

A flexible textile structure based on polymeric photovoltaics using transparent cathode

Ayşe Bedelloğlu^{a,*}, Ali Demir^b, Yalcın Bozkurt^a, Niyazi Serdar Sarıçiftçi^c

^a Dokuz Eylül University, Textile Engineering Department, Tinaztepe Yerleşkesi, Buca, İzmir, Turkey

^b Istanbul Technical University, School of Textile Technologies and Design, Istanbul, Turkey

^c Linz Institute for Organic Solar Cells (LIOS), Physical Chemistry, Johannes Kepler University of Linz, A-4040 Linz, Austria

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ABSTRACT

This paper presents results for photovoltaic performance obtained from the application of different bulk heterojunction blends onto flexible polypropylene (PP) substrates for textile applications. Organic photovoltaic devices were fabricated onto non-transparent PP tapes and ITO coated glasses. The layer of poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonate) (PEDOT:PSS) and PEDOT:PSS with 100 nm of silver (Ag) metal layer constituted anode structure and substituted indium tin oxide (ITO) layer in this study. The blends of poly(3-hexylthiophene) and 1-(3-methoxycarbonyl)-propyl-1-phenyl(6,6)C₆₁ (P3HT:PCBM) or poly [2-methoxy-5-(3',7'-dimethyloctyloxy)-1-4-phenylene vinylene] and 1-(3-methoxycarbonyl)-propyl-1-phenyl(6,6)C₆₁ (MDMO-PPV:PCBM) were utilized as the absorbing materials. The thin metal layers of lithium fluoride (LiF) and aluminum (Al) were deposited on top of the devices by evaporation. All photovoltaic devices were characterized by measuring current–voltage (*I*–*V*) characteristics under simulated AM 1.5 conditions. The morphology of these devices using MDMO-PPV:PCBM and P3HT:PCBM blends was also investigated using atomic force microscopy (AFM).

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1. Introduction

In recent years alternative renewable energies including that obtained by solar cells have attracted much attention due to exhaustion of other conventional energy resources especially fossil-based fuels and due to global warming they caused [1]. Photovoltaic energy is one of the cleanest, most applicable and promising alternative energy using limitless sun light to generate electricity [2]. Even though, inorganic solar cells dominate in the world photovoltaic market, organic solar cells as the new emerging photovoltaic technologies can open new possibilities for different applications with their advanced properties including flexibility, light-weight, graded transparency [3,4]. Despite the fact that they have still problems with lower efficiency and lifetimes [3,5], low cost production and easy processing of organic solar cells comparing to conventional silicon-based technologies make them interesting and worth employing for personal use and large scale applications [2,6,7].

Technical textiles are produced for various industrial and functional requirements, in recent years based on information from

different scientific disciplines. Medical, agriculture, automotive and packing industries, protective and sportive clothing, ecology are the main fields where technical textiles are being used. Today, the smart textiles as the part of technical textiles using smart materials including photoactive materials, conductive polymers, shape memory materials, etc. are developed to mimic the nature in order to form novel textile materials with high functions. Though the solar cell-based textile phenomenon [8,9] is a novel field and a promising development obtaining new features and various applications, inorganic solar cells have already started to be used effectively, especially in military applications, where the soldiers need electricity for the portable devices. For example, photovoltaic textile materials can power wearable, mobile and stationary electronic devices to communicate, lighten, cool, heat, etc. by converting sun light into electrical energy [10–12]. The photovoltaic materials can be integrated onto textile structures especially on clothes. However, the best promising results can be taken from an efficient photovoltaic fiber which can constitute every type of smart textile structures and related products.

Indium tin oxide which is being almost exhausted and has crucial difficulties in application, is used as a common transparent electrode in polymer-based solar cells due to its good efficiency and transparency properties. However, it is also quite expensive

* Corresponding author. Tel.: +90 2324127712; fax: +90 2324127750.
E-mail address: ayse.celik@deu.edu.tr (A. Bedelloğlu).

and generally too brittle to be used for flexible substrates [12–14]. Therefore, highly conductive PEDOT:PSS, carbon nanotube or metal layers are used to substitute ITO electrode [12,13,15–22]. This can be a promising way due to its low cost and easy application features [23] for future textile applications. In this paper, fabrication of ITO-free organic solar cells on non-transparent flexible PP textile tapes, having a transparent cathode, is explained and results concerning the structural, optical and electrical properties of these devices are presented.

