



Photovoltaic Properties of Polyaniline-copoly(butyl acrylate/vinyl acetate) Composite

Habib Ashassi-Sorkhabi^{1*}, Elnaz Asghari¹, and Abdolreza Mirmohseni²

(1) Electrochemistry Research Laboratory, Department of Physical Chemistry;

(2) Polymer Technology Research Laboratory, Department of Applied Chemistry
Faculty of Chemistry, University of Tabriz, Tabriz, Iran

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ABSTRACT

In recent years, there has been considerable interest in the fabrication of photovoltaic devices using polymeric materials. Polyaniline and its composites with other polymers are promising candidates for industrial application of conducting polymers. In this study the photoelectrochemical behaviour of the novel conductive polyaniline-copoly(butyl acrylate/vinyl acetate), (PAN-poly(BuA/VAc)), composite has been investigated using linear sweep voltammetry (LSV) measurements. PAN-copoly(BuA/VAc) films, containing 40% polyaniline, were sprayed on indium-doped tin-oxide (ITO) coated flexible plastic sheets, as working electrode, using a simple spraying method; a Pt coated ITO coated glass was used as counter electrode and the electrolyte as a liquid electrolyte containing I_3^-/I^- redox couple sandwiched between them. The photovoltaic parameters, including energy conversion efficiency (ECE%), fill factor (FF), open circuit voltage (V_{oc}), and short circuit current (I_{sc}), were obtained from current-voltage (I-V) curves. The cells were prepared using different composite film thicknesses from 10 to 40 μm . The best energy conversion efficiency (ECE%) was obtained about 0.115% for a cell prepared with composite film thickness of 30 μm for which $V_{oc} = -140$ mV, $I_{sc} = 22 \mu\text{Acm}^{-2}$ and FF= 0.22 were obtained. The effect of composite film thickness and illumination time on photovoltages and photocurrents were investigated. It was observed that the photovoltages and photocurrents reached a maximum value at the 20 th minute.

Key Words:

photoelectrochemical cells;
polyaniline-copoly(butyl
acrylate/vinyl acetate);
conductive polymers;
photovoltaic.

INTRODUCTION

Although commercial photovoltaics are made mostly from inorganic semiconductors [1], organic photovoltaic cells have been a recent research focus due to their potential advantages of low cost fabrication, flexibility and large dimension [2].

Since the discovery of poly-

acetylene in 1977, semiconducting polymers have been investigated for various applications including artificial muscles, biosensors, drug delivery systems, heat shutters [3], light emitting diodes (LED) and photovoltaics due to their promise of the above advantages, less toxic manufacturing methods, tunable

(*) To whom correspondence to be addressed.

E-mail: habib_ashassi@yahoo.com
ashassi@tabrizu.ac.ir

optical properties and the possibility of light weight flexible panels' production. Polymer solar cell efficiencies are still far below those of amorphous silicon or dye sensitized electrochemical cells [4]. The main difference between devices made from these materials and silicon devices is that, whereas the absorption of a photon in silicon produces a free electron-hole pair at room temperature, in conducting polymers tightly bound excitons are created. In order to produce photocurrent, the exciton must be dissociated before it decays by radiation and/or no radiation so that the charges can be collected by their respective electrodes [5].

Many organic cells using dyes with *p*-type organic semiconductors have been investigated such as polythiophenes [6], polypyrrole [7,8], polythiocyanogene [9], poly(*p*-phenylene-vinylene) [10], fullerene/conjugated polymer composites [11,12], poly(*N*-vinyl carbazole)/porphyrin [13], etc.

