiations like gamma rays, accelerated electrons, etc., thus some blends of PANI with PVC were tried under various irradiation conditions. It was found that increasing irradiation dose resulted in increase in the conductivity of PANI/PVC blends. This result prompted us to investigate the effect of PVDC on the conductivity of PANI under irradiation. However, PVDC is not an easy polymer to prepare perfect films mainly caused by its very limited solubility due to its high crystallinity. Because of this particular problem we decided to prepare random copolymers of PVDC and synthesized P(VDC-co-VAc) in various compositions. Among various compositions P(VDC-co-VAc) containing 43% vinyl acetate having better solubility and sufficiently high level of PVDC has lead us to prepare PANI blends using this copolymer composition for further studies. P(VDC-co-VC)/PANI and PVC/PANI blends were also prepared for comparison purposes. In order to check the effect of radiation on the conductivity of pure PANI, conductivities of the pure PANI-salt and -base were measured after exposure to gamma radiation. Radiation-induced conductivity in PANI-base was quite small, less than an order of magnitude for absorbed doses of up to 800 kGy. The conductivity of PANI-base remained at around $10^{-9}$ Sc m$^{-1}$ for several hundreds kGy of doses. The conductivity of PANI-salt, however, decreased with dose from 2.00 to $6 \times 10^{-2}$ Sc m$^{-1}$ when irradiated up to 800 kGy.

When P(VDC-co-VAc)/PANI blend films were irradiated, a steady increase in conductivity has been observed for all blend compositions with dose, very fast initially reaching a plateau value at around 200 kGy dose followed by a small decrease at very high doses. A maximum value of $10^{-1}$ Sc m$^{-1}$ was reached for sample with 0.5 blend ratio indicating a saturation point for doping of this system. Increasing the content of copolymer in P(VDC-co-VAc)/PANI blend results in an initially steep increase followed by a decrease in the conductivity beyond a certain composition as can be seen for a given dose in Fig. 4. The composition corresponding to maximum conductivity is the optimum ratio of the two polymeric species namely, chlorine-containing polymers as the source for HCl and PANI as the polymer providing conductivity. FT-IR spectra of the blend films prepared from both homo and copolymers were taken and area of the bands at 1149 cm$^{-1}$, which characterizes the conductivity and 814 cm$^{-1}$ signifying the amount of chlorine added to PANI 0 backbone were determined (Kang et al., 1998). The information collected from FT-IR spectra of irradiated blends also support the results of conductivity measurements in a way that increasing amount of PVC or copolymer results in an increase in the band area of 1149 cm$^{-1}$ up to a certain blend ratio beyond which a decrease was observed in the respective band areas caused by the decrease in the availability of doping centers (PANI) in the blends. The general agreement obtained from FT-IR and conductivity measurements, relating chemical changes induced by radiation with the changes observed in conductivity is striking (Bodugöz and Güven, 2005).

In order to elaborate further the idea of using chlorine-containing copolymers for the preparation of radiation
responsive PANI blends, new films comprising PANI/P(VDC-co-VC) in various ratios were also prepared. Among the blend systems tested the highest conductivity values were thus obtained at 0.5 mol ratio for P(VDC-co-VAc)/PANI, 0.4 for P(VDC-co-VC)/PANI and 1.0 for PVC/PANI systems studied here as $3.7 \times 10^{-2}$, $9.7 \times 10^{-3}$, and $7.8 \times 10^{-5}$ S cm$^{-1}$, respectively (Bodugöz and Güven, 2005). The most characteristic feature of PANI blends prepared in this work is the possibility of maintaining the mechanical properties of the blends at a level essentially equivalent to the host bulk polymer. From this point of view we can conclude that all host polymers resulted in the formation of a free-standing highly stable polymer films as compared to inferior properties of PANI alone.

The results shown and discussed so far had clearly shown that the idea of in situ doping of PANI-base in the presence of chlorine-containing polymers and copolymers by radiation-induced release of HCl works very well to increase the conductivity of starting blend system by 7–8 orders of magnitude. The idea of HCl release upon irradiation can also be extended to consider some small molecular weight compounds instead of polymers. This approach was further developed to test chloroalkanes or similar compounds within PANI-base matrix. One such compound known as chloral hydrate $\text{CCl}_3\text{CH}(_2)\text{OH}$ has a very high radiation $G$-value of HCl release, reaching up to $100 \mu$mol/J depending on the conditions (Woods and Akhtar, 1974). We have therefore prepared composites of PANI-base with chloral hydrate to test the suitability of this compound in inducing conductivity in gamma-irradiated PANI matrices. The data points given in Fig. 5 below show that an increase of 8 orders of magnitude was obtained in the conductivity of a composite prepared from 100 mg of PANI-base with 30 mg of chloral hydrate (Uzun et al., 2006). The response shown up to 100 kGy of gamma irradiation is quite promising to consider this system as a radiation dosimeter after some modifications.

4. Conclusions

In this work, our aim was to prepare PANI blends with chlorine-containing polymer and copolymers and investigate their radiation response in terms of induced conductivities. Blends of non-conductive PANI with poly(vinylidene chloride-co-vinyl acetate), [P(VDC-co-VAc)], poly(vinylidene chloride-co-vinyl chloride), [P(VDC-co-VC)] and poly(vinyl chloride), (PVC) were prepared in the form of as-cast films. A number of blends which are different in composition were exposed to gamma radiation to various doses and the effect of irradiation type and composition of polymers used in the blends on the conductivity of films were
investigated by using conductivity measurements, FT-IR and UV–vis spectroscopy. Besides using chlorine-containing polymers together with PANI-base, a small molecular weight compound, chloral hydrate, which is rather easy to mix with PANI-base has also been found to be very efficient in inducing conductivity in gamma-irradiated PANI-base. The results clearly showed that ionizing radiation is an effective tool to induce conductivity in the blends of PANI with chlorine-carrying compounds and polymers. The main mechanism behind this radiation-induced conductivity is in situ doping of PANI-base with HCl released from partner polymers and compounds by the effect of radiation.

Our approach, the radiation-induced doping via an acid–base chemistry within the chloride-containing polymer matrix is similar in essence but totally different from the usual chemical/electrochemical methods of preparation of conductive PANI and is a novel method with unique and unforeseen possibilities.

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