ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE ENGINEERING AND TECHNOLOGY

DEVELOPMENT OF ORGANIC BASED PHOTOVOLTAIC FIBER

M.Sc. THESIS

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Department of Textile Engineering

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JULY 2012

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Thesis Advisor: Prof. Dr. Ali DEMİR

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

ORGANİK ESASLI FOTOVOLTAİK LİF GELİŞTİRİLMESİ

YÜKSEK LİSANS TEZİ

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TEMMUZ 2012

İsmail Borazan, a **M.Sc.** student of ITU **Institute of Science** 503101805 successfully defended the **thesis** entitled "**DEVELOPMENT OF ORGANIC BASED PHOTOVOLTAIC FIBER**", which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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To my family,

FOREWORD

Energy and environment are two of the most crucial issues of wide concern nowadays. With increasing population and energy consumption, renewable energy sources have a great attraction on researchers. Organic photovoltaics has a distinct place among all types of solar cells with plenty of advanteges, such as being organic and cheap, ease of prosess, flexibility, large scale applicability, color variety, graded transparency etc.

In this work, it is proved that textiles in our daily life can generate electricity. With various deposition techniques, a textile fiber is coated with photoactive materials in order to harvest energy from the sun light.

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IMPORTANT REMARKS:

This thesis work has been carried out within the following projects:

1. SANTEZ Project Number: 00568.STZ.2010-1, entitled "Güneş Işığını Elektrik Enerjisine Dönüştüren (Fotovoltaik) Lif Yapısının Tekstil Amaçlı Uygulanabilir Boyuta Getirilmesi " under the guidance of the Project Manager Prof. Dr. Ali Demir.
2. ITU BAP Project Number: 36537, entitled "Polimer Esaslı Fotovoltaik Lif Tasarımı" under the guidance of the Project Manager Prof. Dr. Ali Demir.

Both projects provided Research Student Scholarship, material, as well as participation fee and travel expenses for the congresses attended to present al the results of this research work.

The data, figures as well as pictures included in this thesis have also been included in the interim as well as the final reports of the above mentioned projects and no citation has been reciprocally made.

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ABBREVIATIONS

CdSe : Cadmium Selenide
CdTe : Cadmium Telluride
CIGS : Copper indium gallium selenide ($CuIn_xGa_{(1-x)}Se_2$)
DSSC : Dye sensitized solar cell
ITO : Indium tin oxide
IZTECH : Izmir Institute of Technology
MDMO-PPV : Poly[2-methoxy-5-(3,7-dimethyloctyloxy)]-1,4-phenylenevinylene
OPV : Organic photovoltaic
P3HT : Poly (3-hexylthiophene)
PCBM : Poly [6,6]-phenyl-C_{61}-butyric acid methyl ester
PEDOT:PSS : Poly(ethylene-dioxythiophene):polystyrenesulfonate
PEO : Poly (ethylene oxide)
PET : Polyester
PV : Photovoltaic
R2R : Roll to roll, reel to reel
ZnO : Zinc oxide

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DEVELOPMENT OF ORGANIC PHOTOVOLTAIC-BASED FIBER

SUMMARY

The aim of this study is to present a textile fibre which will produce electricity by photovoltaic effect. In the future, photovoltaic fibre produced, will be used to manufacture textile products (clothings, tents, etc.) which will produce electricity itself. In the study, by using various chemical materials and methods, photovoltaic effect is developed on polyester filaments. The photovoltaic fibres, which are produced using easier techniques and materials compared to silicon based solar cells, can be used to produce yarns and fabrics. The photovoltaic fibres can be also integrated into fabrics or clothes.

Renewable energy technologies including solar cells attract considerable attention due to the inevitable end of fossil fuels and due to global warming and other environmental problems they caused, in recent years. Ongoing efforts focus on for reducing the fabrication cost of solar cells and for improving the efficiencies of existing devices. In this respect, an organic solar cell using organic semiconductors which are cheaper than inorganic semiconductors and can be synthesized with easier processes is a promising approach owing to its unique features including low-cost, flexibility and lightness for solar energy conversion. Additionally, their chemical and physical properties can be changed or tuned easier.

People who are working, living or being apart from the electrical grids, will be able to produce electricity by using these photovoltaic fibres/textile structures for the electricity requirements of small electrical devices.
Preliminary studies on developing a fibre showing photovoltaic effect were done previously. In this work, by changing and improving existing photovoltaic fibre structures with new materials and techniques, an advanced photovoltaic fibre structure is developed.

The existing methods which are used to produce conventional glass-based solar cells will be modified and applied to produce fibre based solar cell.

In this work, the first aim is to get a photovoltaic effect on a textile fibre/filament. Organic materials which have many advantages such as being lightweight, low-cost and graded transparency are used in this study. Serial production issue will be also discussed for mass production, after repeatable manufacturing and test procedures are developed and efficient results are taken.

This study will present results about developing and measuring photovoltaic effect on textile structures by using different specific materials and techniques. Photovoltaic fibres will be very useful in both industrial and daily life, due to the fact that they only use abundant and limitless sunlight.

Produced photovoltaic fibres/filaments can be used to form larger textile structures by weaving or knitting techniques or integrating into a fabric.

In this thesis, organic based solar cell materials were applied onto textile fibres. Photovoltaic performances of produced flexible devices were measured and compared to conventional solar cells consist of glass and plastic substrates. PET tapes and PET monofilament are employed as textile based materials, as bottom electrode polymer based matieral (PEDOT:PSS) and metal layers (Al, Au, Ag), P3HT:PCBM and MDMO-PPV:PCBM blends were used as photoactive layer, different metal oxides and polymers (ZnO-NPs and PEO) were used as a buffer layer between bottom electrode and photoactive layer, several metal layers (Al, Ag, Au) were employed as semi-transparent top electrode. Counter to standard solar cells, semi-transparent cathodes as top electrode and luminous light comes from top electrode side. Therefore, 0,3 % efficiency for fiber based and 0,03% efficiency for reference cells were obtained, as polymeric anode and in some experiments, PEDOT:PSS layer were used to instead of ITO. Results obtained from measurement of all solar cells were evaluated by drawing graphs. In order to understand surface structure, scanning electron microscope (SEM) and atomic force microscobe (AFM) was used. Photovoltaic textile fibers producing electricity by using solar energy, can meet the power requirements of portable electronic devices such as ipod, mp3 player etc. After development of these devices, all power demand for various applications such as heating, cooling, lighting, communicating etc. can be met.

ORGANİK ESASLI FOTOVOLTAİK LİF GELİŞTİRİLMESİ

ÖZET

Son yıllarda, küresel ısınma ve kirlilik, enerji elde etmek için fosil madde esaslı yakıtların ağırlıklı olarak kullanılmasının da etkisiyle, dünyadaki yaşamsal faaliyetleri tehdit edecek bir boyuta ulaşmıştır. Bu nedenle günümüzde, günlük hayatta ve sanayide kullanılması zorunlu elektrik enerjisinin, çevreye en az zarar verecek biçimde üretimi, iletimi ve tüketiminin gerçekleştirilmesi konusu çözülmesi gereken en önemli sorunlardan biri haline gelmiştir. Yenilenebilir ve temiz enerji teknolojileri arasında belki de en fazla dikkat çekenlerden bir tanesi, sınırsız güneş enerjisini kullanarak elektrik enerjisi üretilmesini sağlayan fotovoltaik teknolojisidir.

Dünya genelinde, son yıllarda tekstil sektörü yapısının hızla değişmesi ile Türkiye de diğer Avrupa ülkeleri gibi katma değeri yüksek, daha özel ve kaliteli tekstil ürünlerinin üretimine yönelmiştir. Gerekli araştırma-geliştirme çalışmalarının yürütülmesi konusunda hem üniversiteler hem de özel sektördeki firmalar ilk adımları atmıştır, atmaya da devam etmektedir. Çeşitli akıllı malzemelerin tekstillerle birlikte kullanılması ile farklı özelliklere ve kullanım alanlarına sahip fonksiyonel tekstil malzemeleri elde edilmeye ve kullanılmaya başlanmıştır. Enerji üreten veya dönüştüren, kendi kendini temizleyen, belirli ortam koşullarında faz, şekil ve renk değiştiren, iletken ve benzeri özellikteki akıllı malzemeler kullanılarak üretilen tekstil ürünleri günümüzün vazgeçilmezleri arasına girmeye başlamıştır.

Fotovoltaik teknolojisi ağırlıklı olarak silikon esaslı pahalı malzemeleri kullansa da günümüzde daha ucuz yöntem ve malzemeleri kullanan güneş pilleri de (örn. Organik madde esaslı güneş pilleri) üretilmeye başlanmıştır. Organik güneş pilleri, silikon esaslılara göre hafiflik, ucuz malzeme ve daha kolay yöntemleri kullanma, düşük sıcaklıklarda çalışabilme, esneklik, çok küçük ve ya çok büyük yüzeylere uygulanabilirlik gibi çeşitli avantajlara sahiptir. Organik güneş pillerinin verimleri şuan silikon esaslılara göre düşük olmasına rağmen, taşıdığı özellikler nedeniyle tekstil yapılarına çok uygundur.

Bu çalışmada fotovoltaik etki sağlanması için güneş enerjisini kullanarak elektrik enerjisi üretebilecek bir tekstil lifi elde edilmesini amaçlamaktadır. Üretilecek fotovoltaik lif, ileride kendi elektriğini üreten akıllı tekstillerin (giysiler ve çadırlar gibi) imalatında kullanılabilecektir. Bu çalışma kapsamında, çeşitli kimyasal maddeler ve yöntemler kullanılarak polyester tekstil lifi üzerinde, fotovoltaik etki geliştirilecektir. Silikon esaslı güneş pillerine göre nispeten kolay yöntem ve daha ucuz malzemelerle geliştirilecek olan fotovoltaik lifler ile ileride iplikler ve kumaşlar üretilebilecektir ya da fotovoltaik lifler kumaş ya da giysiler içerisine entegre edilebilecektir. Böylece, elektrik kaynağından uzak yerlerde spor yapmak için veya görevleri nedeniyle bulunmak durumunda kalan insanlar elektrikli cihazları için gerekli enerjiyi kendileri, fotovoltaik tekstillerle elde edebileceklerdir.

Çalışmanın temel amacı, tekstil lifi üzerinde seçilmiş farklı malzemeler kullanılarak fotovoltaik etkinin sağlanması ve ölçülmesidir. Diğer amaç ise genel kullanım

alanına uygun bir koruyucu bir tabakanın fotovoltaik lif yapısını bozmadan yapıya eklenmesidir.

Güneş, insanlar ve doğadaki diğer canlılar tarafından farklı amaçlar için kullanılan, enerji üretimi için kullanıldığında çevreye zarar vermeyen ve tükenmeyen bir enerji kaynağıdır. Güneş pilleri ise, güneş enerjisini elektrik enerjisine dönüştüren yapılardır. Güneş enerjisinin her yerde bulunabilir, pratik, temiz ve çevre dostu olması nedeniyle, dünyada, güneş pillerine olan talep gün geçtikçe artmaktadır.

Fotovoltaik malzemelerin tekstillerle çeşitli yöntemler kullanılarak kombine edilmesi son yıllarda tüm dünyadaki araştırmacıların ilgilendikleri bir konu olmuştur. Günümüzde, ağırlıklı olarak silikon esaslı güneş pillerinin tekstillere entegre edilerek kullanıldığı fotovoltaik tekstil yapıları gibi güneş ışığını kullanarak elektrik enerjisi üreten ticari ürünler mevcuttur.

Fotovoltaik enerji, temiz (enerji üretimi sırasında veya sonrasında, çevreye zehirli kimyasal maddeler vermeyen), güvenilir ve pratik bir enerji teknolojisidir. Fotovoltaik tekstiller, günlük hayatın yanında özellikle elektrik kaynaklarından uzak yerlerde çalışmak durumunda olan (askerler gibi) ya da spor faliyetleri yapmak isteyen insanların, yanlarındaki cihazlar için gerekli elektrik enerjisi ihityacını karşılayarak, hayatımızdaki önemli bir boşluğu dolduracaklardır.

Fotovoltaik tekstiller küresel tekstil endüstrisinde önemli bir konuma gelmeye başlamıştır ve dünya genelinde gelişen teknoloji ile birlikte talep de artmaktadır. Eşsiz bir ürün olarak yüksek katma değere ve ileri fonksiyonlara sahip olması, tekstil endüstrisinin gelişmesi için gelecek vaat etmektedir. Ayrıca böyle bir ürünün Türkiye'de üretilmesi ve geliştirilmesi, ülkemizin diğer dünya ülkeleri arasında rekabet edebilirliğini arttıracaktır.

Bu tez kapsamında üretilen esnek fotovoltaik lifler, ileride fotovoltaik tekstil üretiminde kullanıldığında esnek, hafif, kolay taşınabilir, rulo yapılabilir veya katlanabilir, fotovoltaik ürünler elde edilebilecektir.

Bu tez çalışmasında organik güneş pili malzemeleri kullanılarak fotovoltaik bir tekstil lifi geliştirilmesi amaçlanmıştır. Literatürdeki mevcut çalışmalar göz önüne alındığında, bu konuda yapılan çalışmalarda tekstil liflerinin kullanılmadığı görülmektedir. Türkiye'de tamamlanan doktora tezinde, (Bedeloğlu, 2009) ilk defa organik fotovoltaik malzemeler kullanılarak fotovoltaik tekstil lif ve şeritleri geliştirilmiştir. Bu çalışmada ise daha önceki deneyimler de göz önünde tutularak farklı kimyasal maddeler ve tekstil lifleri ile denemeler yapılmıştır.

Üretilen fotovoltaik lif hem tekstil lifinin esneklik, hafiflik, incelik gibi özelliklerini taşıyan hem de güneş enerjisini elektrik enerjisine dönüştüren bir güneş pili yapısındadır. Fotovoltaik lif herhangi bir tekstil malzemesinin (iplik ve kumaş gibi) üretilmesinde veya sonradan yapının içine katılması şeklinde kullanılabilir.

Dünya genelinde fotovoltaik lifler konusunda yapılmış çok sınırlı sayıda çalışma ve yeni başlayan çalışmalar/projeler mevcuttur. Organik güneş pili malzemeleri kullarak gerçekleştirilen çalışmalarda taşıyıcı tabaka olarak metal tel, optik lif, polyimid kaplı optik lif, polipropilen şeritler ve polipropilen lif kullanılmıştır. Optik lifler, tekstil yapısına çok uyumlu değildir. Metal tel ise tekstil lifine göre daha ağır ve daha az esnektir. Üretimden rastgele alınmış polipropilen yapılar ise pürüzlülüğü ve ıslanma davranışları nedeniyle metal ve çözelti kaplanması sırasında bazı problemler çıkartmıştır. Ayrıca tüm mevcut çalışmalarda, verimin düşük olması söz konusudur.

Fotovoltaik bir lifin elde edilmesi konusu, hem Türkiye hem de dünya için yeni ve ilginç bir konudur. Üretim yöntemi olarak, önceki çalışmaların çoğunda standart bir güneş pilinin üretim aşamalarına benzer yöntemler kullanılarak lif elde edilmeye çalışılmıştır. Bu çalışmada ise kullanılan malzemeler (akıllı malzemelerin ve koruyucu tabakanın seçilmesi) açısından farklılıklar bulunmaktadır.