Too et al. have studied some photovoltaic and Schottky diodes based on polythiophenes. In 2001, they studied photovoltaic devices based on polythiophenes and substituted polythiophenes with both solid and liquid electrolytes [1]. Cutler et al. have studied the effect of electron withdrawing nitro substituents on the behaviour of the photoelectrochemical cells based on nitrostyrylterthiophene [6]. Recently other researchers have reported the use of poly(3,3-didodecylquaterthiophene) blended with [6,6]-phenyl-C61 butyric acid methyl ester in a photovoltaic cell [14]. The highest power conversion efficiencies of their cells were in the range of 0.3-0.4%. The use of nanocrystalline materials and nanoparticles for improvement of photovoltaic properties in polymer solar cells has also been reported in recent years [15,16]. Strange et al. have prepared a polymer solar cell using the biodegradable poly(*L*-lactic acid) substrate loaded with nanoclay to improve the thermal properties and reduce permeation of water and oxygen [17].

Polyaniline (PAn) is one of the most promising candidates for industrial application of conducting polymers. It is formed via simple chemical or electrochemical oxidation of aniline. The electrochemical method can be used to produce thin films directly on conductive substrates such as ITO (indium-tin oxide). The chemical method can be used to produce a mate-

rial with the de-doped emeraldine base form soluble in solvents such as 1-methyl-2-pyrrolidone and some doped forms [18,19]. PAn has been predicted as a promising electronic material due to its unique conduction mechanism and high environmental stability. By electrochemical oxidation or reduction the colour of a PAn film can be reversibly switched between yellow and green at relatively low voltages (-0.2 to 0.1 V); this property has been represented as a new electrochromic material [20]. PAn has also been used as microwave absorbing and shielding material [21] and also in sensing applications [22]. This polymer has been used as a hole transport material and as a sensitizer in dye sensitized solid state solar cells [23,24]. In addition, Schottky diodes of Al/polyaniline/ITO with large area have been reported in literature [25]. Polyaniline composite films with inorganic materials such as CdS, Cu₂S nanoparticles and nanocrystalline TiO₂ have been used as an active layer in solar cells [20,26]. Polyaniline derivatives such as *o*-methoxy aniline have also been used in photovoltaic systems [27,28].

However, poor mechanical properties of pure polyaniline do not meet the requirements of a number of applications because, it is not readily processable. Therefore, researchers have attempted to form PAn composites with improved processability and mechanical properties while maintaining the inherent electroactive properties of the polymer [29]. Conducting PAn blends and composites with other polymers are prepared mostly via the chemical oxidation route, although electrochemical synthesis is also employed in some cases [30]. Using the chemical approach in situ polymerization of monomer in the presence of a host polymeric matrix has been reported [31-33]. PAn-poly(ethylene terephthalate) [31] and PAn-polystyrene [32] composites were both prepared using this approach.

Preparation and characterization of colloidal dispersions consisting of PAn and polyvinyl alcohol (PVA) have been investigated in recent years. The mechanism of polymerization [34], polymerization yield [35] and the size uniformity of particles [36] has been reported. Electrochemical behaviour in non-aqueous media [37], resistivity changes in relation to dispersion concentration [38], photoconductivity [39] and conductivity studies [40] have all been considered

in detail. The use of these PAN-PVA composites to produce a humidity [41] or carbon dioxide sensor [42] has also been reported.

Mirmohseni et al. [43] have reported the preparation of electroactive PAN-PVA composite. They have also reported the preparation of a PAN-poly(BuA/VAc) composite as a novel conducting polymer composite using emulsion polymerization of aniline in a medium containing poly(BuA/VAc) [29]. They also studied the properties of the resultant composite and showed that the prepared films (cast from an aqueous medium) had excellent mechanical properties and could be stretched up to 900%. They also indicated that the composite is soluble in common organic solvents, and a stable water-based dispersion could be prepared. An electrical conductivity of 2.2 S.cm^{-1} was obtained for films prepared from composite containing 40% polyaniline. Electroactivity of the composite was confirmed using cyclic voltammetry studies. It had excellent adhesion on either glass or steel plates [29].