2. Experimental

Six different types of devices were fabricated: three of them used MDMO-PPV:PCBM active layer including PP tape-based (a), 100 nm of Ag coated PP tape-based (b) and ITO coated glass-based (c) substrates. The other three types used P3HT:PCBM active layer including PP tape-based (d), 100 nm of Ag coated PP tape-based (e) and ITO coated glass-based (f) substrates.

2.1. Materials

Highly conductive PEDOT:PSS (Baytron PH 500) solution was used in this work. Chemical structure of PEDOT:PSS is shown in Fig. 1(a). 5% dimethylsulfoxide (DMSO) and 0.1% Triton X-100 (from Union Carbide) by volume were mixed with PEDOT:PSS solution to enhance the conductivity and wetting properties, respectively. The mixed solutions were stirred continuously for 24 h at room temperature.

The photoactive material solutions were prepared using blends of P3HT:PCBM and MDMO-PPV:PCBM, separately. A blend of P3HT (from Rieke Metals) and PCBM (from Nano-C) with a weight ratio of 1:0.8 in 27 mg/ml chlorobenzene solution was stirred for 24 h at room temperature. Meanwhile the blend of MDMO-PPV (from Covion) and PCBM with a weight ratio of 1:4 was also dissolved in chlorobenzene (17.5 mg/ml) and stirred for 24 h at temperature of 40 °C. Chemical structures of P3HT, MDMO-PPV and PCBM are given in Fig. 1(b–d), respectively.

2.2. Photovoltaic device fabrication

Non-transparent (black coloured) and non-conductive flexible PP textile tapes (from SUNJÜT) of 0.4 cm × 5 cm were used without ITO layer, as textile-based substrates. The glass sheets of 1.5 cm × 1.5 cm covered with ca. 120 nm ITO (from Merck KG) layer

were used as substrate of reference cells with a sheet resistance less than 15 Ω cm⁻².

For device preparation, flexible textile substrates were gently cleaned in methanol, isopropanol and distilled water, respectively, and dried in a nitrogen flow. In order to substitute ITO layer, 100 nm of Ag layer was thermally evaporated onto half part of the PP substrates. Fig. 1(e and f) presents the schematic drawings of the devices used in this study. For glass samples, approximately half of the ITO layer was etched from glass with an acid mixture consisting of HCl, HNO₃, and H₂O (4.6:0.4:5) for ca. 30 min. Then, the glass substrates were cleaned in ultrasonic bath (15 min for every solution) by using organic solvents such as acetone, isopropanol, ethanol and methanol, respectively and finally, washed with water and dried in a nitrogen flow.

In the next step, a thin layer of PEDOT:PSS mixture solution, explained before, was dip-coated on flexible PP tapes and spin-coated onto ITO coated glasses at 1500 RPM as bottom contact (100–150 nm). Substrates with PEDOT:PSS were annealed on the hot plate for 3 h at 50 °C.

Subsequently, solutions of MDMO-PPV:PCBM or P3HT:PCBM blends were dip-coated onto PP tapes and spin-coated onto ITO coated glasses at 1500 RPM, as photoactive layer (200–250 nm). Afterwards, all devices were heated on the hot plate for 15 min at 50 °C. The samples were manufactured on ambient conditions. Finally, transparent outer electrode consisting of thin layers of LiF (0.7 nm) and Al (10 nm) were thermally evaporated through a suitable shadow mask in a vacuum below 10⁻⁵ mbar. Due to undurable structures of textile substrates at high temperatures (>60 °C), all devices were measured without thermal post-treatment. 30 devices were prepared for each type of photovoltaic tapes using P3HT:PCBM and MDMO-PPV:PCBM-based solar cells including PP tape and Ag coated PP tape substrate configurations and 15 devices were manufactured for each type of reference cells based on P3HT:PCBM and MDMO-PPV:PCBM organic solar cells. The active areas for both textile-based and reference cells were between 10 and 14 mm².