Bu tez çalışması ile fotovoltaik lif konusunda akademi ve sanayi bir araya gelerek ilk adımı atmıştır. Türkiye'de bu konuda Ağustos 2009 yılında tamamlanan "Photovoltaik etki gösteren bir lif geliştirilmesi" isimli doktora tezi mevcuttur; ancak araştırmacılar tarafından alınmış bir patent henüz bulunmamaktadır. Öte yandan bu tez çalışması ile yapılmış özgün çalışma sonucunda patent başvurusu yapılmıştır.

1. INTRODUCTION

Optimization of the performance of photovoltaic and other systems that convert sunlight into other useful forms of energy is contingent on the knowledge of the properties of sunlight. This chapter provides a synopsis of the important solar phenomena, including the solar spectrum, atmospheric effects, solar radiation components, determination of sun position, measurement of solar parameters and positioning of the solar collectors.

1.1 Photovoltaic Technology

1.1.1 Solar energy

Due to the exhaustion of oil sources and rising oil prices and environmental issues spawning political momentum for renewable energy, solar electricity takes a crucial poisition in the global energy economy (Figure 1.1).

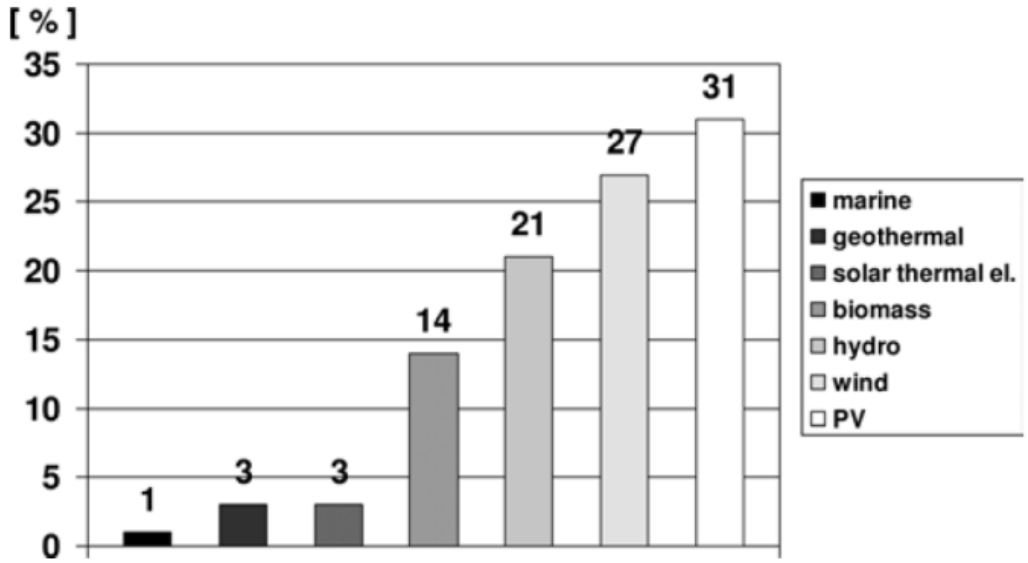


Figure 1.1 : Predicted scenario for the energy sources by 2040 (Url-1).

1.1.2 Sun light and its radiation

The sun is surrounded by gas heated by nuclear fusion reactions at its centre (Quasching, 2003). Internal temperatures reach 20 million K. The intense radiation

from the interior is absorbed by a layer of hydrogen ions closer to the sun's surface, as shown in Figure 1.2.

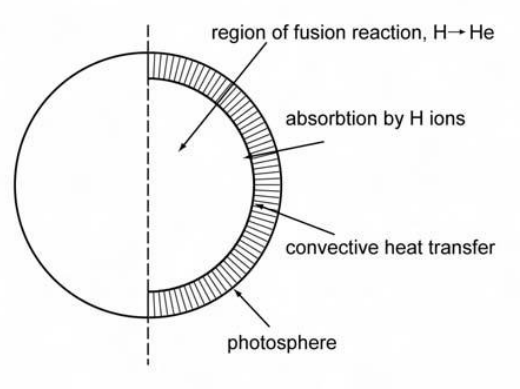


Figure 1.2 : Regions in the sun's interior (Corkish et al., 2007)

Through this optical barrier, energy is transferred by convection and then re-radiated from the outer surface of the sun, the photosphere. This emits radiation approximating to a blackbody with a temperature of nearly 6000 K, as shown in Figure 1.3 (Corkish et al., 2007).

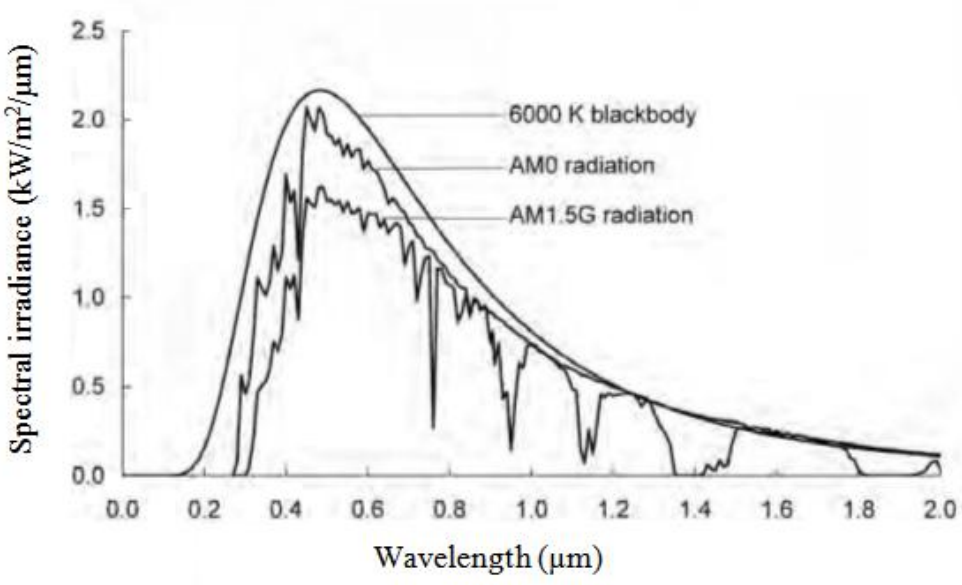


Figure 1.3 : The spectral irradiance (AM1.5G) (Corkish et al., 2007).

The spectrum of the Sun's solar radiation is close to that of a blackbody with a temperature of about 5,800 K. The Sun emits EM radiation across most of the electromagnetic spectrum. Although the Sun produces Gamma rays as a result of the nuclear fusion process, these super high energy photons are converted to lower energy photons before they reach the Sun's surface and are emitted out into space, so the Sun doesn't give off any gamma rays to speak of. The Sun does, however,

emit X-rays, ultraviolet, visible light, infrared, and even Radio waves. When ultraviolet radiation is not absorbed by the atmosphere or other protective coating, it can cause damage to the skin known as sunburn or trigger an adaptive change in human skin pigmentation.

The spectrum of electromagnetic radiation striking the Earth's atmosphere spans a range of 100 nm to about 1 mm. This can be divided into five regions in increasing order of wavelengths (Anonymous, 2009a) shown in Figure 1.4.

Ultraviolet C or (UVC) range, which spans a range of 100 to 280 nm. The term *ultraviolet* refers to the fact that the radiation is at higher frequency than violet light (and, hence also invisible to the human eye). Owing to absorption by the atmosphere very little reaches the Earth's surface (Lithosphere). This spectrum of radiation has germicidal properties, and is used in germicidal lamps.

Ultraviolet B or (UVB) range spans 280 to 315 nm. It is also greatly absorbed by the atmosphere, and along with UVC is responsible for the photochemical reaction leading to the production of the ozone layer.

Ultraviolet A or (UVA) spans 315 to 400 nm. It has been traditionally held as less damaging to the DNA, and hence used in tanning and PUVA therapy for psoriasis.

Visible range or light spans 380 to 780 nm. As the name suggests, it is this range that is visible to the naked eye.

Infrared range that spans 700 nm to 10^6 nm (1 mm). It is responsible for an important part of the electromagnetic radiation that reaches the Earth. It is also divided into three types on the basis of wavelength:

- Infrared-A: 700 nm to 1,400 nm
- Infrared-B: 1,400 nm to 3,000 nm
- Infrared-C: 3,000 nm to 1 mm.

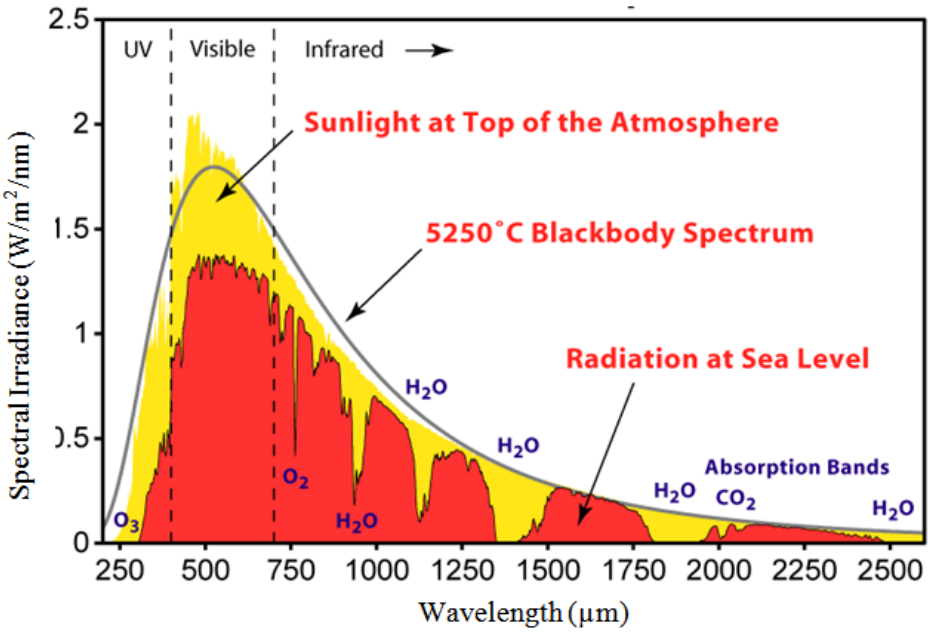


Figure 1.4 : Solar irradiance spectrum above atmosphere and at surface (Markvarti, 1994).

Illumination or irradiance is a measure of energy density in W/m^2/unit wavelength in meter unit. Luminous or irradiation is energy densty in kWh/m^2. Illumination is an amount of light in a moment. This energy has a 150 million km distance to the earth, and the sum of extraterrestrial energy density is 1367 W/m^2, refers to as the solar constant and shown as AM0 and it has a range between 0-1100 W/m^2 (Markvarti 1994).

When sunlight comes to Earth's atmosphere, some is absorbed while some is scattered and the rest passes through uninfluenced by the molecules in the atmosphere and is either absorbed or reflected by objects at ground level.

Various molecules behaves different. Carbon dioxide, water vapour and ozone have several substantial absorbtion wavelengths. Ozone has an important role by absorbing a substantial amount of radiation in the ultraviolet region of the spectrum, whereas carbon dioxide and water vapour absorbs primarily in the visible and infrared parts of the spectrum as shown in Figure 1.5.

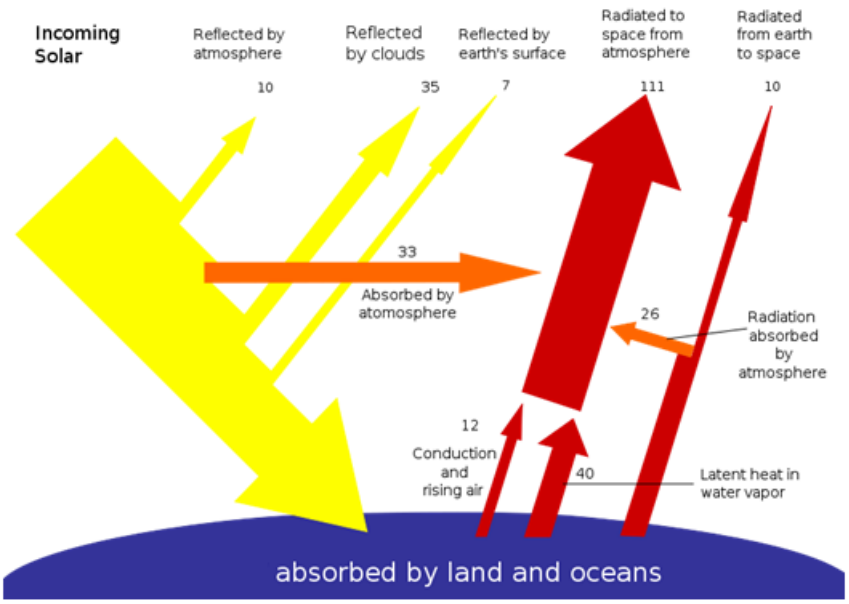


Figure 1.5 : Breakdown of the incoming solar energy[Url-2]

Length of path through the atmosphere defines the amount of sunlight which are absorbed or scattered. This path length is generally compared with a vertical path directly to sea level, which is defined as air mass = 1 (AM1). This radiance reduces 70% to 1000 W/m^2 at sea level which is AM0 of its original value (Messenger et al, 2004).

1.1.3 The photovoltaic technology

Photovoltaic, as a word, refers to light electricity. “Photo” from Greek roots, meaning light, and “voltaic” from “volt”, that takes the name from Italian scientist Alessandro Volta who worked on electrical fields, which is the unit used to measure electric potential at a given point.

Photovoltaic, when it is exposed to light, is the capability to produce electrical potential (voltage). Photovoltaic device refers to the devices which can produce electricity with photovoltaic effect.

Photovoltaics is the technology that generates direct current (DC) electrical power measured in Watts (W) or kiloWatts (kW) from semiconductors when they are illuminated by photons. As long as light is shining on the solar cell (the name for the individual PV element), it generates electrical power. When the light stops, the electricity stops. Solar cells never need recharging like a battery (Hegedus and Luque, 2003).

Conventionally, photovoltaic technologies are thin constructions using sun light. But recent studies shows that new generation photovoltaic technologies produced from new polymers can use the energy from other parts of solar spectrum, such as infrared (Janssen, 2006) and ultraviolet (Yamaura, Muraoka, Yamauchi, Muramatsu and Hiroi, 2003) (Bedeloglu, 2009).

1.1.4 The photovoltaic effect

Photovoltaic effect can be defined in many ways as given below:

i. It occurs in a material illuminated with a radiance at a comprehensive wavelength.
ii. Photovoltaic effect, refers to current in a semiconductor like nonhomogenius silicon or at a junction between two types of materials.
iii. It refers to voltage producing with a cause of emitting photon energy along a pn junction.
iv. It refers to a current between two electrods when one is exposed to light (Graf, 1999).

1.1.5 History of photovoltaics

Researchers have been working on photovoltaics since 1800s. The first functional and intentionally made photovoltaic device was made by Fritts in 1883. It was melted into a thin layer on a metal substrate and pressed a Au-leaf film as the top contact on an aproxximately 30 cm^2 area by him.

First research on photoconductivity are reported by Smith in 1873 and Adams in 1876 by using Sellenium with a 1-2%. Pochettino in 1906 and Volmer in 1913 worked on first organic heterojunction having photoconductivity. First solar cell containing Silisium in 1918, and Germanium based solar cell in 1951 were developed. First Silica based inorganic solar cell was developed in Bell Labs by Chapin et al. in 1954 with a 6% efficiency and this efficiency is overcome increased to 10% in a short while, and used on space technology applications as power generator (Goetzberger et al., 2002). Mono crystal silica based solar cells has reached an approximately 24% efficient in laboratory conditions (Green, Emery, King, Igari and Warta, 2003). Silica based solar cells has a 99% part in all solar cell types.