In the present work we have reported studies on photoelectrochemical properties of the novel conductive PAN-poly(BuA/VAc) composite prepared by Mirmohseni et al. [29]; as mentioned above, this composite has shown good adhesion and mechanical properties as well as electrical conductivity. Combining the electrical conductivity of PAN with the adhesion and mechanical properties of poly(BuA/VAc) can be very useful in practical applications; therefore, this composite may be a potential alternative for pure PAN in most of its applications such as photovoltaic cells. On the other hand, there is no report in literatures on the photoelectrochemical properties of this composite. Thus, in this work the photoelectrochemical behaviour of the composite has been studied. The effect of thickness and illumination time on the photovoltaic properties of the constructed cells are also investigated using current-voltage curves obtained from linear sweep voltammetry (LSV) measurements.

EXPERIMENTAL

Composite Preparation

Sodium lauryl sulphate, ammonium persulphate,

sodium hydrogen carbonate and *p*-TSA were used in preparation of the PAN-poly(BuA/VAc) composite; the monomers consisting of butyl acrylate, aniline (Merck) and vinyl acetate (in commercial grade from Kimidarou Co.) were distilled prior to use. At the first step, copoly(BuA/VAc) was synthesized by emulsion polymerization, according to literatures [29], and then composite was prepared using the resultant copolymer as insulation polymer, aniline as the monomer of conductive polymer, ammonium persulphate as starter and *p*-TSA solution as dopant. Full description of preparation method has been illustrated elsewhere [29]. A mixture of 2 g composite in 40 mL dichloromethane and a 1 M *p*-TSA solution was stirred using a magnetic stirrer for 24 h to obtain a homogeneous doped polymer solution.

For conductivity measurements, stand-alone PAN-poly(BuA/VAc) composite films were prepared by casting the solution onto a glass slide; film was doped by immersion in a 1 M HCl solution for 24 h and was then placed between two sheets of filter paper and dried under high vacuum for 48 h, the conductivity reached a constant value after this period; the conductivity tests were repeated six times and the average value was reported. The thickness of all films for conductivity measurements were $25 \mu\text{m}$. According to the previous work reported by Mirmohseni et al. [29], conductivity of the composite films increases from 0.2 S.cm^{-1} for a composite film containing 10% polyaniline up to 2.2 S.cm^{-1} for a composite containing 40% polyaniline both with the same thickness. Thus we used the films with 40% polyaniline containing composite to have higher conductivity.

In order to confirm the electroactivity of the films PAN-poly(BuA/VAc) composite coatings were prepared on the working electrode (Au), and the cast films were subjected to cyclic voltammetry (CV) in 0.5 M HCl.

Preparation and Test of Photoelectrochemical Cells

Indium-doped tin-oxide (ITO) coated flexible plastic sheets, each of area 2 cm^2 were cleaned successively with detergent and distilled water, dried with an air gun and were used as substrates for composite films. The polymer solution in dichloromethane ($2 \text{ g}/40 \text{ cm}^3$) was then sprayed using a spray gun (air brush kit

SB 1104) on ITO substrates. Area of the polymer film on ITO substrate was 1 cm^2 . Thickness of polymer films was measured using a micrometer (Teclock Corporation SM-1201) with the precision of $\pm 1 \text{ }\mu\text{m}$. In order to use a uniform film in the tests, we determined the thickness in different points of the coated film and only the films that were uniform were selected for photoelectrochemical cells preparation. The electrolyte was prepared by dissolving 0.145 g iodine (Merck) and 1.488 g tetrapropylammonium iodide 98% (ACROS) in a 1:1 (by weight) mixture of propylene carbonate and ethylene carbonate.

A two electrode configuration was used for electrochemical tests; the polymer coated ITO substrate as working electrode and a Pt coated ITO coated glass as counter electrode, the liquid electrolyte was sandwiched between them. A piece of parafilm was used as spacer to prevent short-circuiting between working and counter electrodes. Figure 1 shows the structure of fabricated photovoltaic cell.

The devices were tested after fabrication in a dark box ($30 \times 30 \times 40 \text{ cm}$). A potentiostat-galvanostat (Autolab PGSTAT30) was used to measure and record the current-voltage (I-V) response of cells both in the dark and under illumination. The source of white light was a 50 W halogen lamp. Intensity of light was measured using a luxmeter (Leybold 53076). I-V curves were obtained using LSV method with a scan rate of $5 \text{ mV}\cdot\text{s}^{-1}$. The current versus the potential differences between working and counter electrodes were recorded first in the dark and then under illumination and the photovoltaic parameters, including short circuit current (I_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and energy conversion efficiency (ECE%), were obtained from I-V curves analysis. Each electrochemical test was repeated at least three times to verify the reproducibility of results.