2.3. Photovoltaic device characterization

Current–voltage (*I*–*V*) characteristics of the photovoltaic devices were measured using a Keithley SMU 236 in a glove box (MB 200 from MBraun) under argon atmosphere immediately after production. The devices were illuminated by a solar simulator (Steuernagel Lichttechnik GmbH) through the top transparent electrode in AM1.5

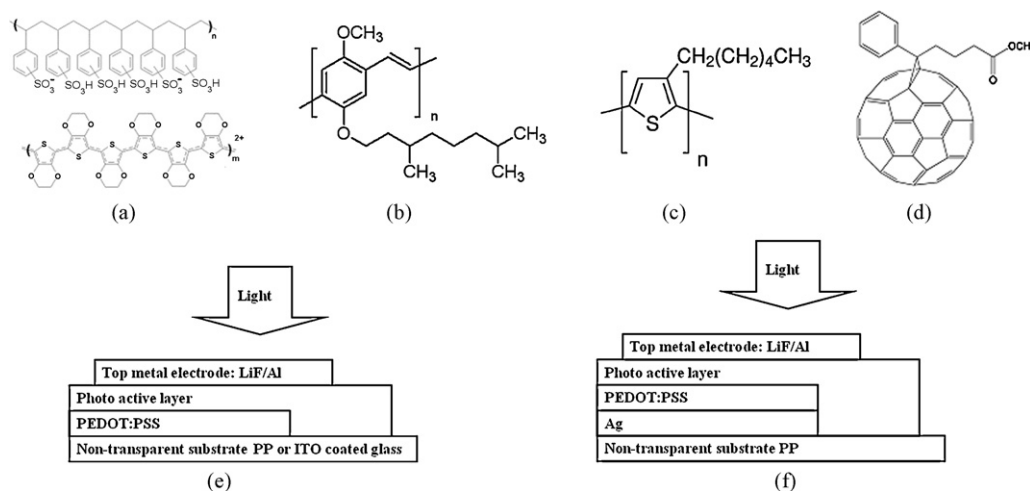


Fig. 1. Chemical structures of PEDOT:PSS transparent electrode (a), MDMO-PPV (b), P3HT (c) and PCBM (d), and also schematic representation of device structures standard ITO coated glass (e) and PP substrate itself with bottom Ag metal electrode instead of ITO (f).

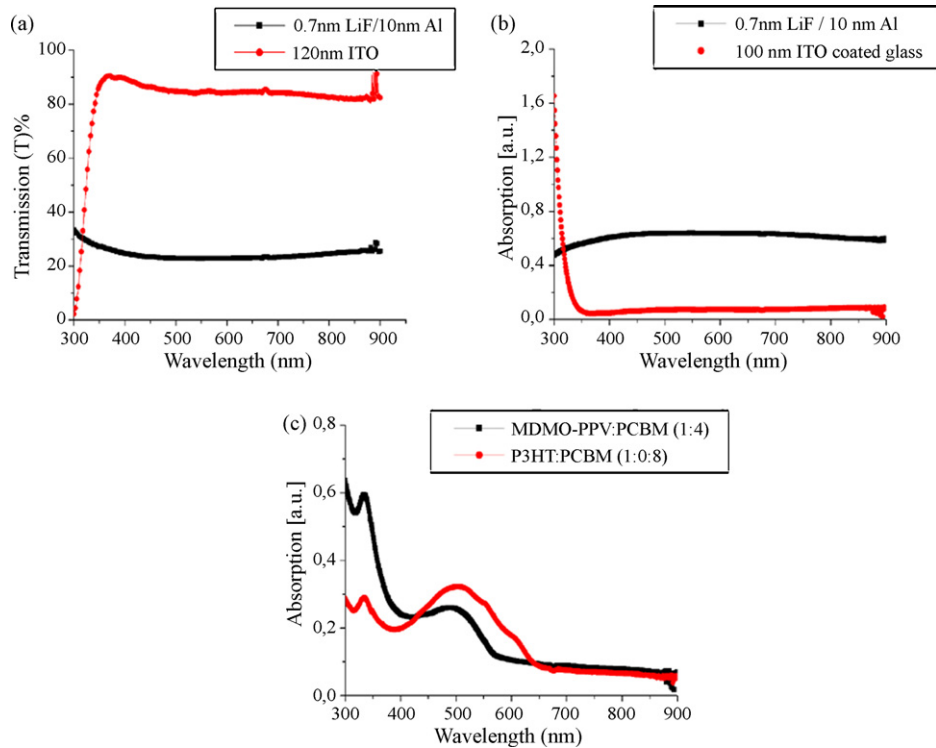


Fig. 2. The transmission (a) and absorption (b) spectra of LiF/Al and ITO layers and absorption spectra of MDMO-PPV:PCBM and P3HT:PCBM blends in chlorobenzene (c).