The modern era of photovoltaics started in 1954 accidentally by Bell Labs researchers in USA as the room lights were on, they found out pn junction diodes generated a voltage. In a year, They had carried out a 6% efficienct Si pn junction solar cell (Chapin et al., 1954). In the same year, a thin film heterojunction solar cell based on Cu2S/CdS having 6% efficiency results were published by a group at Wright Patterson Air Force Base in the US (Reynolds et al., 1954). Next year, RCA Lab in the US reported 6% GaAs pn junction solar cell (Jenny et al. 1956). After 1960, several key papers explaining fundamentals of pn junction solar cell operation including the theoretical relation between band gap, incident spectrum, temperature, thermodynamics, and efficiency by Prince (1955), Loferski (1956), Rappaort and Wysoski (1960), Shockley (a Nobel laureate) and Queisser (1961) (Chapin et al., 1954).

At the beginning of 1960s, a lot of dyes are found out having semi conducting property (Bube, 1960) and later on, these are included in first organic materials showing photovoltaic effect. First amorphous silicon solar cell is reported by Carlson and Wronski in 1976 with a 1,1% efficiency (Goetzberger, Hebling and Schock, 2003).

A solar cell is used on a satellite called Vanguard-1 in 1958 for the first time as energy (0,1 watt) generator. Occuring oil crisis in 1973 effected the idea that photovoltaics can be used on application on the world, though. Since 1970s, photovoltaic modules firstly on the roof of buildings, later on planes and solar cars, traffic lights, calculators, tents and all kind of mobile constructions including textile, army, sport and electronic industry and daily life, often are used. In 1980, first plane journey with solar energy, first plane without human (Pathfinder) which its wings equipped photovoltaic modules in 2002 are significant examples for photovoltaics (Altın, 2005).

The milestones on improving organic solar cells are shown in Table 1.1.

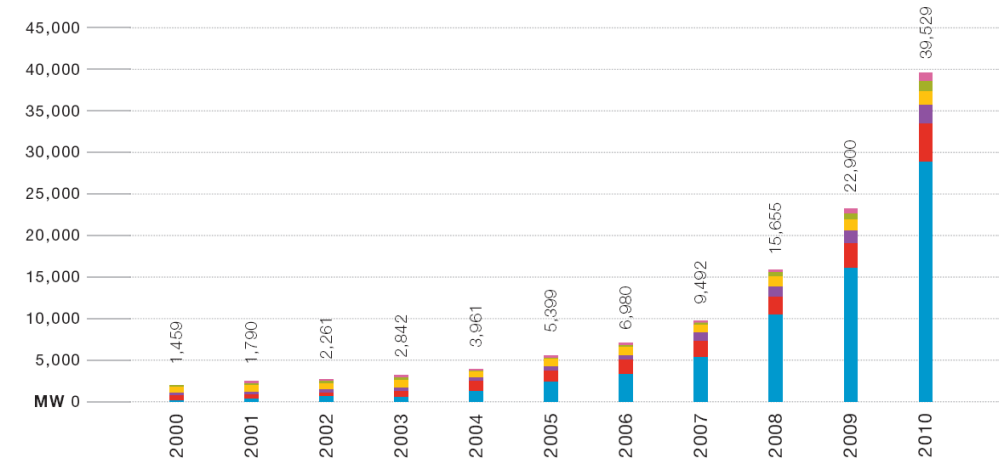
Table 1.1 : Significiant dates for organic solar cells (Bedeloglu, 2009).

1839	Observation of photoelectrochemical event by Becquerel
1906	Photoconductivitiy studies by Pochettino
1958	Kearns and Calvin reported 200 mV by employing magnesium phtalocyanine (MgPh)
1986	The first heterojunction photovoltaic device was improved by Tang
1991	Hiramoto's first dye/dye blend realization heterojunction photovoltaic construction by sublimation
1993	The first polymer/C60 heterojunction photovoltaic device by Sariciftci
1994	The first polymer/C60 blend heterojunction photovoltaic device by Yu
1995	The first polymer/polymer blend heterojunction photovoltaic device by Yu and Hall
2000	Using oligomer C60 double and triples as photoactive materials in photovoltaic by Peters and van Hal
2001	Double wire polymers used in photovoltaics by Ramos
2003	The first MDMO-PPV:PCBM heterojunction device by Sariciftci et al.

1.1.6 Photovoltaic market

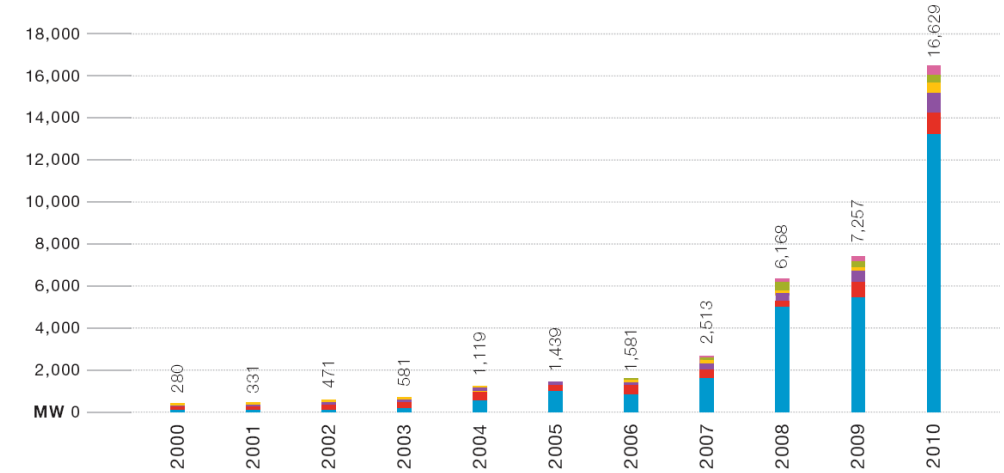
Over the past decade, the photovoltaic (PV) market has experienced unprecedented growth. In particular in 2010, the photovoltaic market has reached a cumulative installed capacity of roughly 40 GW world-wide, with an annual added capacity of 16.6 GW. The photovoltaic power is well on the way to becoming a fully competitive part of the electricity system in the European Union (EU) and an increasingly important part of the energy mix around the Globe. But much of the progress in recent years has been very heterogeneous, varying from country to country, due to several factors, the most important being different national regulations and incentive schemes as well as varying availability of financing facilities.

The PV industry experienced significant growth in 2010. Capacity additions grew from 7.2 gigawatts (GW) installed in 2009 to 16.6 GW in 2010. The total installed capacity in the world now amounts to around 40 GW, producing some 50 terawatt-hours (TWh) of electrical power every year (Url-7) as seen in Figure 1.6, 1.7 and 1.8.



	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010
China	19	30	45	55	64	68	80	100	145	373	893
APEC	38	43	49	57	66	80	112	170	466	718	1,191
Rest of the world	758	814	894	971	1,000	1,010	1,128	1,190	1,303	1,427	1,844
North America	146	177	222	287	379	496	645	856	1,205	1,744	2,727
Japan	318	452	637	860	1,132	1,422	1,708	1,919	2,149	2,632	3,622
EU	181	275	414	613	1,319	2,324	3,307	5,257	10,387	16,006	29,252
Total	**1,459**	**1,790**	**2,261**	**2,842**	**3,961**	**5,399**	**6,980**	**9,492**	**15,655**	**22,900**	**39,529**

Figure 1.6 : Evolution of global cumulative installed capacity - 2000-2010 (Url-7).



	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010
China	0	11	15	10	9	4	12	20	45	228	520
APEC	5	5	7	8	10	13	33	59	300	258	473
Rest of the world	88	56	80	77	29	10	118	63	115	130	417
North America	23	31	46	65	92	117	149	212	349	539	983
Japan	112	135	185	223	272	290	287	210	230	483	990
EU	52	94	139	199	707	1,005	983	1,950	5,130	5,619	13,246
Total	**280**	**331**	**471**	**581**	**1,119**	**1,439**	**1,581**	**2,513**	**6,168**	**7,257**	**16,629**

Figure 1.7 : Evolution of global annual PV market - 2000-2010 (Url-7).

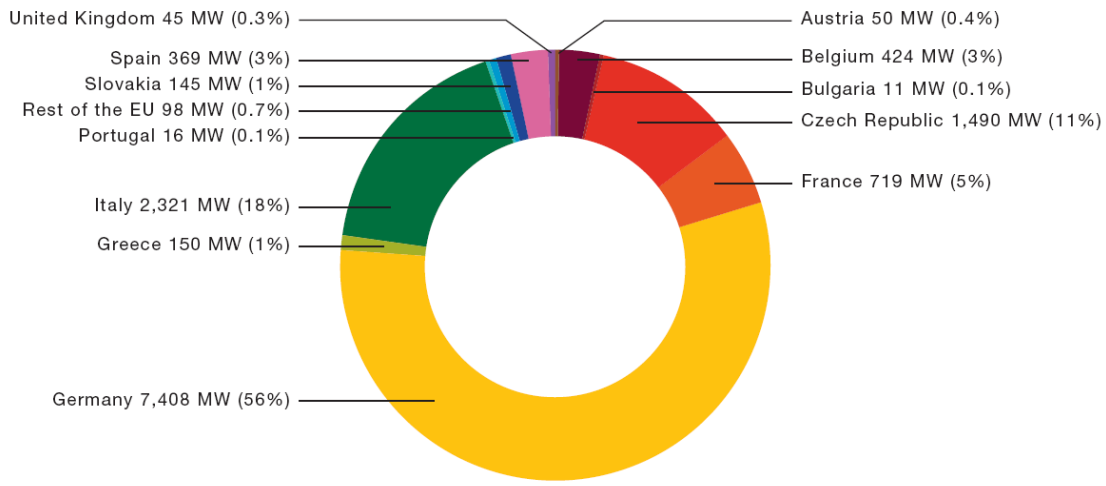


Figure 1.8 : 2010 EU market share (MW, %) (Url-7).

1.2 Solar Cells and Collectors in Turkey

Solar collectors, mostly on Aegean an Mediterranean regions in Turkey, are hot water generating systems that converts solar energy into heat energy. So far, installed solar collectors capacity in Turkey is approximately 12 million m^2 and annual production is 750 thousand m^2 which has a significiant amount in whole producting on the world. Some part of this production is used domestic and some part is exported. Heat energy from solar energy is annually 420 thousand TEP(=Ton Equivalent Petroleum). These collectors contribution to Turkey's primary energy consumption by years is shown in Table 1.2 (Bedeloglu, 2009).

Table 1.2 : Annual production of solar connectors in Turkey (Url-6)

Year	Solar Energy Production (thousand TEP)
1998	210
1999	236
2000	262
2001	290
2004	375
2007	420

TEP: Ton Equivalent Petroleum

Solar cells are used far from grids, countryside regions for signalling and low electric required usages in Turkey in economical way.

Figure 1.9 : Installed PV system for daily electricity (4,8 kWp) (EİE, 2011).

Solar Energy Research Center (GUNAM), Middle East Technical University (ODTU), Nanoscience and Nanotechnology Advanced Research Institute, Istanbul Technical University, Advanced Lithographic Methods Laboratory, Istanbul University, Infrastructure Laboratories Center, Mugla University, ENAR Program, Republic of Turkey Ministry of Energy and Natural Resources (ETKB), Energy Data and Technology Management Center (EBITEM), General Directorate of Electrical Power Resources Survey and Development Administration (Url-6), Environmental Tests Center, TUBITAK-UME, Electrical Energy Storage Technologies R&D, Diagnosis and Risk Evaluation Center, TUBITAK-MAM have been studying solar cells and photovoltaic applications in Turkey in recent years (Icli et al., 2010).

1.2.1 Solar energy and photovoltaic technology in Turkey

With a surface area of 78 Mha and 73 Million population, Turkey's production and consumption based on primary energy resources are projected to increase by 76 % during 2010-2020 period according to the “Blue Book” published by Turkish Ministry of Energy and Natural Resources at the end of 2010 (Url-3).

Gross electric energy consumption of Turkey in 2009 decreased by 2,4 % while the production decreased by 2,0 % in reference to 2008. These figures are 193,3 billion kWh and 194,1 billion kWh respectively. Total installed capacity of electricity is 46.126 MW as of July 2010. Total electric production in 2009, broken down by specific resources, stands at 48,6 % natural gas, 28,3 % coal, 18,8 % hydro, 3,4 %

liquid fuels and 1,1 % renewables. The cumulative installed PV power in Turkey at the end of 2010 was estimated to be about 6 MW (Icli et al., 2010).

1.3 Photovoltaic technologies

1.3.1 Single crystalline (sc-Si) and multi-crystalline (mc-Si) silicon based solar cells

Single crystalline (sc-Si) and multi-crystalline (mc-Si) silicon based solar cells are first generation solar cells. Silicon technology has been improved much more before photovoltaics had been developed and has been used for microelectronic industry in big amounts. Therefore the studies in this field started and are continuing with these materials. The best efficiency for single crystalline silicon is 24,7% in laboratory conditions. Researchers are aimed to new materials due to high purified silicon requirement, thick crystalline silicon layer in order to absorb light (100 nm for 90% absorbtion) and also inexpensive module invesment for this type of solar cells (Goetzberger et al., 2002).

1.3.2 Thin film technology solar cells

Thin films, such as thin silicon films (amorphous silicon (a-Si), protocrsytalline, nanocrystalline (nc-Si), microcrystalline and crystalline silicon (c-Si), cadmium telluride (CdTe), copper indium gallium selenide (CIGS), are expressed as second generation solar cells. Researchers tended to thin films on account of cheap production costs. Thin film solar cells can be produced in required space whereas silicon based has to be at least 100 cm^2 areas. While in laboratory conditions produced cells having 17,7% efficiency, prototype modules in terms of generating power has 10,2% efficiency. There are advantages of this type of solar cells such as high efficiency with gathering crystalline and amorphous technologies in heterojunctions, rather lower processing temperatures (<200°C) and low cost technology. CdTe, a high crystalline material, has a 16% efficiency of laboratory type small cells, and commercial modules has approximately 7% efficiency. The production cost of CdTe based solar cells is lower comparing to silicon based cells (Url-7). Semiconductors used in thin films has higher absorbance coefficient compared to silicon. Hence inexpensive semiconductors are used rather less in this types of cells (Goetzberger et al., 2002).

1.3.3 Multi junction (emerging) technologies

Semiconductors such as GaAs, GaAlAs, GaInAsPO, InAs, InSb, and InP used in multi junction (emerging) solar cells which are connected to each other with various band ranges have a wider range in order to use more energy of solar spectrum and shows better performance. But these materials are expensive, and therefore the most important usages are available on space applications. For worldwide applications, low energy generating optical condenser technology is developed (Swanson, 2002). Such condenser cells have a 30% efficiency. For example, Gallium Arsenide (GaAs) performs 25-28% (with an optical condenser) efficiency in laboratory conditions. Multi junctional GaAs constituted with other semiconductors have a 30% efficiency. GaAs solar cells are used in space applications and optical condensed systems (Goetzberger et al. 2002).