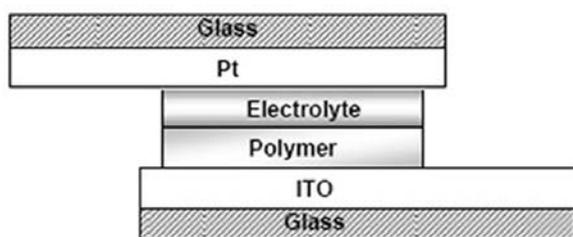


Figure 1. The structure of fabricated photoelectrochemical cells.

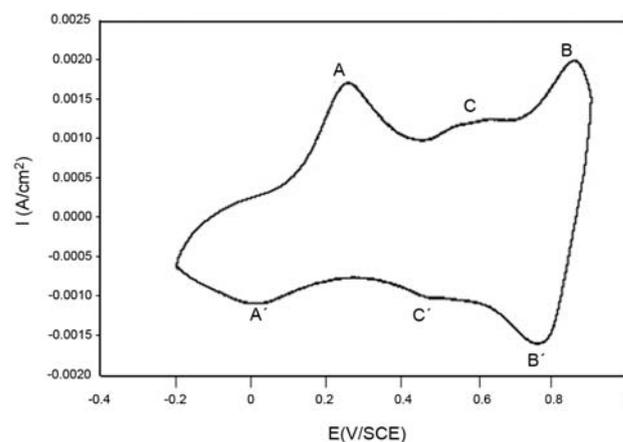


Figure 2. Cyclic voltammogram of PAN-copoly(BuA/VAc) composite film on Au electrode in 0.5 M HCl.

RESULTS AND DISCUSSION

Conductivity and Electroactivity of the Composite Films

The conductivity of PAN-copoly(BuA/VAc) composite films was measured six times and the average value of $2.2 \text{ S}\cdot\text{cm}^{-1}$ was obtained which is of the same order of magnitude obtained in the previous work [29].

Cyclic voltammetry was used to confirm the electroactivity of composite films. Figure 2 shows the cyclic voltammogram of PAN-copoly(BuA/VAc) composite film, with thickness of $25 \text{ }\mu\text{m}$, on Au electrode in 0.5 M HCl. It is well known that PAN undergoes two separate oxidation and reduction processes. This is clearly found to be occurring in the films prepared here. The well defined oxidation-reduction responses indicate that composite is electroactive. The first response (A and A') is due to oxidation-reduction of leucoemeraldine to emeraldine and vice-versa. The second response (B and B') is due to oxidation of emeraldine to pernigraniline (fully oxidized form) and vice-versa. Peaks C and C' are attributed to polyaniline breakdown products obtained upon excursion to the potentials necessary to observe the B-B' couple [43].

Current-voltage Characteristics

I-V curves were recorded both in the dark and under illumination for cells prepared with different thicknesses of PAN-copoly(BuA/VAc) composite films.

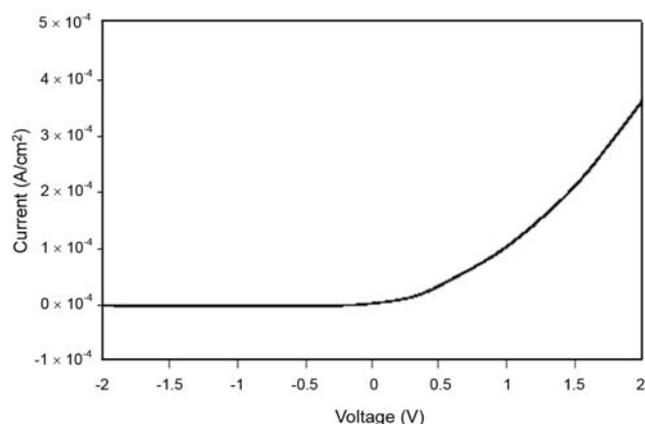


Figure 3. I-V characteristics for a photoelectrochemical cell prepared of PAN-copoly(BuA/VAc) composite film with 30 μm thickness in dark.