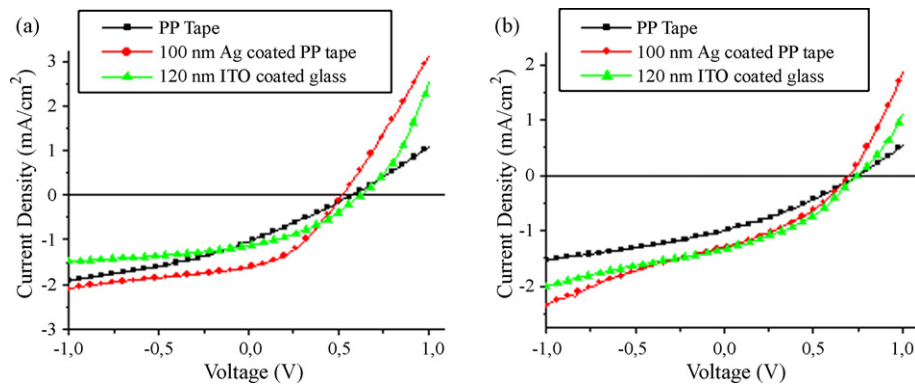


Fig. 3. *I*-*V* characteristics of organic solar cells using P3HT:PCBM (a) and MDMO-PPV:PCBM (b): (■) PP tape, (●) 100 nm Ag coated PP tape, (▲) 120 nm ITO coated glass as substrates, respectively.

conditions (100 mW/cm² power intensity of white light). Solar cell efficiencies were calculated according to the following formula (1):

$$\eta = \frac{I_{sc}V_{oc}FF}{P_{in}} \quad (1)$$

Here, I_{sc} is the short-circuit current density (mA/cm²), V_{oc} is the open-circuit voltage (mV), FF is the fill factor and P_{in} is the incident light intensity.

Table 1
I-*V* characteristics of the photovoltaic devices.

Devices	Substrate type	Photoactive layer	<i>I</i> (mA cm ⁻²)	<i>V</i> (mV)	FF (%)	η (%)
a	PP tape	MDMO-PPV:PCBM	0.98	760	~31	0.23
b	Ag coated PP tape	MDMO-PPV:PCBM	1.28	700	~37	0.33
c	ITO coated glass	MDMO-PPV:PCBM	1.33	740	~38	0.37
d	PP tape	P3HT:PCBM	1.04	580	~27	0.17
e	Ag coated PP tape	P3HT:PCBM	1.60	520	~37	0.33
f	ITO coated glass	P3HT:PCBM	1.12	620	~36	0.25

The surface morphology was determined by Digital Instruments DIMENSION 3100 atomic force microscope (AFM) in the tapping mode.

Scanning electron microscopy (SEM) analysis of cross-section was done by using a LEO Supra 35 scanning electron microscope.

The absorption and transmission spectra of LiF/Al metal electrode were obtained by evaluating the metal layers evaporated on only glass and compared with spectra of ITO coated glass. The absorption spectra of P3HT:PCBM and MDMO-PPV:PCBM blends in

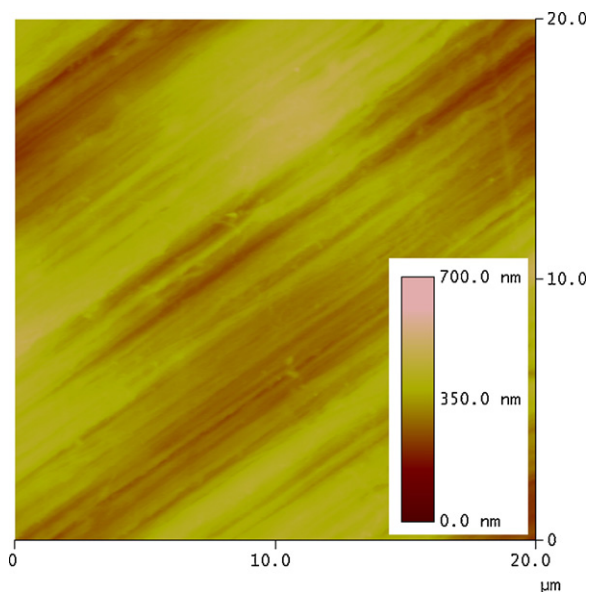


Fig. 4. AFM image of PP tape (surface roughness is ca. 530 nm).