1.3.4 Organic solar cells

Molecular and polymer photovoltaics are distinguished by the type of material and fabrication methods. Molecular photovoltaic technologies are generally fabricated by sublimation under vacuum of successive layers of electron- and hole-transporting materials. Charge photogeneration occurs at the interface between the two layers, also known as the organic heterojunction. Figure 1.10 shows the chemical structures of some small molecules commonly used in OPVs. These include materials primarily used as dopants in polymer OPVs as well as charge transport layers in hybrid organic–inorganic devices. The first organic solar cells exhibiting reasonable power conversion efficiencies were fabricated by Tang (1986) using phthalocyanine and perylene derivatives; these families of materials have accordingly been heavily investigated. Buckminsterfullerene (C_{60}) and its derivatives have also been widely investigated, both as separate layers in molecular OPVs and in bulk heterojunction polymer OPVs (Sun and Sariciftci, 2005).

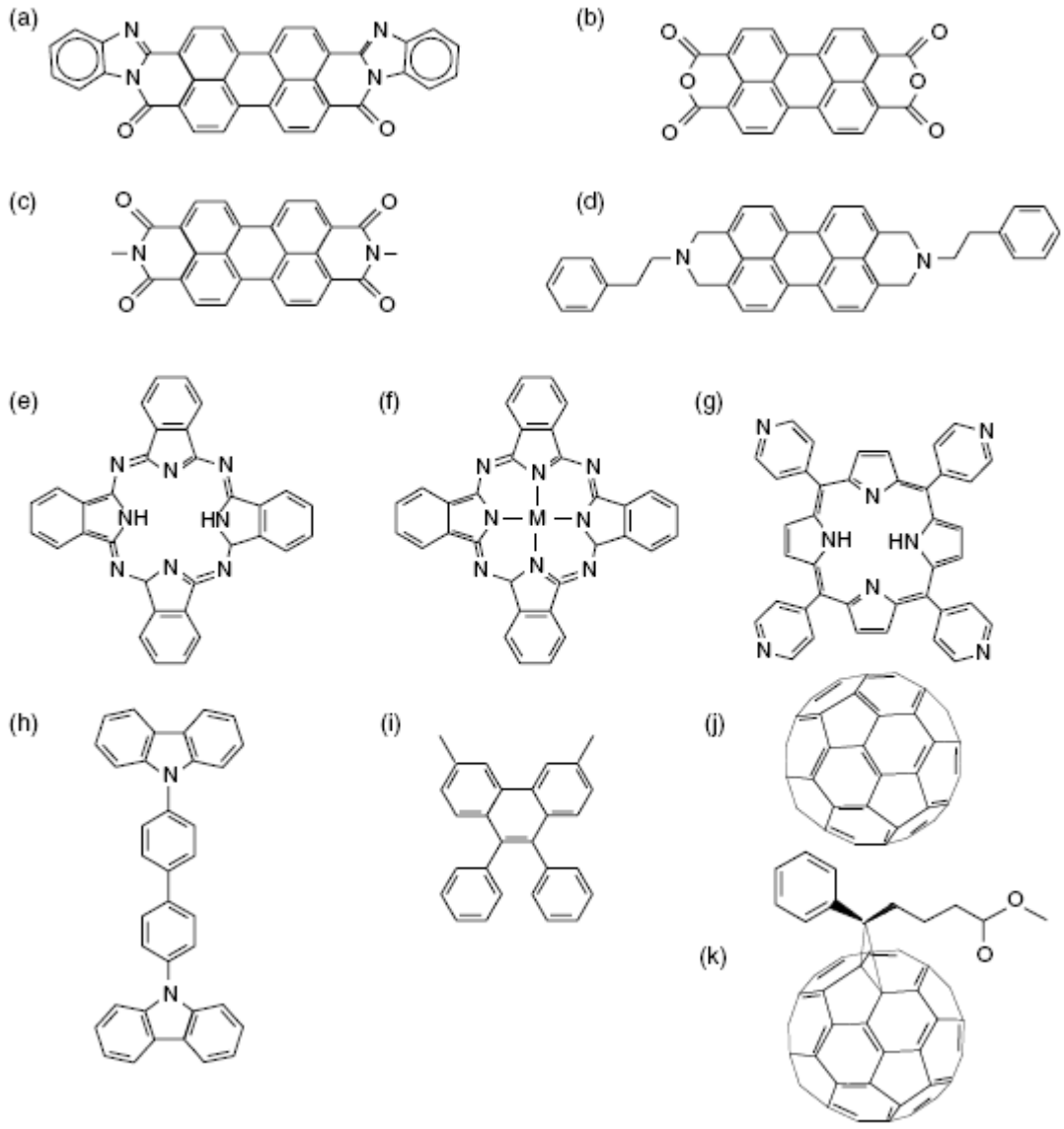


Figure 1.10 : Chemical structures of molecular semiconductors used in PVs. (a) PTCBI, (b) PTCDA, (c) Me-PTCDI, (d) Pe-PTCDI, (e) H2Pc, (f) MPc (M¼Zn, Cu), (g) TPyP, (h) TPD, (i) CBP, (j) C60, (k) 5,6-PCBM (Sun and Sariciftci, 2005).

In contrast, polymer OPVs are generally prepared by solution processing. The most efficient devices consist of blends of a conjugated polymer and a molecular sensitizer, or blends of two different conjugated polymers. Such blends have interfaces throughout the active layer, known as a bulk heterojunction. Multilayer devices consisting of two different materials, most commonly two different polymers, have also been fabricated and are discussed. Figure 1.11 shows repeat units of various conjugated polymers used in active layers of organic solar cells. Poly(p-phenylene vinylene) (PPV) and various derivatives with different side-chain substitution have been most widely used in the active layer of polymer OPVs.

Derivatives of polythiophene (PT) and, more recently, polyfluorene have also been investigated by a number of research groups (Sun and Sariciftci, 2005).

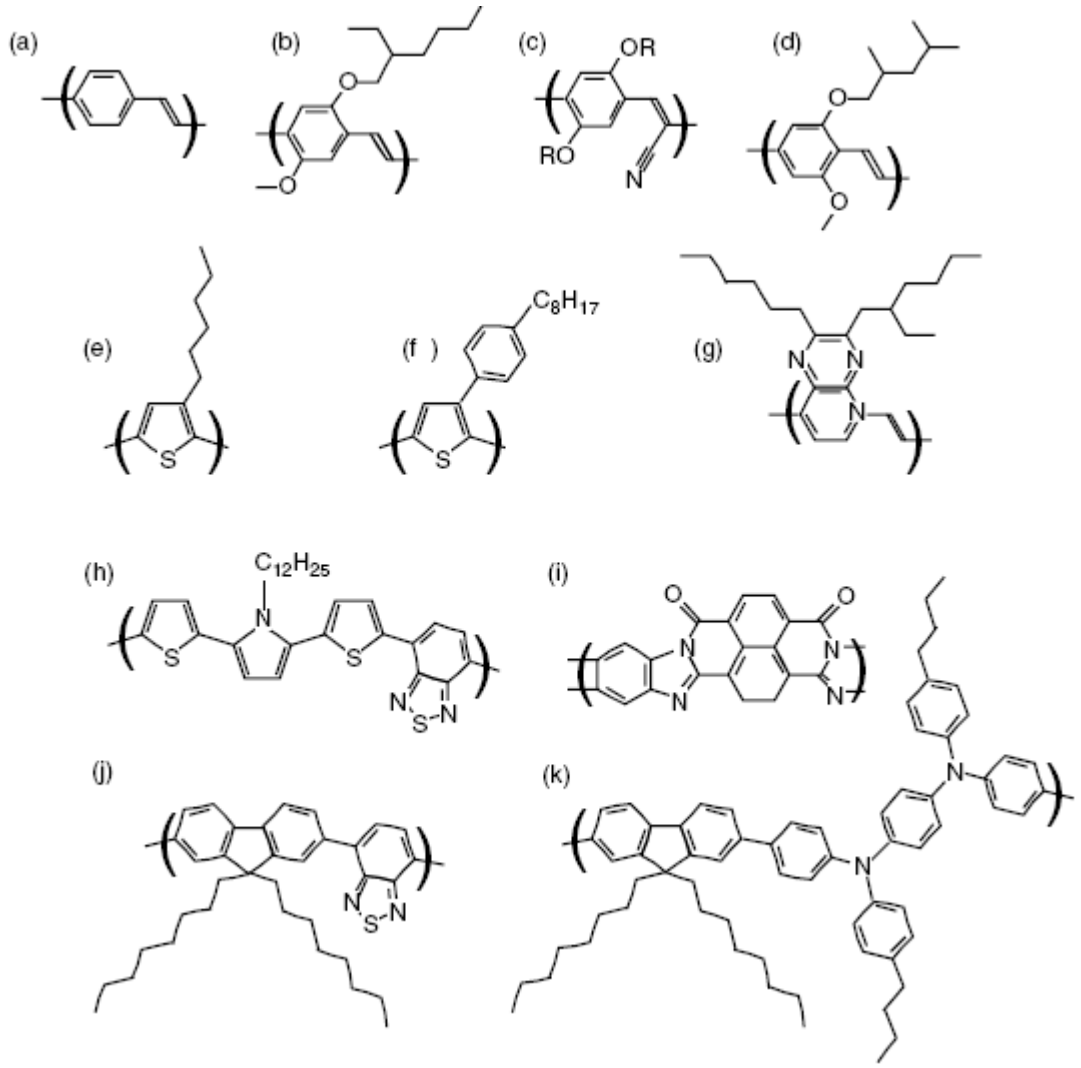


Figure 1.11 : Chemical structures of conjugated polymers used in OPVs: (a) PPV, (b) MEHPPV, (c) CN–PPV (various alkoxy cyano-derivatives have been prepared), (d) MDMO-PPV, (e) P3HT, (f) POPT, (g) EHH–PpyPz, (h) PTPTB, (i) BBL, (j) F8BT, (k) PFMO (Sun and Sariciftci, 2005).

Organic semiconductors, conductive polymers, dyes, pigments, and liquid crystallines are used in organic solar cells. Solar cells efficiency table is given in Figure 1.12.

Classification[a]	Effic.[b] (%)	Area[c] (cm^2)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF[d] (%)	Test centre[e] (and date)	Description
Silicon							
Si (crystalline)	25.0 ± 0.5	4.00 (da)	0.706	42.7[f]	82.8	Sandia (3/99)[g]	UNSW PERL [18]
Si (multicrystalline)	20.4 ± 0.5	1.002 (ap)	0.664	38.0	80.9	NREL (5/04)[g]	FhG-ISE [19]
Si (thin film transfer)	19.1 ± 0.4	3.983 (ap)	0.650	37.8[h]	77.6	FhG-ISE (2/11)	ISFH (43-μm thick) [20]
Si (thin film submodule)	10.5 ± 0.3	94.0 (ap)	0.492[i]	29.7[i]	72.1	FhG-ISE (8/07)[g]	CSG Solar (1–2 μm on glass; 20 cells) [21]
III-V cells							
GaAs (thin film)	**28.3 ± 0.8**	**0.9944 (ap)**	**1.107**	**29.47[i]**	**86.7**	**NREL (8/11)**	**Alta devices [3]**
GaAs (multicrystalline)	18.4 ± 0.5	4.011 (t)	0.994	23.2	79.7	NREL (11/95)[g]	RTI, Ge substrate [22]
InP (crystalline)	22.1 ± 0.7	4.02 (t)	0.878	29.5	85.4	NREL (4/90)[g]	Spire, epitaxial [23]
Thin film chalcogenide							
CIGS (cell)	19.6 ± 0.6[k]	0.996 (ap)	0.713	34.8[l]	79.2	NREL (4/09)	NREL, CIGS on glass [24]
CIGS (submodule)	**17.4 ± 0.5**	**15.993 (da)**	**0.6815[i]**	**33.84[i]**	**75.5**	**FhG-ISE (10/11)**	**Solibro, four serial cells [4]**
CdTe (cell)	16.7 ± 0.5[k]	1.032 (ap)	0.845	26.1	75.5	NREL (9/01)[g]	NREL, mesa on glass [25]
Amorphous/nanocrystalline Si							
Si (amorphous)	10.1 ± 0.3[m]	1.036 (ap)	0.886	16.75[f]	67.0	NREL (7/09)	Oerlikon Solar Lab, Neuchatel [26]
Si (nanocrystalline)	10.1 ± 0.2[n]	1.199 (ap)	0.539	24.4	76.6	JQA (12/97)	Kaneka (2 μm on glass) [27]
Photochemical							
Dye sensitised	**11.0 ± 0.3[o]**	**1.007 (da)**	**0.714**	**21.93[h]**	**70.3**	**AIST (9/11)**	**Sharp [5]**
Dye sensitised (submodule)	9.9 ±0.4[o]	17.11 (ap)	0.719[j]	19.4[i,l]	71.4	AIST (8/10)	Sony, eight parallel cells [28]
Organic							
Organic thin film	**10.0 ± 0.3[o]**	**1.021 (ap)**	**0.899**	**16.75[j]**	**66.1**	**AIST (10/11)**	**Mitsubishi Chemical [6]**
Organic (submodule)	**4.2 ± 0.2[o]**	**294.5 (da)**	**0.714**	**12.26[j]**	**47.7**	**AIST (9/11)**	**Sumitomo Chemical (10 series cells) [7]**
Multijunction devices							
GaInP/GaInAs/Ge	**34.1 ± 1.2**	**30.17 (t)**	**2.691**	**14.7[j]**	**86.0**	**FhG-ISE (9/09)**	**AZUR (monolithic) [8]**
a-Si/nc-Si/nc-Si (thin film)	12.4 ± 0.7[p]	1.050 (ap)	1.936	8.96[h]	71.5	NREL (3/11)	United Solar [29]
a-Si/nc-Si (thin film cell)	**12.3 ± 0.3[q]**	**0.962(ap)**	**1.365**	**12.93[j]**	**69.4**	**AIST (7/11)**	**Kaneka [9]**
a-Si/nc-Si (thin film submodule)[j]	11.7 ± 0.4[n,r]	14.23 (ap)	5.462	2.99	71.3	AIST (9/04)	Kaneka [30]

[a] CIGS, CuInGaSe2; a-Si, amorphous silicon/hydrogen alloy.
[b] Effic., efficiency.
[b] (ap), aperture area; (t), total area; (da), designated illumination area.
[d] FF, fill factor.
[e] FhG-ISE, Fraunhofer Institut fùr Solare Energiesysteme; JQA, Japan Quality Assurance; AIST, Japanese National Institute of Advanced Industrial Science and Technology.
[f] Spectral response reported in Version 36 of these Tables.
[g] Recalibrated from original measurement.
[h] Spectral response and current–voltage curve reported in Version 38 of these Tables.
[i] Reported on a "per cell" basis.
[j] Spectral response and current–voltage curve reported in present version of these Tables.
[k] Not measured at an external laboratory.
[l] Spectral response reported in Version 37 of these Tables.
[m] Light soaked at Oerlikon prior to testing at NREL (1000 h, one sun, 50 ºC).
[n] Measured under IEC 60904–3 Ed. 1: 1989 reference spectrum.
[o] Stability not investigated. References 31 and 32 review the stability of similar devices.
[p] Light soaked under 100 mW/cm2 white light at 50 ºC for over 1000 h.
[q] Stabilised by manufacturer.
[r] Stabilised by 174 h, one sun illumination after 20 h, five sun illumination at a sample temperature of 50 ºC.