The I-V characteristic of a cell prepared with composite film thickness of 30 μm in dark is shown in Figure 3. Figure 4 shows typical I-V curves for some tested photoelectrochemical cells under illumination. The I_{sc} and V_{oc} were obtained from I-V curves; I_{sc} is the current when the voltage is zero and V_{oc} is the voltage when the current is zero. The values of FF, which is a measure of the squareness of output characteristics, and ECE% were calculated using eqns (1) and (2), respectively [1,6]:

$$\text{FF} = [V_{\text{pp}} \cdot I_{\text{pp}}] / V_{\text{oc}} \cdot I_{\text{sc}} \quad (1)$$

$$\begin{aligned} \text{ECE}\% &= [V_{\text{pp}} \cdot I_{\text{pp}}] \times 100 / P_{\text{IN}} \\ &= [V_{\text{oc}} \cdot I_{\text{sc}} \cdot \text{FF}] \times 100 / P_{\text{IN}} \end{aligned} \quad (2)$$

where $I_{\text{pp}} \cdot V_{\text{pp}}$ is the maximum output power which is obtained when the potential drop across the load is

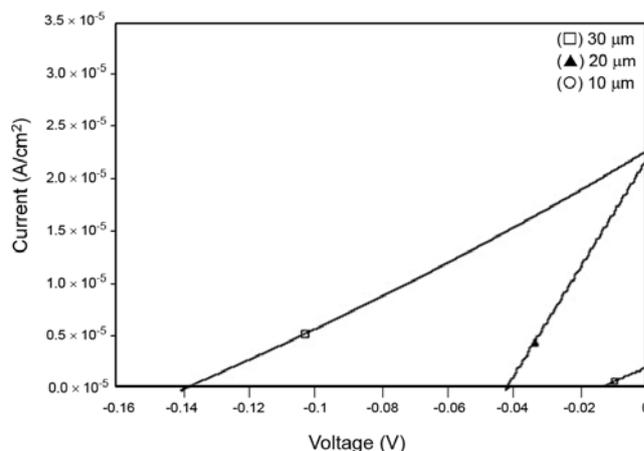


Figure 4. Typical I-V curves for some tested cells under illumination.

about 80% of V_{oc} . The I_{pp} and V_{pp} are mentioned as peak power current and peak power voltage, respectively. P_{IN} is the total power of illumination on the cell area (1 cm^2). The photovoltaic parameters for all tested cells are summarized in Table 1. It is clear from these data that all tested cells in this study showed much lower energy conversion efficiencies in comparison with conventional silicon solar cells. However, new photovoltaic devices using organic materials in active layer usually showed lower values than 1% energy conversion efficiency, which is the reason why scientists are seeking new cheap and easy producible photovoltaic materials and devices [1,6,44].

The best ECE% was calculated for the cell prepared with polymer thickness of 30 μm to be 0.115%. In order to understand the reasons for such low efficiencies we should notice the mechanism of photocur-

Table 1. The photovoltaic parameters obtained for all tested cells obtained from I-V curves.

Polymer film thickness ($\pm 1 \mu\text{m}$)	V_{oc} (mV)	I_{sc} ($\mu\text{A} \cdot \text{cm}^{-2}$)	FF	$V_{\text{pp}} \cdot I_{\text{pp}}$ ($10^{-9} \text{W} \cdot \text{cm}^{-2}$)	ECE (%)
10	-12	2.0	0.28	6.72	0.001
15	-30	15	0.26	117	0.020
20	-41	17	0.24	167	0.033
25	-100	20	0.22	440	0.073
30	-140	22	0.22	692	0.115
35	-70	16	0.26	291	0.048
40	-20	3.0	0.27	16.2	0.003