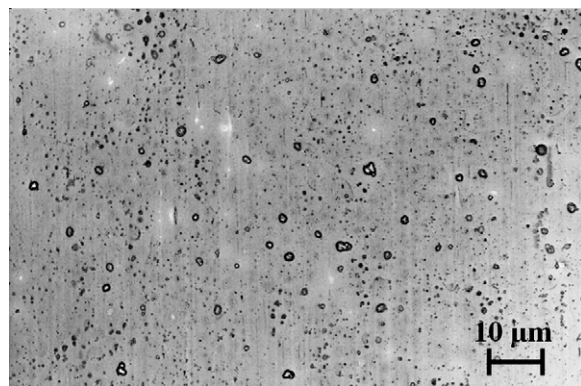


Fig. 6. SEM picture of surface of top metal electrode (LiF/Al).

chlorobenzene were also recorded using Cary 3G Varian UV Spectrophotometer.

3. Results and discussion

3.1. Absorption and transmission characteristics

The absorption and transmission spectra of evaporated thin LiF/Al layer compared with ITO are shown in Fig. 2. The absorption spectra of MDMO-PPV:PCBM and P3HT:PCBM blends in chlorobenzene are also given in Fig. 2c. As can be seen in Fig. 2a and b, absorption and transmission properties of ITO layer are better than