Figure 1.12 : Confirmed terrestrial cell and submodule efficiencies measured under the global AM1.5 spectrum (1000 W/m^2) at 25 ºC(IEC 60904-3İ 2008, ASTM G-173-03 global) (Green et al, 2011).

1.3.5 Dye-sensitized solar cells

A dye-sensitized solar cell (DSSC, DSC or DYSC) (Haiying, 2011) is a group of low-cost thin film solar cells (Url-7). It is a photoelectrochemical system which is based on a semiconductor formed between an electrolyte and a photo-sensitized anode. Michael Gratzel and Brian O'Regan invented a later version of a dye solar cell called Gratzel cell, won the 2010 Millenium Technology Prize for this invention, at the Ecole Polytechnique Federale de Lausanne in 1991 (Gratzel, 2003).

However in conventional photovoltaic technologies where the semiconductor undertakes light absorption and charge carrier transport the two functions are

seperated here. Light is absorbed by a sensitizer bonded on the top of a wide band semiconductor. Charge seperation comes out between photo-induced electron injection from the dye into the conduction band of the solid. Carriers are transported in the conduction band of the semiconductor to the charge collector. Sensitizers having a large absorption band in conjunction with oxide films of nanocrystalline construction are used in order to harvest a broad fraction of sunlight. Current conversion efficiencies (IPCE) over 10% (standard AM 1.5) have been reached (Gratzel, 2003).

1.4 Photovoltaic Textiles

1.4.1 Technical-smart textiles

As parallel to growing population worldwide, variety of goods, changes in fashion and new applications have been increasing day by day. Like in every field, textiles have been used to meet many requirements in industry and daily life other than conventional functionalities such as covering and protecting. Out of functionalities especially like appearence and aesthetic facilities, technical textiles produced for various technical performances and functionalities are improved very fast by 1980s and have been one of substantial fields nowadays (Url-9).

Smart textiles can be defined as textile materials having smart materials that sense and react to various environmental conditions or stimuli, such as mechanical, thermal, chemical, electrical, magnetic or other effects .

Smart textiles as smart materials can be classified in three groups according to manner of reaction as given below :

- Passive smart materials can only sense the environmental conditions or stimuli.
- Active smart materials can only sense and react to the conditions or stimuli.
- Very smart materials can sense, react and adapt themselves accordingly .

Smart materials are between metallic, vitreous, polymeric, liquid crystalline and composit material types. Polymeric materials are rather prefferred in terms of flexibility, multifunctionality and especially coherence to textile constructions. Smart

materials can be applied in textiles and industry with scientists's joint working. Some of the research areas can be grouped as follows :

For sensors/actuators:

- Photo-sensitive materials
- Fibre-optics
- Conductive polymers
- Thermal sensitive materials
- Shape memory materials
- Intelligent coating/membrane
- Chemical responsive polymers
- Mechanical responsive materials
- Microcapsules
- Micro and nanomaterials.

For signal transmission, processing and controls:

- Neural network and control systems
- Cognition theory and systems.

For integrated processes and products:

- Wearable electronics and photonics
- Adaptive and responsive structures
- Biomimetics
- Bioprocessing
- Tissue engineering
- Chemical/drug releasing (Tao, 2000).

Photovoltaic textiles works in the same way as solar cells which generates electricity by converting photon energy integrated into a textile structure. It can be obtained in two ways: A solar cell is manufactured seperately and integrated onto a textile structure or it can be formed on textile based substrates; such as polymer based substrates, fibres, yarns etc to provide a photovoltaic effect. Out of integrated thin film production, in order to produce a photovoltaic effect on textiles that is suitable, flexible, and thin; it can be achieved by producing an efficient and flexible fiber meeting those requirements mentioned above. It can be possible to produce such a fiber with special materials and special processes (Bedeloglu et al., 2010).

1.4.2 Applications of photovoltaic technology on textiles

Photovoltaic textiles can be grouped in two categories according to studies on this field: First, solar cell construction intregrated onto textiles and the second is solar cell formed in fiber or textile form.

Hynek et al. in 2005, integrated a flexible silica-based solar panels onto a plain jacket and a tie produced from cotton. They used digital printing for coherence of patterns. It was covered with a suitable lamination to protect solar panels. In spite of disadvantages; such as shiny, knot of the tie and width, they claimed it can be overcomed with digital printing. Some images related are shown in Figure 1.13 (Hynek et al., 2005).

Figure 1.13 : Plain jacket with thin film photovoltaic modules adhered to back and arms (a), Jacket concept with digitally printed pattern to mask photovoltaic modules (b) (Hynek et al., 2005).

Krebs et al. (2006) integrated a polymer based organic solar cells into textile structures in two ways: Firstly, they coated PET substrates with ITO, MEH-PPV, C_{60} and Al, respectively, and then laminated the structure with PET. The other was laminated with PE layer onto textile substrate and then, deposition of PEDOT, active material and top electrode, respectively. The last form of devices were integrated into clothes as shown in Figure 1.18 (Bedeloglu, 2009).

Figure 1.14 : Organic polymer solar cells integrated into clothes (Krebs, 2006).

1.4.3 Organic photovoltaic fibers

There are several studies about organic photovoltaic fibers in the literature.

A photovoltaic fiber (0) patented by Forrest et al in 2003 shown in Figure 1.15. In this study, a core fiber is having a primary electrode (1: substrate, 2: primary electrode). Photoactive layer (3) is surrounding the core and having an electrical contact with primary electrode (2). Transparent secondary electrode (4) is enclosing the phovoactive layer and having and electrical contact with this layer. A counter electrode (5) has a contact with transparent electrode. There is a protective layer (6) on the outer surface (Forrest et al., 2003).

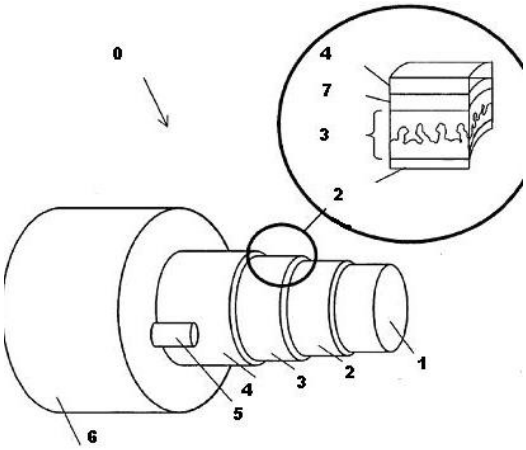


Figure 1.15 : Photovoltaic fiber (Forrest et al., 2003).

Liu et al (2007) deposited photoactive materials onto optical fibers with a diameter of 0,6-1,4 mm (Figure 1.16). They used thin film techniques in this study. 0,1% and 0,6% efficiencies obtained from optical fibers having 1,5 mm and 0,6 mm diameter, respectively. In the study, optical fibers are deposited ITO, PEDOT:PSS; P3HT:PCBM, LiF and Al, respectively.

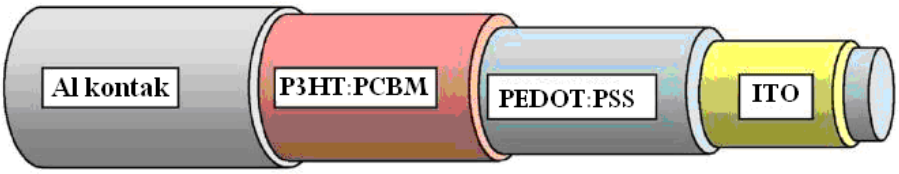


Figure 1.16 : Photovoltaic optical fiber (Liu et al., 2007).

A fiber-shaped, ITO-free organic solar cell using molecular organic compounds was substantiated by Shtein and co-workers (O'connor et al, 2008). Light is absorbed through a semitransparent outer electrode in the fiber-based photovoltaic cell. The construction has thin films of Mg/Mg:Au/CuPc/C_{60}/Alq_3/Mg:Ag/Ag by thermal evaporation under vacuum conditions onto 0,48 mm diameter polyimide coated silica fibers as shown in Figure 1.17. The device demonstrated 0,5% efficiency. Fiber length was limited by the experimental deposition chamber size.

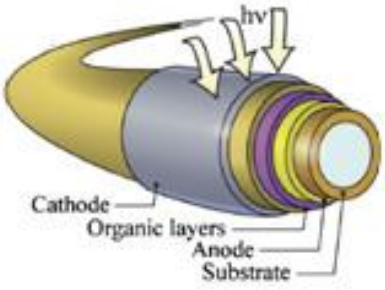


Figure 1.17 : Fiber based organic device (O'Connor, B., Pipe, K. P. & Shtein, M.; 2008).

A flexible ITO-free photovoltaic device was developed by Bedeloglu et al. (Bedeloglu et al., 2009, 2010a, 2010b, 2010c, 2011). The non-transparent and non-conductive PP tapes and fiber substrates were deposited by dip coating and thermal evaporation techniques. The construction consists of PP/Ag/PEDOT:PSS/:P3HT:PCBM/LiF/Al layers, respectively in photovoltaic tape; in photovoltaic fiber PP/PEDOT:PSS/P3HT:PCBM/LiF/Al, respectively as shown in Figure 1.18. The semi-transparent cathode with a thickness of 10 nm LiF/Al

permitted the light pass through into photoactive layer. Obtained devices had a promising technologies for further studies about photovoltaic textile structures.

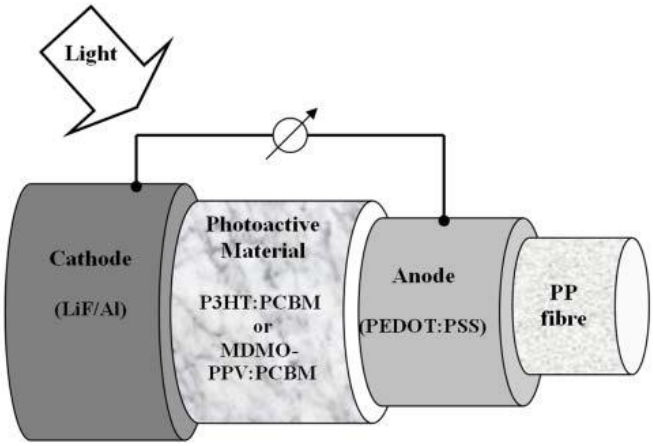


Figure 1.18 : Schmetaic drawing of a photovoltaic fiber (Bedeloglu et al., 2009).

2. MATERIALS AND METHODS

2.1 Substrates for Polymer Based Organic Solar Cells

In this study, glass based reference cells are produced in order to compare flexible organic solar cell performances. As a substrate, indium tin oxide coated (ITO) 25x25 mm^2 sized having transmittance over 83% and 1,1 mm thickness square glasses purchased from Sigma-Aldrich are employed. ITO thickness on the glass is ca.120-160 nm and surface recistivity is ca. 8-12 Ω/cm^2 (Url-5).

In order to produce polymer based organic solar cells, ca. 100 nm indium tin oxide coated (ITO) polyester (PET) tapes (l=25 mm, w=5 mm) from Sigma-Aldrich having 0,08 mm thickness, 60 Ω/cm^2 surface resistivity, and transmittance over 79%, polyester silver (Ag) coated polyester (PET) monofilaments (60 denier) (Courtesy of Korteks)and polyamide (PA) monofilaments (D=0,9 mm) were purchased from the market.

2.2 Bottom Electrodes for Polymer Based Organic Solar Cells

In this study, several types of metal and polymer anodes are employed. Metal based materials (Au, Ag) were deposited in ambient atmopshere by thermal vacuum evaporation technique. Polymer based electrodes (PEDOT:PSS and PH 1000) were coated by using dip-coating and spin coating techniques.

2.2.1 PEDOT:PSS polymer as a flexible anode

For flexible organic solar cells production, poly (3,4-ethylenedioxythiophene) poly (styrenesulfonicacid) (PEDOT:PSS) is used as a flexible polymer anode. PEDOT is a conjugated polymer carrying positive charges based on thiophene. PEDOT and PSS together charged macromolecules form a macromolecular salt. Chemical structure of PEDOT:PSS is given in Figure 2.1.

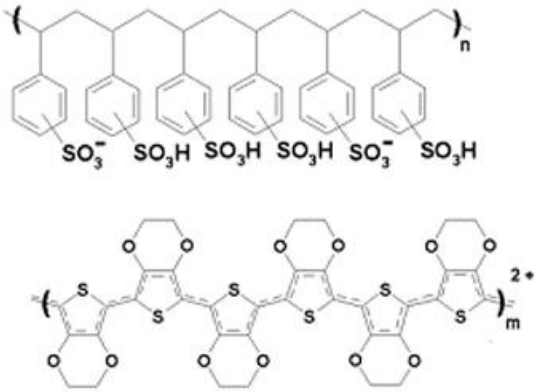


Figure 2.1 : Chemical structure of PEDOT:PSS.

PEDOT:PSS is more advantageous in terms of production and usage features comparing to ITO. A comparison table is given below in Table 3.1.

PEDOT:PSS is a hydrophobic material so in order to coat textile materials, a small amount of Triton X 100 chemical was added before stirring.

Table 3.1: Comparison of PEDOT:PSS and ITO (Url-5).

Features	**ITO**	**PEDOT:PSS (Clevious PH 1000)**
Composition	Indium-tin-oxide	poly (3, 4 ethylene di oxy thiophene : poly (styrene sulfonic acid)
Deposition techniques	Spraying, evaporation, sol-gel application	Spin coating, dip-coating, printing
Flexibility	Low	High
Surface resistivity at 90% transmittance	5-20 Ω	200 Ω* (with addition of DMSO)
Conductivity	6000 S/cm	900 S/cm*

*with addition of 5% DMSO

2.2.2 Low-conductivity grade PEDOT:PSS

PEDOT:PSS (weight ratio 1:2,8), purchased from Sigma-Aldrich, is dispersed in H_20 and its conductivity is approximately 1E-5 S/cm.

2.2.3 Conductivity grade PEDOT:PSS

PEDOT:PSS (weight ratio 1:1,3), purchased from Sigma-Aldrich, is dispersed in H_20 and its conductivity is approximately 1 S/cm.

2.2.4 High conductivity grade PEDOT:PSS (Clevious PH 1000)

PEDOT:PSS (weight ratio 1:2,5), purchased from Clevious, is dispersed in H_20 and its conductivity is minimum 900 S/cm after addition of 5% DMSO (dimethylsulphoxide).

2.3 Photoactive Materials for Polymeric Based Organic Solar Cells

2.3.1 Electron donor: P3HT

Poly(3-hexylthiophen-2,5-diyl) or poly (3-hexylthiophene) (Figure 2.2), is used in the rechargable battery electrodes, electronic devices, chemical and optical sensors, light emitting diodes, field effectted transistors and especially in photovoltaic applications. P3HT is soluble in toluene, chloroform, chlorobenzen, dichlorobenzene etc. solvents and has the highest absorption value at 550 nm wavelength. It is a positive type, donor, in photovoltaic devices. It is a conjugated polymer which is semicrystalline at room temperature (Yang, Orfino, and Holdcroft, 1996). In this study, P3HT purchased from Sigma-Aldrich is used.

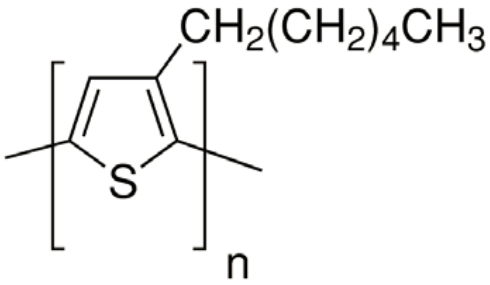


Figure 2.2 : Chemical structure of P3HT.