rent and photovoltage generation in a polymer photovoltaic cell. The charge conduction mechanism appears to be more complex for conducting polymers than for inorganic semiconductors. The efficiencies for polymer photovoltaics are low; when a conducting polymer is illuminated, the photons excite an electron from valence band into conduction band, the resulting electron and hole are bound, and their motion through material is coupled. These coupled moieties are known as excitons and are responsible for many of the electronic properties found in the most common and efficient polymer-based electronic devices. The bound exciton can then be split at interfaces. The simplest interface is created at the junction between electrode and conducting polymer. Under open-circuit conditions, holes are collected at high work function electrode, and electrons are collected at low work function electrode. The V_{oc} generated by these devices depends on the work function difference between two electrodes. Unfortunately, the exciton-splitting process that occurs at polymer-electrode interface is not very efficient and is one of the causes of low quality of these devices. Another reason of very low efficiency is the effect of impurities, such as oxygen, which acts as traps for the migrating excitons. The lifetime of excitons is short, and only excitons that are formed within ~ 10 nm of the junction will ever reach it. This short exciton range clearly limits the efficiency of these photovoltaic devices [19].

It can also be observed that the I_{sc} increases from 10 to 30 μm and then decreases with increase of polymer film thickness. The I_{sc} values obtained from the constructed cells are comparable with the photocurrents reported by Too et al. [1]. They were studied photoelectrochemical cells constructed from electro-synthesized polythiophene and polyetherthiophene with a structure similar to the structure used in our work; they showed that the I_{sc} values, depending on the electrosynthesis conditions vary from 1.39 to 13.4 $\mu\text{A}\cdot\text{cm}^{-2}$ for polythiophenes, and from 1.86 to 15.1 $\mu\text{A}\cdot\text{cm}^{-2}$ for polyetherthiophene [1]. Cutler et al. could improve the I_{sc} values up to 141.8 $\mu\text{A}\cdot\text{cm}^{-2}$ obtained from cells using polyetherthiophenes grown in -250 mV. The cells based on poly ((E)-3''(p-nitrostyryl) therthiophene exhibit an I_{sc} value of 21.6 $\mu\text{A}\cdot\text{cm}^{-2}$ [6]. This initial enhancement of I_{sc} with polymer film thickness from 10 to 30 μm can be due

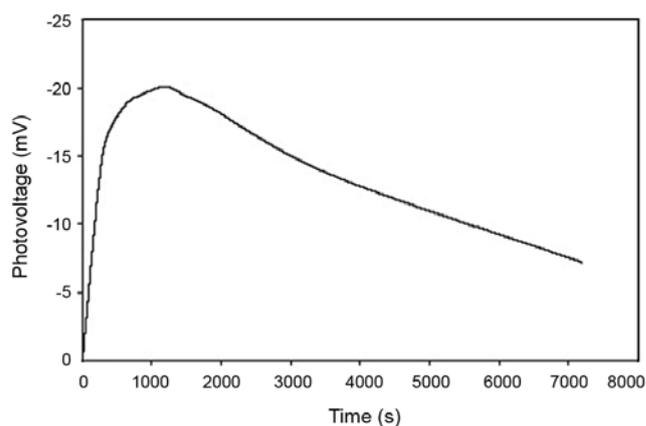


Figure 5. Variation of photovoltage versus illumination time for a photoelectrochemical cell prepared of PAN-poly(BuA/VAc) composite film with 30 μm thickness.

to more excitons production in the polymer film. On the other hand, we can interpret the decrease of I_{sc} in higher polymer film thicknesses, to mean that the performance of the polymer blend samples is limited by charge transport, most likely resistive losses and low carrier mobilities across the polymer layer, rather than by light absorption [4].