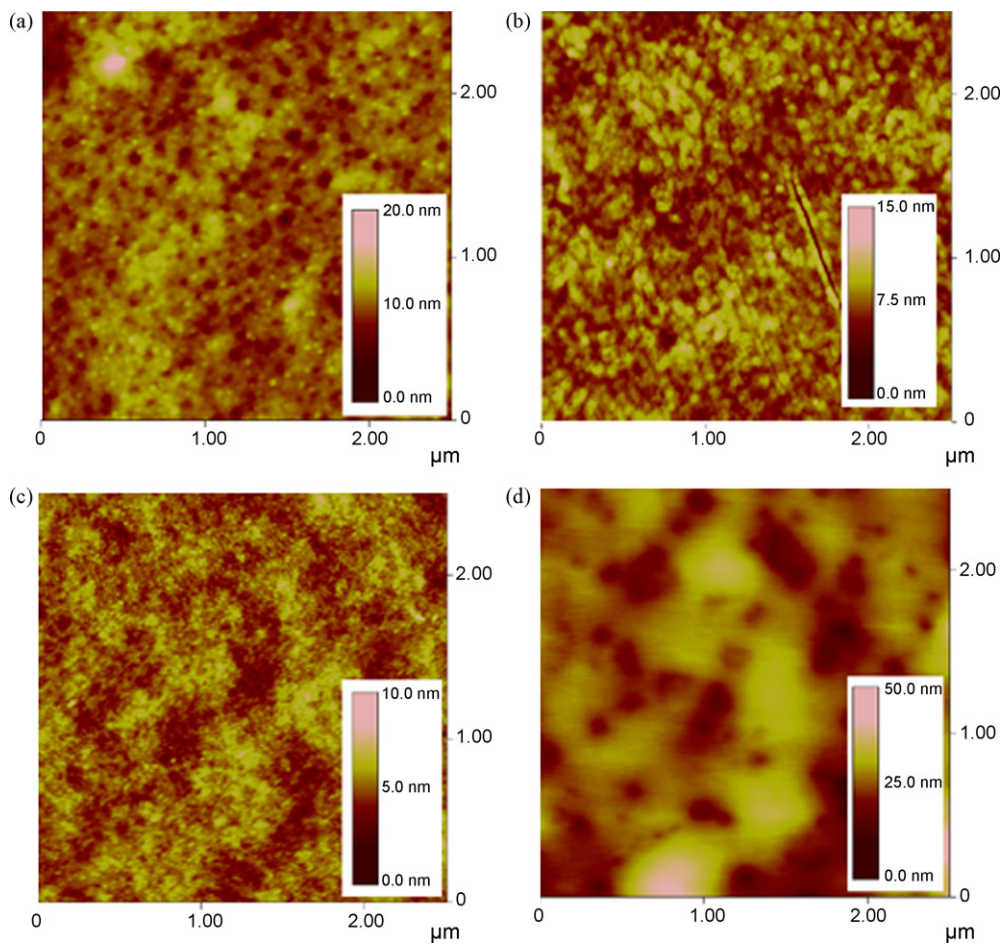


Fig. 5. AFM images of organic photovoltaic cells based on PP tape substrates using P3HT:PCBM (a) and MDMO-PPV:PCBM (b), and organic photovoltaic cells based on ITO coated glass substrates using P3HT:PCBM (c) and MDMO-PPV:PCBM (d).

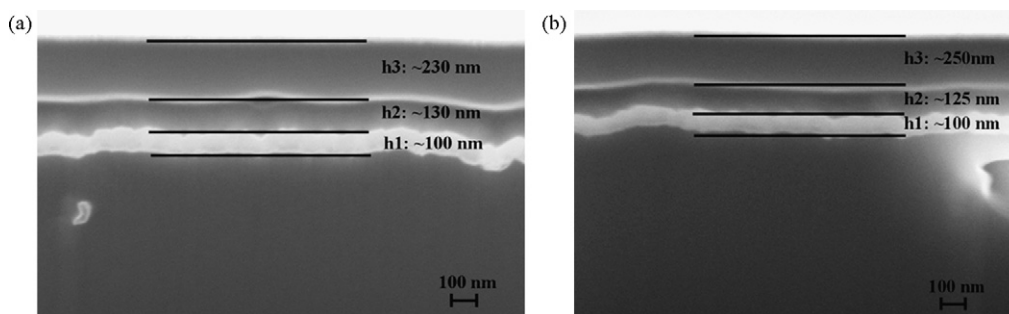


Fig. 7. SEM pictures of cross-sections of photovoltaic devices using MDMO-PPV:PCBM (a) and P3HT:PCBM (b) with PP tape substrate (h1: 100 nm Ag, h2: PEDOT:PSS, h3: photoactive layer).

LiF/Al layer when they are used as bottom electrode on glass substrate. However, due to non-transparent substrate, photovoltaic textile structure takes the light from its outer surface. Therefore, in this study, outer electrode (top contact) is a transparent metal layer, so that light can enter into the photoactive layer and electricity can be produced.

3.2. Photovoltaic performance of devices

P3HT:PCBM and MDMO-PPV:PCBM composite materials were evaluated as electron donor/acceptor materials in ITO-free organic bulk heterojunction solar cells by using PP tapes as substrates. In this study, all solar cells including reference cells were illuminated through the top electrode side and compared in terms of substrate and active layer types. Current–voltage (I – V) characteristics of photovoltaic devices having two different photoactive materials (MDMO-PPV:PCBM and P3HT:PCBM) are shown in Fig. 3. Detailed characteristics of devices such as short-circuit current density, open-circuit voltage, fill factor and efficiency values are also given in Table 1, respectively.

As can be seen in Table 1, maximum current density, obtained from P3HT:PCBM-based solar cells using 100 nm of Ag coated PP tape as substrate, is 1.6 mA cm^{-2} . Maximum voltage obtained from MDMO-PPV:PCBM-based reference solar cells on ITO coated glass is 740 mV.

It was observed that, when 100 nm of Ag coated substrate was used in both MDMO-PPV:PCBM and P3HT:PCBM solar cells, current density, fill factor and efficiency values of these devices increased slightly compared with the values of solar cells using only PP tapes substrates and their performance approached to reference cells. The thin and transparent outer electrode (ca. 10 nm LiF/Al), letting photon transmission into the device and collecting the produced electrons, performed its duty, successfully. Some possible reasons for the low efficiency can be rough surface of the textile substrate when compared with results of some previous studies [1,24,25] and thickness of the cathode which affects the collection of electrons from the device. The rough surface can affect the PEDOT:PSS and active layer coatings and may result in short-circuit problems in device.