2.3.2 Electron donor: MDMO-PPV

MDMO-PPV {Poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene]}, is a conjugated polymer performing as an electron donor in photovoltaic devices. The chemical structure of MDMO-PPV is given in Figure 2.3. It is soluble in various solvents such as toluene, xylene, chloroform, chlorobenzene etc. (Bedeloglu, 2009).

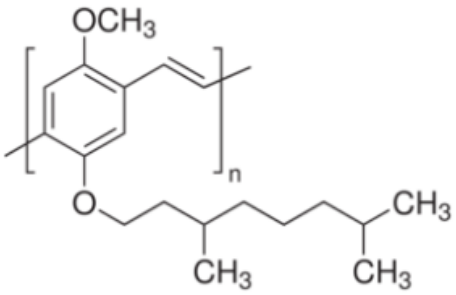


Figure 2.3 : Chemical structure of MDMO-PPV.

2.3.3 Electron acceptor: PCBM

PCBM {[6,6]-Phenyl C_{61} butyric acid methyl ester} is a negative type organic semiconductor that can be soluble in organic solvents. It is used in organic based electronics, negative type layer of photovoltaic devices and OFET, as electron acceptor material. In this study, PCBM purchased from Sigma-Aldrich was used. Chemical structure of PCBM is given in Figure 2.4.

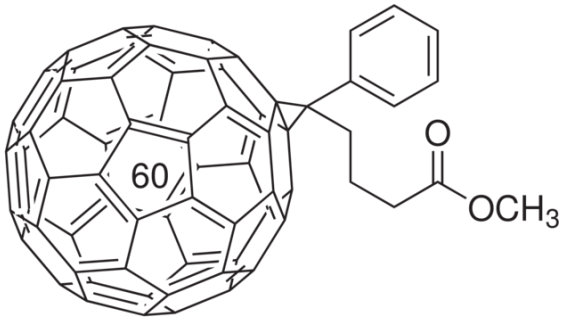


Figure 2.4 : Chemical structure of PCBM.

2.4 Buffer Layers

Organic (PEO and PEDOT:PSS) and inorganic (ZnO) based materials were used for buffer layers between active layer and one of the electodes.

PEO {poly [ethyleneoxide]} solution (aq) has been used to modify interface between active layer and cathode by F. Zhang et al. in 2007. Polymer based PEO purchased from Sigma-Aldrich was employed in order to modify the WF (work function) of bottom electrode so that increase the efficiency of solar cells (Borazan et al., 2011). PEO (aq) solution was prepared at 1 mg/ml concentration in distilled water and stirred at least one hour before use.

Polymer based PEDOT:PSS, purchased from Sigma-aldrich, material was used for hole transporting layer and surface smoothness (Bedeloglu et al., 2009). PEDOT:PSS

polymer was used after 5% DMSO added and stirred at least three hours at room temperature.

Inorganic based ZnO nanoparticles purchased from Sigma-Aldrich was dissolved in chloroform:methanol (volume ratio 4:1) solution and stirred at least 24 hours at room temperature. ZnO-nanoparticles was employed for electron selective layer in inverted solar cells (Borazan et al., 2012).

2.5 Top Electrodes for Polymer Based Organic Solar Cells

After deposition of polymeric layers, PEDOT:PSS polymer by dip-coating or spin coating according to subsrate geometry, or one of Ag, Au and Al metals by using thermal vacuum evaporation was deposited as top electrode for polymer based organic solar cells.

Ag and Au materials caused short-circuit in photovoltaic devices by influencing into photoactive layer due to atomic structure of the material after evaporation.

3. EXPERIMENTAL SECTION

In experimental section, five different types of solar cell combinations are compared for the efficiencies. Constructions of the produced devices are given in Table 3.2.

Table 3.2: Produced organic solar cells combinations in this study.

Substrate	Bottom electrode	Buffer layer	Photoactive layer	Buffer layer	Top electrode
Glass/ PET foil/ Fiber	ITO/Au/Ag	PEDOT:PSS	P3HT:PCBM / MDMO-PPV:PCBM		Au/Ag/Al
	ITO/Au/Ag	PEO	P3HT:PCBM / MDMO-PPV:PCBM	PEDOT:PSS	Au/Ag/Al
	PH 1000/ PEDOT:PSS		P3HT:PCBM / MDMO-PPV:PCBM		Al
	ITO/Au/ Ag/ PH 1000	ZnO	P3HT:PCBM / MDMO-PPV:PCBM	PEDOT:PSS	Au/Ag/Al
	ITO/Au/ Ag/ PH 1000	ZnO	P3HT:PCBM / MDMO-PPV:PCBM	PEDOT:PSS	PEDOT:PSS

3.1 Deposition of Thin Films

The photoactive materials solution was prepared by using blends of P3HT:PCBM or MDMO-PPV:PCBM. A blend of P3HT and PCBM (weight ratio 1:0,8) was dissolved in 2 ml chlorobenzen solvent and stirred at room temperature at least 24 hours. MDMO-PPV and PCBM (weight ratio 1:4) was dissolved in 1 ml chlorobenzene and stirred at 40 °C over 24 hours.

For device preparation, ITO coated glass and PET foil substrates, approximately half of the ITO layer was etched from glass with an acid solution of 36% HCl (in distilled

water) for 15 minutes. Then, etched (Figure 3.1) ITO coated glasses, flexible PET foils and fiber substrates were gently cleaned in acetone, isopropanol, methanol and distilled water respectively and dried in nitrogen air.

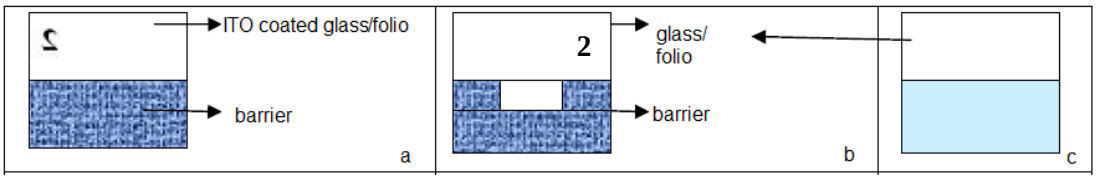


Figure 3.1 : Front (a), back (b) view of ITO coated substrates before etching, and view of ITO coated substrates after etching process.

Ag or Au bottom electrodes were deposited onto PET fibers, PET tapes and glasses by magnetic sputtering or thermal vacuum evaporation tecniques in order to substitute the ITO layer. Highly conductive PH 1000 or PEDOT:PSS was spin coated at 1500 rpm for 60 seconds onto flat surfaces or dip-coated onto fiber shaped substrates. Then, glass substrates at 120 °C, polymer based flexible substrates at 60 °C were thermally annealed on hot-plate for 5 minutes.

After bottom electrode deposition, PEO solution was spin coated onto flat surfaces at 3000 rpm for 60 seconds, and fiber shaped substrates was dip-coated at room temperature and subsequently left on hot-plate at 70 °C for thermal annealing for 10 minutes.

ZnO-nps solution was coated onto flat surfaces at 8000 rpm for 60 seconds by spin coating, for fiber shaped substrates by dip-coating. Afterwards, all the substrates were thermally annealed at 80 °C for 10 minutes on hot-plate.

Nano-blends of active materials solution was spin coated onto flat substrates at 800 rpm for 60 seconds, dip coated onto fiber shaped substrates, then all the substrates thermally annealed at 120 °C for 15 minutes.

For the top electrode deposition, all the substrates were mounted onto a shadow mask and one of Ag, Au, or Al metals was deposited approximately 10 nm by thermal evaporation at approximately 10^{-6} mbar vacuum conditions. After top electrode deposition all the substrates were thermally annealed on hot plate at 80 °C for 10 minutes.

After all depositions of thin films, the view of flat (a) and fiber shaped (b) organic photovoltaic devices is given in Figure 3.2.

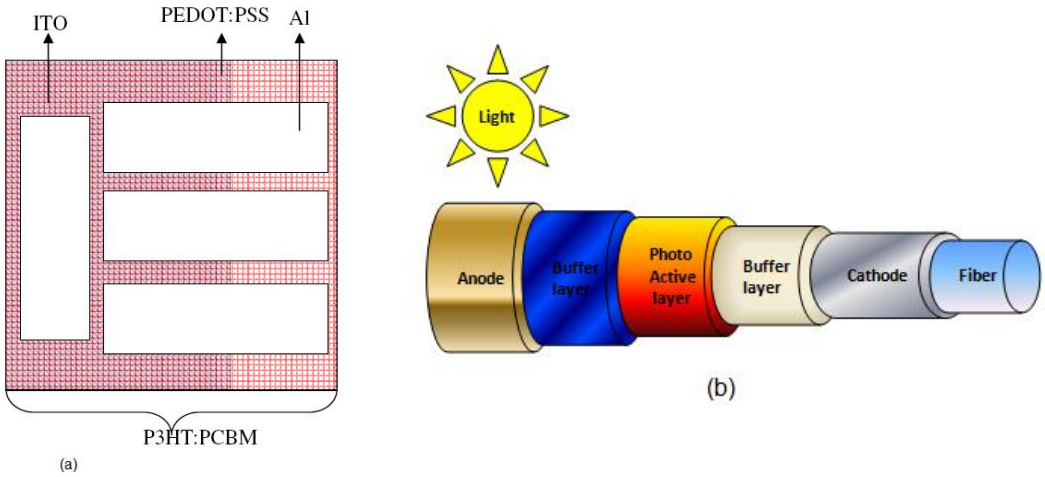


Figure 3.2 : Schematic view of reference (a) and fiber shaped (b) photovoltaic devices.

3.2 Characterization of Produced Organic Solar Cells

All characterizations were carried out in ambient atmosphere. All current–voltage (*I–V*) characteristics of the photovoltaic devices were measured with a Keithley 2400 source measure unit in the dark and under simulated AM (Air Mass) 1.5 global solar conditions at an intensity of 100 mW/cm^2 by using a LOT Oriel solar simulator according to ASTM Standards, E 892, Sun1, AM 1.5 conditions.

In this study, all the produced devices were illuminated through the cathode side.

Performances of solar cells are calculated by using formula given below:

$$\eta = \frac{I_{sc} * V_{oc} * FF}{P_{in}} \quad \textbf{(3.1)}$$

Where;

Isc : Short circuit current density,

Voc : Open circuit voltage,

FF : Fill factor, and

Pin : Incident light indensity is represented.

$$FF = \frac{Impp * Vmpp}{Isc * Voc} \quad \textbf{(3.2)}$$

In the equation (3.2), Vmpp and Impp represent, the voltage and the current at the maximum power point(MPP), respectively, where the product of the voltage and current is maximized (Güneş et al., 2007).

Surface morphology studies of the devices were carried out both in AFM (Atomic Force Microscopy) and in SEM (Scanning Electron Microscopy) (Zeiss MA10).

Thickness of each layers were evaluated by a Tencor Alpha Step 500 profilometer (Figure 3.3).

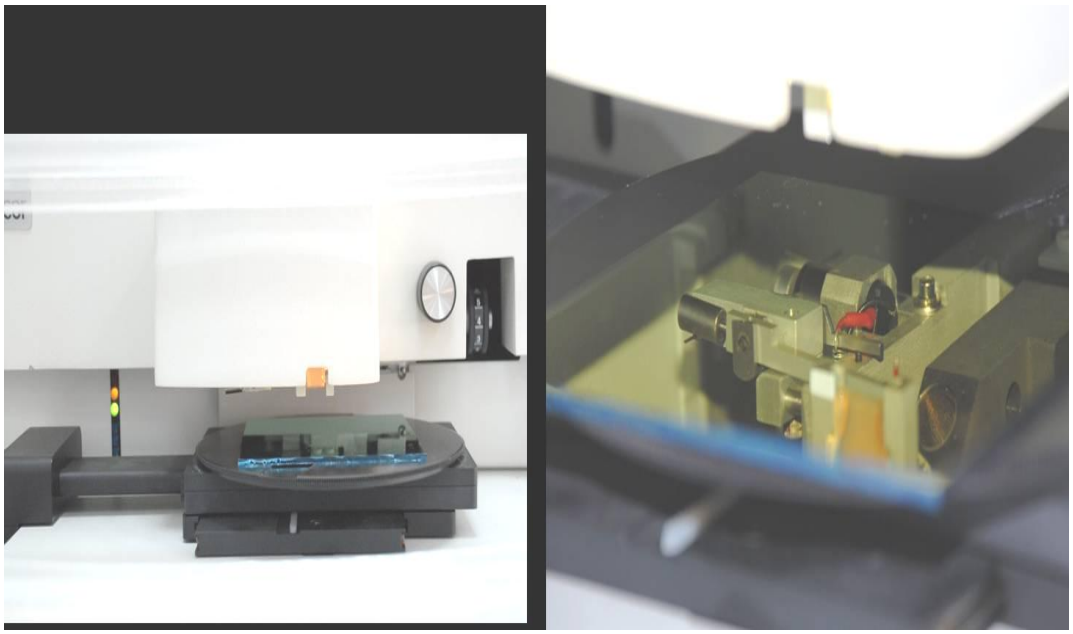


Figure 3.3 : Tencor Alpha Step 500 profilometer.

Light transmittance values were carried out in a PE Lambda 900 UV (Ultraviolet) Spectrophotometer (Figure 3.4) between 200-1600 nm wavelength.

Figure 3.4 : PE Lambda 900 UV (Ultraviolet) Spectrophotometer.

4. RESULTS

In this study, non-conductive and non-transparent polymer based textile materials in fiber and tape forms were employed as substrate. As the luminescent light comes from outer surface needed for photovoltaic mechanism, cathode layer on the top of the device deposited very thin in order to let the light pass through itself into photoactive layer substitute to ITO in standart organic solar cells. Also conductive polymers -having good conductivity, flexibility and easy processible- used in the devices to be convenient for flexible textiles.

Several combinations of photovoltaic devices as mentioned in Table 3.2 and all positive (which are not short-circuit) results are given in Table 4.1.