Effect of illumination time on photovoltage and photocurrent was also investigated. The photovoltages and photocurrents were measured in different illumination times from 0 to 7200 s. Figures 5 and 6 show the photovoltage-illumination time and photocurrent-time curves for a photoelectrochemical cell prepared with a 30 μm PAN-poly(BuA/VAc) composite film, respectively. These results show that both

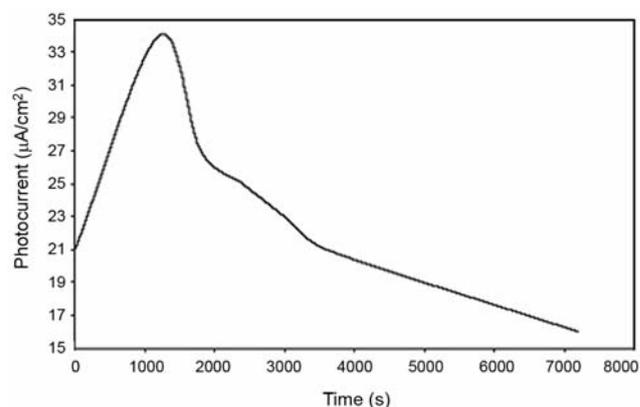


Figure 6. Variation of photocurrent versus illumination time for a photoelectrochemical cell prepared of PAN-poly(BuA/VAc) composite film with 30 μm thickness.

photocurrent and photovoltage have the same trend versus time; they are low in the beginning of illumination and reach a maximum value in 1200 s and then decrease. It means that the efficiency of the cells reaches maximum at 20th minute after the cell begins to work and declines after 20 min. These trends have also been observed in all tested cells. Reduction of voltages and currents in longer illumination times can be attributed to the excitons short lifetime. As mentioned before, only excitons that are formed within ~10 nm of the junction will ever reach it. At initial times of illumination the number of charge carriers enhances with increase of illumination time; although the enhanced dissociation of excitons in longer times, leads to the gradual reduction of photovoltages and photocurrents.

CONCLUSION

The photoelectrochemical behaviour of PAN-copoly(BuA/VAc) composite was studied. The composite films were prepared by a simple spraying method on ITO coated flexible plastic substrates which is an inexpensive, economical and simple method for practical applications. Due to good mechanical properties, which have been confirmed in previous works [29], this composite can be coated on any surface easily, whereas the pure polyaniline has poor mechanical properties. I-V characteristics were recorded both in the dark and under illumination for cells prepared with different PAN-copoly(BuA/VAc) composite film thicknesses and the photovoltaic parameters were obtained. The best ECE% was 0.115% which was obtained for the cells prepared with a PAN-copoly(BuA/VAc) composite film with 30 μm thickness. Low values of ECE% was attributed to the short lifetime of charge carriers, excitons, and existence of impurities such as oxygen molecules which act as traps for excitons. Although, there are efficiencies reported in the literature which are much lower than the ECE% values obtained in the present work [1,6,13]. The decrease of ECE% and I_{sc} with polymer film thickness in higher thicknesses demonstrates that these devices are still limited more by charge transport, likely low mobilities and resistive losses across the polymer layer, than they are by light

absorption in the polymer. The effect of illumination time on photovoltages and photocurrents was also investigated and it was found that the cells efficiency reached its maximum value in 1200 s and then declined gradually with time.

It can be concluded from these studies that the PAN-copoly(BuA/VAc) composite shows photoelectrochemical behaviour but its efficiency is low, similar to the most polymer based photovoltaics [1,6]; thus it will be necessary to improve all the effective factors in order to make viable and applicable plastic solar cells.

Symbols and Abbreviations

Symbol	Description
PAn	Polyaniline
PVA	Poly(vinyl alcohol)
PAn-copoly(BuA/VAc)	Polyaniline-copoly(butyl acrylate/vinyl acetate)
<i>p</i> -TSA	<i>p</i> -Toluenesulphonic acid
ITO	Indium-tin oxide
LSV	Linear sweep voltammetry
CV	Cyclic voltammetry
ECE	Energy conversion efficiency
FF	Fill factor
V_{oc}	Open circuit voltage
I_{sc}	Short circuit current
I_{pp}	Peak power current
V_{pp}	Peak power voltage
P_{IN}	Total power of illumination on the cell area

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