3.3. Morphology of devices by atomic force microscopy (AFM)

The surface characteristics of fabricated flexible and rigid photovoltaic structures were determined via nanomorphology of the bulk heterojunction active layers. To correlate the morphology of the solar cells with photovoltaic performance, an AFM study was performed on textile and glass substrate-based MDMO-PPV:PCBM and P3HT:PCBM solar cells. AFM image of naked PP tape is also given in Fig. 4 to give a clear picture about rough textile substrate. AFM images of MDMO-PPV:PCBM and P3HT:PCBM layers on two different substrates (PP tape itself and ITO coated glass) are shown

in Fig. 5. The roughness, which is the possible reason for low photovoltaic performance, can also be realized from AFM images of samples.

3.4. Scanning electron microscopy (SEM) measurements of devices

The surface view of transparent top metal contact (LiF/Al) is presented in Fig. 6. Cross-sectional pictures of photovoltaic devices demonstrate each layer (100 nm of Ag coated PP tape as substrate, PEDOT:PSS layer and photoactive layer (MDMO-PPV:PCBM or P3HT:PCBM)), clearly, in Fig. 7. However, thin layer (ca. 10 nm) of top metal electrode (LiF/Al) is shadowy. As can be seen from Fig. 7, there is no significant difference between SEM pictures of devices using MDMO-PPV:PCBM and P3HT:PCBM materials.

Surface smoothness, which affects every step, is a serious subject in manufacturing process of a solar cell. In this study, the bobbin of PP tape as a rough textile substrate was chosen from the production flow of the factory named SUNJUT, randomly. In the planned future study, therefore, smoother textile substrates which can help better photovoltaic performance compared with rough surfaces will be considered. For this goal, PP tapes can be covered with a synthetic material by dipping, so that the surface quality can be improved. With adjustments in production processes, the morphology of the PP tapes can also be controlled during the flow and thus PP tapes can be produced with a smoother surface. When solar cell materials are built on that kind of smoother layers as substrate, the device can demonstrate better photovoltaic features.

4. Conclusions

In this study, the possibility of utilizing different conductive layers to substitute ITO anode was investigated. Therefore, PEDOT:PSS mixture (with DMSO and Triton X-100) and PEDOT:PSS coated 100 nm of Ag layers were used in flexible organic photovoltaic devices which had PP tapes as substrates. The maximum values of open circuit voltage obtained from organic solar cell based PP tapes were 760 and 580 mV in MDMO-PPV:PCBM and P3HT:PCBM-based devices, respectively. The maximum obtained short-circuit current density was 1.60 mA/cm^2 on 100 nm Ag coated PP tape using P3HT:PCBM light absorbing layer. The power conversion efficiency of photovoltaic tapes consisting of 100 nm Ag coated PP tape (0.33%) was almost as high as what was obtained with ITO coated glass-based solar cells. The reproducible results show that these materials can be used instead of ITO, in textile structure-based solar cells.

Semiconducting polymers, which are the chief materials of the polymer solar cells are other most serious issues to improve device efficiency. Efficiency of polymer-based organic cells exceeded 5% according to a recent report [26]. However, the use of new materials and new conjugated polymers with wider bandwidths, smaller

(lower) band gaps and higher carrier mobilities in device, can help us to overcome present low photovoltaic efficiencies of organic solar cells [2,14]. Using new electron-accepting materials, multiple layers with different band gaps, right multi-component mixtures expanding the spectral range of the device and light scattering particles (nano or micro) in photoactive layer are interesting points which can be considered in the future studies on photovoltaic textiles. Also using different cathode combinations [27] and further optimizations for thickness of metal layers can achieve higher light transmittance and absorption in photovoltaic tapes.

A new device which employed a transparent metal cathode (ca. 10 nm LiF/Al) and highly conductive PEDOT:PSS and Ag-based anode was achieved in this study. These results show that polymer-based solar cell materials and manufacturing techniques are suitable and applicable for flexible and non-transparent textiles, especially tapes and fibers, with transparent outer electrodes. The electric field in polymer-based photoactive layer is inversely proportional to the polymer layer thickness, for short-circuit conditions. Therefore, thickness of light absorbing layers in both photovoltaic tapes needs to be optimized to improve the power conversion efficiency of devices. Consequently, extended studies are required because of drawbacks in lifetime and efficiency of organic solar cells, to develop practically usable textile products. However, in the near future, the obstacles will be overcome with advancements in materials and technology.

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