4.1 Efficiency Table of All Working Organic Solar Cells

Table 4.1 : Efficiency table of working organic solar cells

Substrate	Construction	V_{oc} (V)	I_{sc} (A)	Active area (m^2)	Jsc (A/m2)	FF (%)	Efficiency (%)
Glass	ITO/PEDOT:PSS/P3HT:PCBM/Al	0,784	7,4E-08	0,000005	1,5E-02	9,99	0,00012
PET foil	ITO/PEDOT:PSS/P3HT:PCBM/LiF:Al	0,481	2,2E-06	0,000005	4,5E-01	94,80	0,02040
PET foil	ITO/PEDOT:PSS/P3HT:PCBM/LiF:Al	0,633	1,8E-06	0,000005	3,6E-01	27,00	0,00612
Glass	PH 1000/ZnO/P3HT:PCBM/Al	0,683	3,1E-06	0,000030	1,1E-01	79,30	0,00545
Glass	PH 1000/ZnO/P3HT:PCBM/Al	0,683	3,1E-06	0,000030	1,1E-01	69,39	0,00501
Glass	PH 1000/ZnO/P3HT:PCBM/Al	0,582	2,1E-06	0,000030	6,9E-02	82,41	0,00331
Glass	PH 1000/ZnO/P3HT:PCBM/PEDOT:PSS/PH 1000/Al	0,582	1,7E-06	0,000030	5,8E-02	71,68	0,00243
Glass	PH 1000/ZnO/P3HT:PCBM/PEDOT:PSS/PH 1000/Al	0,683	1,9E-06	0,000030	6,3E-02	50,87	0,00218
Glass	PH 1000/ZnO/P3HT:PCBM/PEDOT:PSS/PH 1000/Al	0,582	1,7E-06	0,000030	5,7E-02	92,71	0,00309
PET foil	ITO/PH 1000/ZnO/P3HT:PCBM/Al	0,278	5,5E-06	0,000030	1,8E-01	59,57	0,00302
PET foil	PH 1000/ZnO/P3HT:PCBM/Al	0,632	8,6E-08	0,000030	2,8E-03	27,00	0,00005
PET foil	PH 1000/P3HT:PCBM/Al	1,038	1,1E-07	0,000030	3,7E-03	7,16	0,00003
PET foil	Au/PH 1000/P3HT:PCBM/Al	0,835	7,3E-08	0,000030	2,4E-03	38,71	0,00008
PET foil	PH 1000/MDMO-PPV:ZnO/Al	0,734	9,7E-08	0,000040	2,4E-03	74,20	0,00013
PET foil	PH 1000/MDMO-PPV:ZnO/Al	1,139	7,5E-08	0,000040	1,9E-03	72,87	0,00016
PET /PA lif	PH 1000/P3HT:PCBM/Al	0,784	1,2E-06	2,820000E-07	4,3E+00	82,92	0,28333

4.2 Thickness of Each Layer Used in Organic Photovoltaic Devices

Each material was individually deposited onto a glass substrate in order to evaluate thickness in a profilometer. Thickness measurement results are given in Table 4.2.

Table 4.2 : Thickness of each thin films used in the structures.

Layer	Deposition Technique	Deposition Parameter	Thickness
PEDOT:PSS	Spin coating	1500 rpm, 60 sec	110 nm
ZnO	Spin coating	8000 rpm, 60 sec	10 nm
P3HT:PCBM	Spin coating	800 rpm, 60 sec	50 nm
PEDOT:PSS	Spin coating	3000 rpm, 60 sec	45 nm
PH 1000	Spin coating	3000 rpm, 60 sec	45 nm
Al	Thermal vacuum evaporation	10^{-6} mbar	20 nm
Ag	Thermal vacuum evaporation	10^{-6} mbar	10 nm
Au	Thermal vacuum evaporation	10^{-6} mbar	15 nm

4.3 Transmittance of Each Layer Used in Organic Photovoltaic Devices

As thin-film solar cells can consist of many layers, they are optically very complex. Also the fact that layer thicknesses or interface roughnesses can have dimensions comparable to or smaller than the wavelength of solar irradiance, makes it very challenging to model the optical behavious of thin-film solar cells accurately Santbergen, 2008).

The absorption spectrum of the photoactive organic layer should match the solar emission spectrum and the layer should be thick enough in order to absorb most of

the incident light for an efficient photon collection. For the conjugated polymers, such as P3HT, absorption coefficient exceeds 10^5 cm^{-1} in the major part of the visible spectrum (Savenije, 2008).

Absorption of photons and generation of electron-hole pairs occur in photoactive layer (P3HT:PCBM) in the construction of organic solar cells. Therefore absorbancy of photoactive polymer layer is a crucial point, however light illuminates through other outer layers then transmittance of other layers are important. Absorption spectra of P3HT:PCBM layer is given in Figure 4.1.

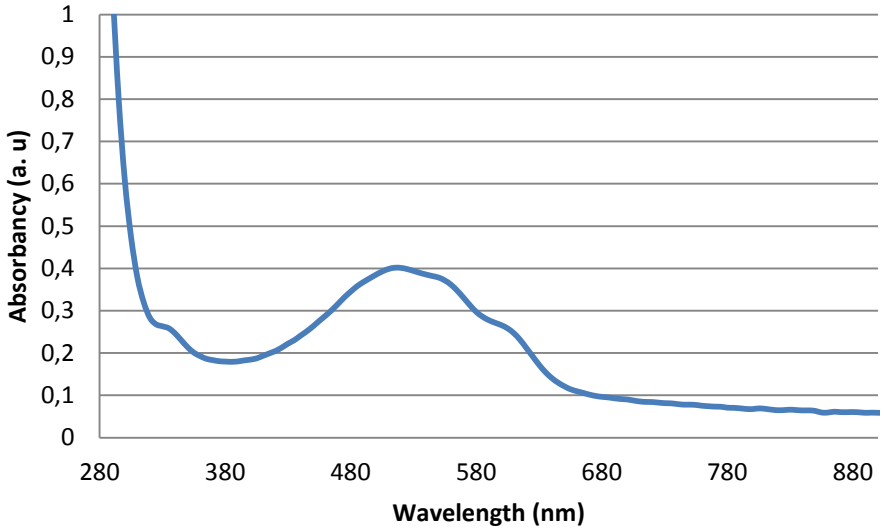


Figure 4.1 : Absorption spectra for P3HT:PCBM layer.

Each material was individually deposited onto a glass substrate in order to measure light transmittance through the substrate and thin film. As substrate microscobe slides were used the same as in this study. And an uncoated glass was also measured to be a reference for other samples. Light transmittance of the layers measured by UV Spectrophotometer is given in Figure 4.2.

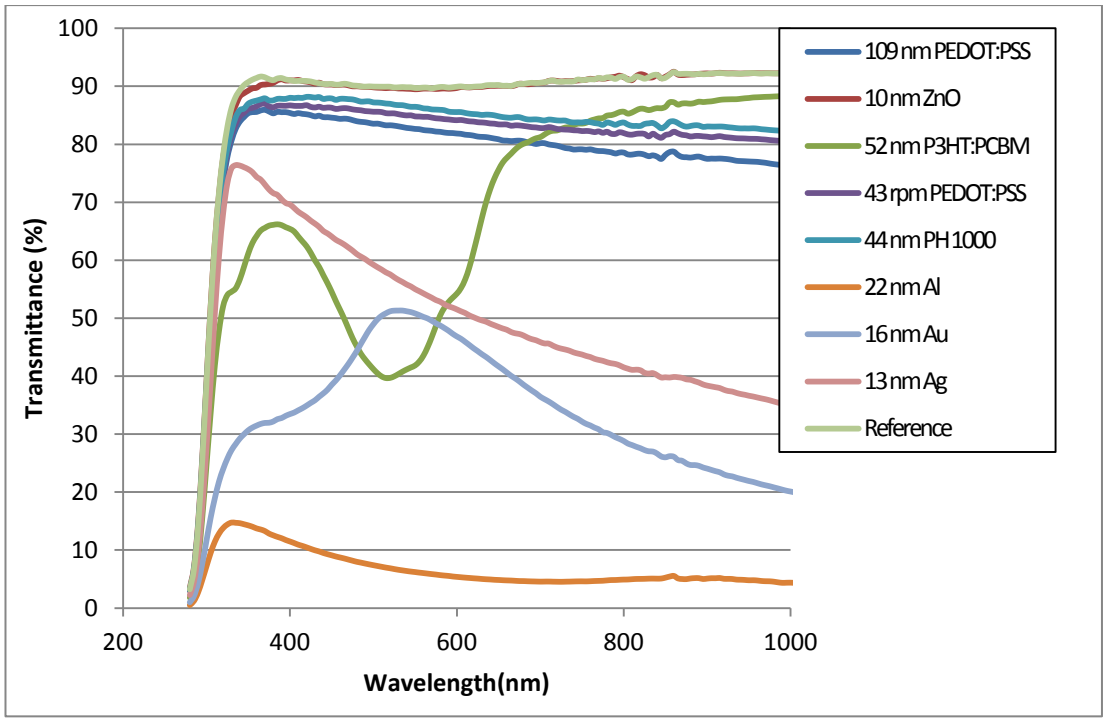


Figure 4.2 : Transmittance of the layers in different wavelengths.

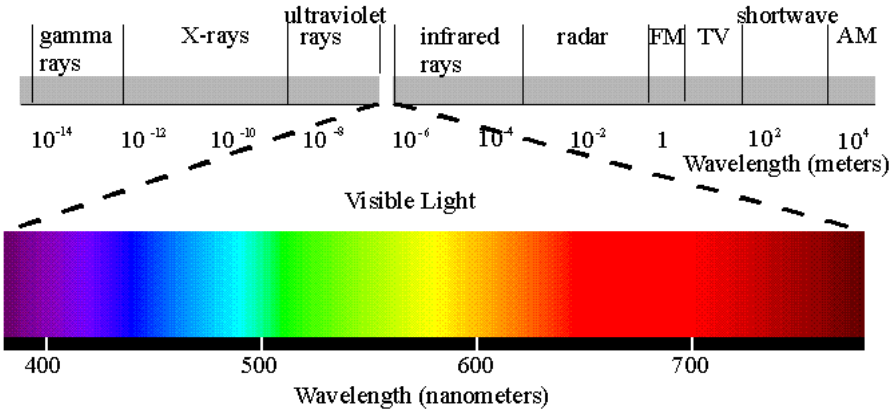


Figure 4.3 : Electromagnetic spectrum (Url-9).

As its shown from the both graph (Figure 4.2 and 4.3), thin films that are produced transmit the light in visible wavelength about 90% so that the textiles will be produced from these organic solar cells will be in use in visible wavelength.

4.4 Produced Organic Solar Cells on Glass Substrates (Reference Cells)

An image of produced organic solar cells on glass substrates (reference cells) is shown in Figure 4.4:

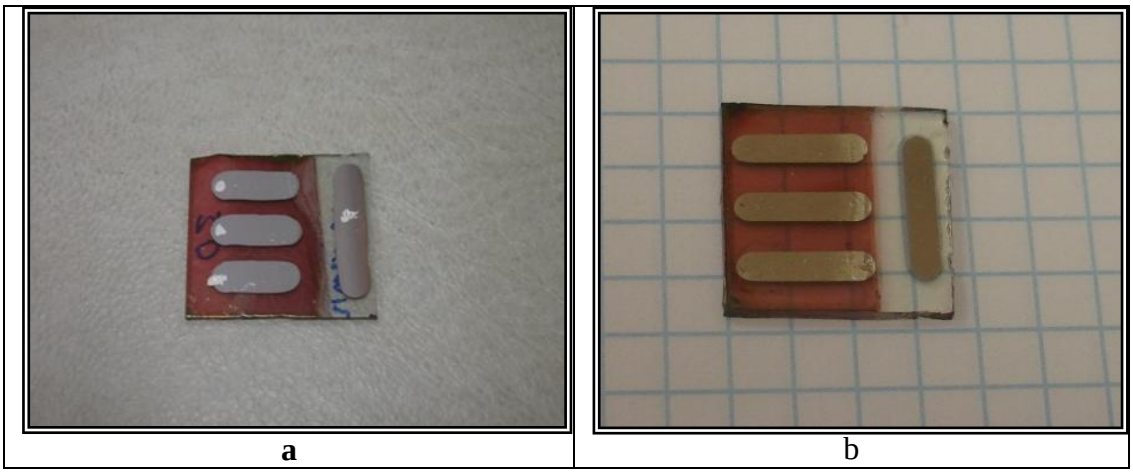


Figure 4.4 : Produced Organic Solar Cells on Glass Substrates (Reference Cells) (Constructions : a, b: ITO coated glass/ PEDOT:PSS/ P3HT:PCBM/ Al).

4.5 Produced Organic Solar Cells on PET Foil Substrates (Flexible Reference Cells)

An image of produced organic solar cells on PET foil substrates (flexible reference cells) is shown in Figure 4.5.

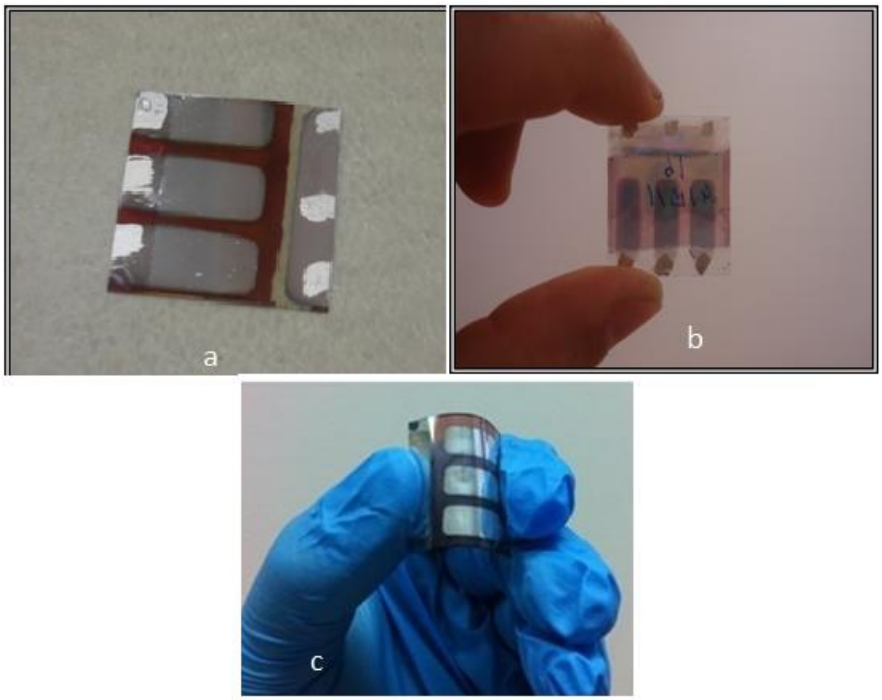


Figure 4.5 : Produced Organic Solar Cells on PET Foil Substrates (Flexible Cells) (Constructions : a,c : ITO coated foil/PEDOT:PSS/P3HT:PCBM/Al, b :PET foil/PEDOT:PSS/P3HT:PCBM/Ag).

4.6 Fiber Shaped Organic Solar Cells

An image of organic based photovoltaic fibers produced in this thesis is shown in Figure 4.6.

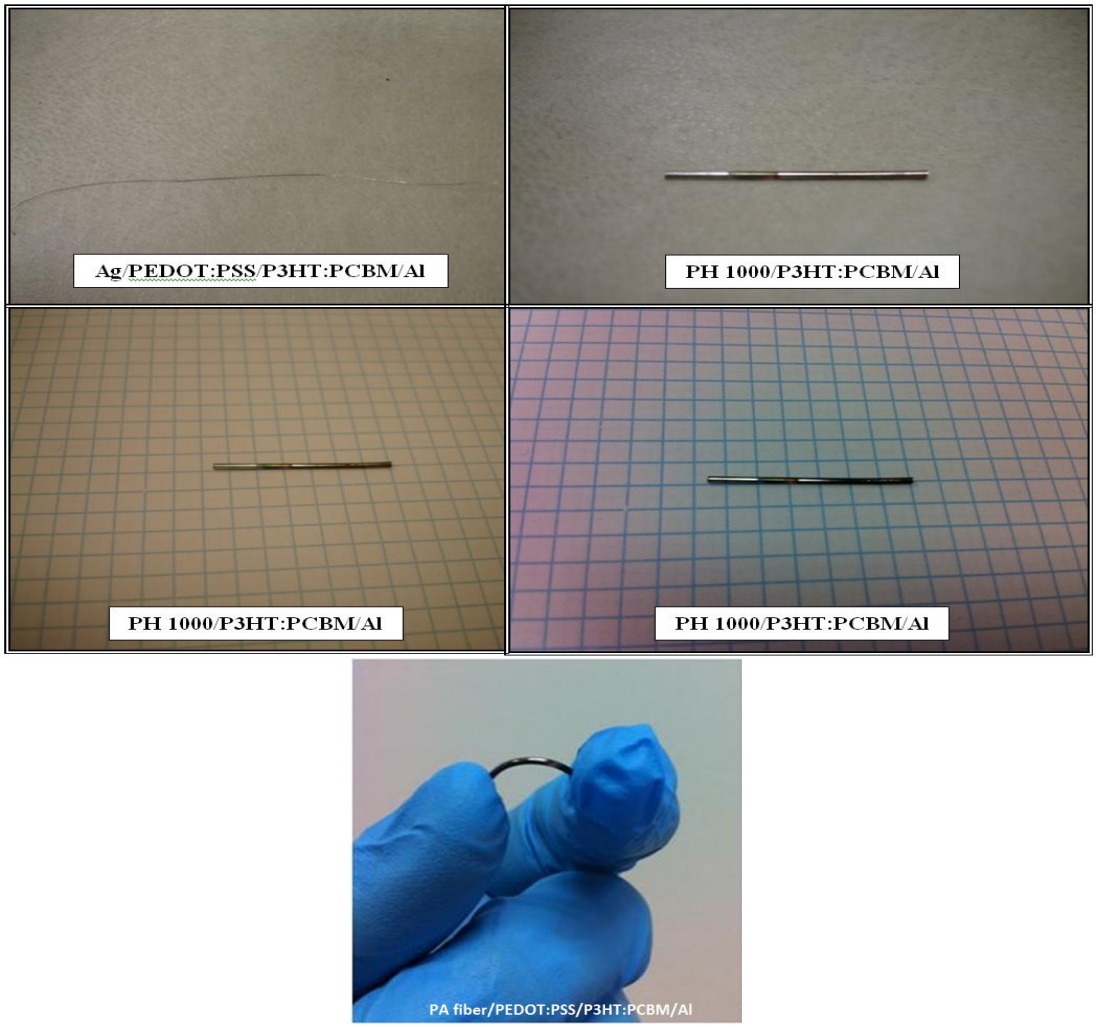


Figure 4.6 : Fiber Shaped Organic Solar Cells

4.7 SEM (Scanning Electron Microscopy) Images

Cross-sections of thin films and surface images were studied in SEM (Scanning Electron Microscopy) and the images are given in Figure 4.7 - Figure 4.10.

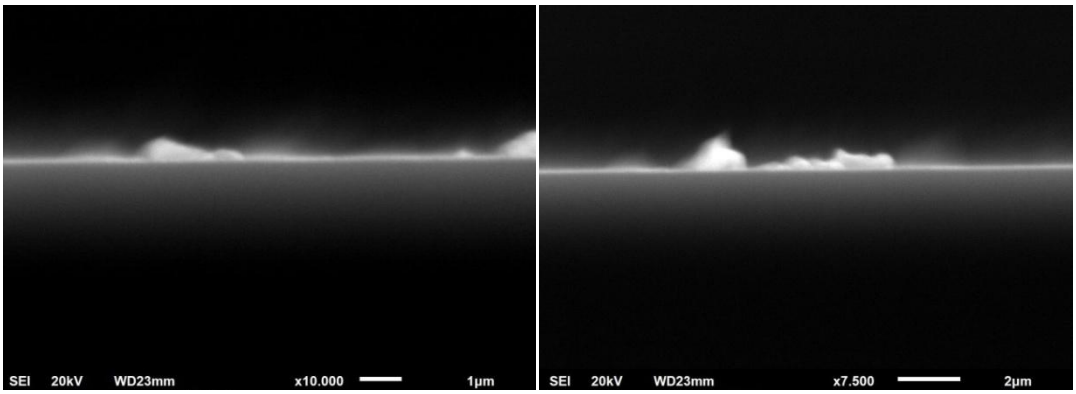


Figure 4.7 : Cross sections of photoactive layers.

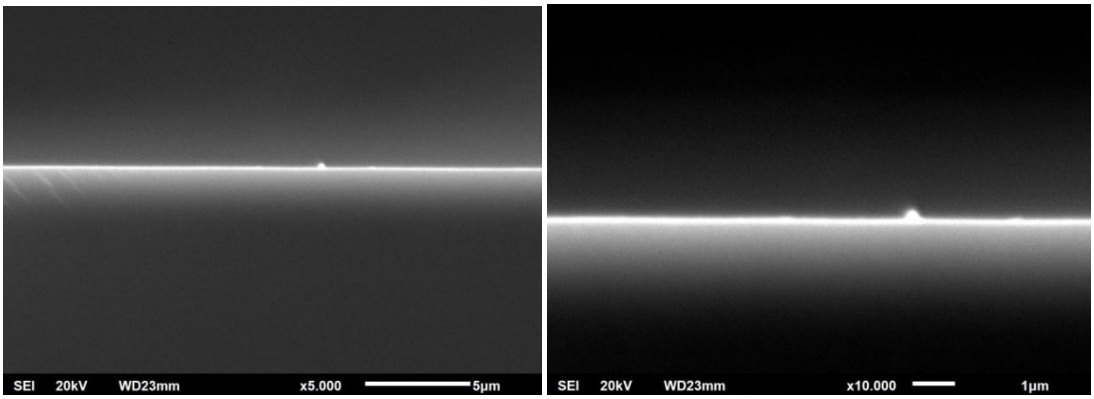


Figure 4.8 : Cross sections of conductive polymer (PEDOT:PSS).

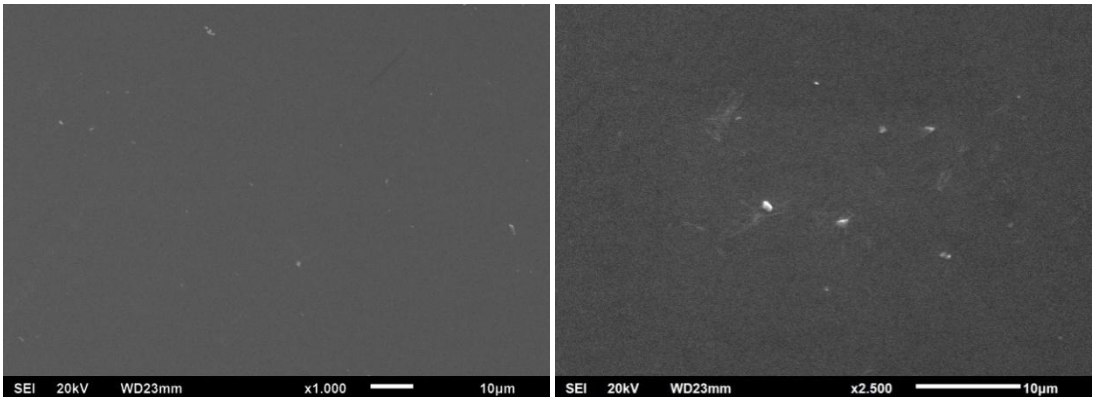


Figure 4.9 : Surface morphology of photoactive layer.

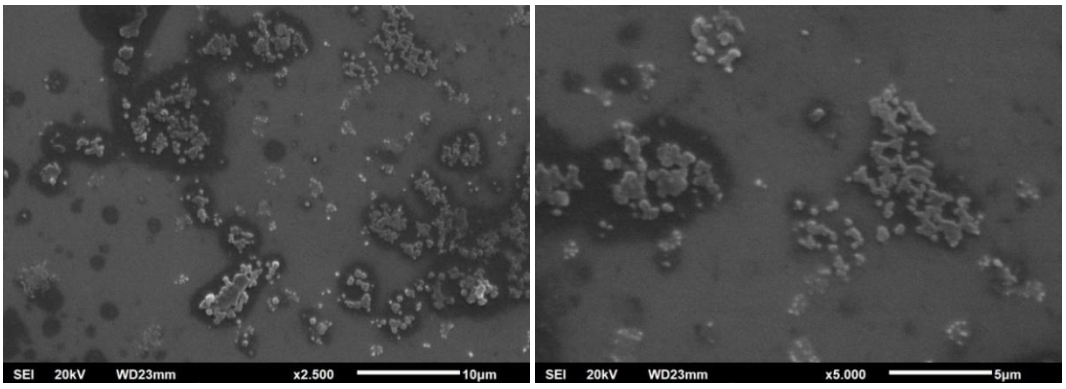


Figure 4.10 : Surface morphology of PEDOT:PSS

4.8 AFM Images

AFM images shows the roughness of thin films. AFM images for PEDOT:PSS layer is shown in Figure 4.11 and P3HT:PCBM layer is shown in Figure 4.12. . Clearly, roughness decreases the efficiency.

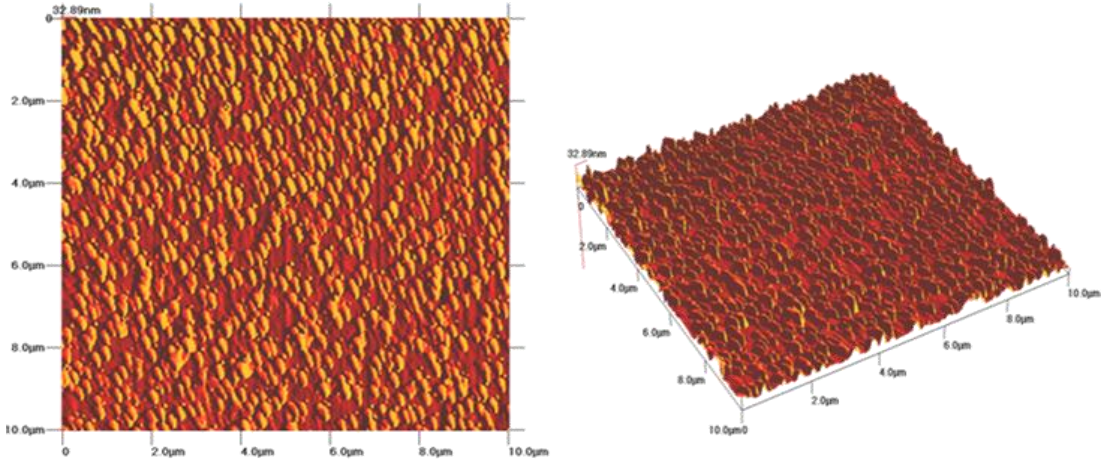


Figure 4.11 : AFM images of PEDOT:PSS layer.

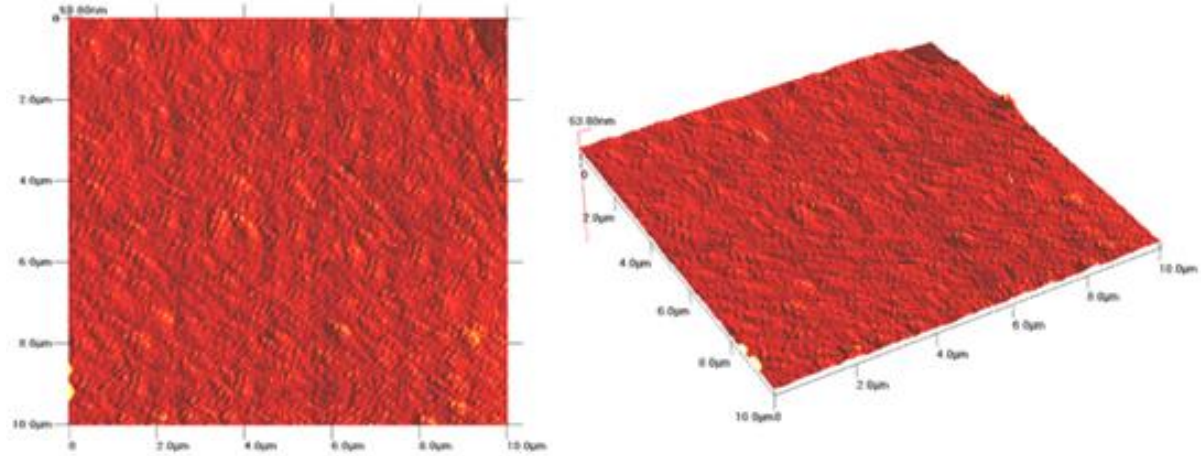


Figure 4.12 : AFM images of P3HT:PCBM layer .

4.9 Discussion

Transparent outer electrode performed its duty and let the photon transmission into photoactive layer and collecting the electrons. The possible reasons for low efficiency can be rough surface of textile substrates, and ambient atmosphere. Since all processes were carried out in ambient atmosphere, polymer based materials in photovoltaic devices begun to decompose due to oxygen and moisture of atmosphere over time so that results was not satisfying as much as expected.

In organic solar cells, the external quantum efficiency of the devices depends on the absorption and charge carrier mobility. The optimal thickness for many material combinations is too small to absorb all photons within the absorption bands. A thick film can absorb more light compared with a thinner film. On the other hand, the film thickness is limited by a low-charge carrier. As the film thickness increases, the electrical field and the number of charge carriers decrease and so, a decrease in the external quantum efficiency of the device is observed. Short-circuit current density is inversely proportional to the thickness of the photoactive layer. Therefore, due to limited charge transport higher currents cannot be obtained generally. The optimum thickness is required to provide both maximum light absorption and maximum charge collection, at the same time. Thus, optimizing the thickness of the photoactive layers in photovoltaic fibers provides the possibility to increase the power conversion efficiency of a polymer based solar cell. The thickness of the layers for optimal photovoltaic fibers can be controlled by solution concentration and dipping time.

5. CONCLUSIONS

In this study, development of photovoltaic fibers using different kind of polymer-based photoactive materials was studied. This approach is especially appropriate for photovoltaic textile structures. This study proves that highly conductive PEDOT: PSS solution and the semi transparent metallic layer can be used successfully as the anode and cathode of the organic solar cells, respectively, for flexible devices. Also possibility of utilizing different conductive layers to substitute ITO anode was investigated, too. The best results obtained from this study for each types of substrates given in Table 6.1.

Table 5.1 : The best results obtained from each types of substrates.

Construction	**V_{oc} (V)**	**J_{sc} (A/m^2)**	**FF (%)**	**Efficiency (%)**
Glass/ITO/PEDOT:PSS/P3HT:PCBM/Al	0,734	1,40E-02	34	0,03
PET foil/Ag/PEDOT:PSS/P3HT:PCBM/Al	0,328	5,84E-02	42	0,03
Fiber/PH 1000/P3HT:PCBM/Al	0,784	4,36	83	0,3

Semiconducting polymers, which are the major materials of the polymer solar cells are other most serious issues to improve device efficiency. However, the use of new materials and new conjugated polymers with wider bandwidths, narrow band gaps and higher carrier mobilities in device, can avoid to overcome present low photovoltaic efficiencies of organic solar cells. 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 and further optimizations for thickness of metal layers can achieve higher light transmittance and absorption in photovoltaic tapes.

Although these flexible and cylindrical shaped devices produced modest power conversion efficiencies due to the materials and modified preparation techniques of solar cells, using flexible fiber as a substrate and a semi transparent metal layer as the

cathode shows promise for future wearable photovoltaic textile applications. For future optimization of the commercial scale production that enhances the optimized power conversion efficiecny of the photovoltaic fibers, some alternatives such as reducing the thickness of the light absorbing layer and the PEDOT: PSS layer, using low band gap materials, infrared light activated materials which would generate power at night may be applied. After optimization this photovoltaic fiber design can be produced in the industry with techniques similar to the textile manufacturing processes to produce smart textiles.

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