Journal of International Scientific Publications: Materials, Methods and Technologies

Volume 8, ISSN 1314-7269 (Online), Published at: http://www.scientific-publications.net

FLEXIBLE UV-ABSORBING FILMS - DEPOSITION AND CHARATERIZATION

Emil Bubev, Valentin Bozhilov, Stefan Kozhukharov, Maria Machkova, Vladimir Kozhukharov

University of Chemical Technology and Metallurgy, Sofia, 1756, Bulgaria

Abstract

Solar UV radiation is a well-known cause of degradation in various organic materials. This leads to unwanted changes in color, strength and other physic-chemical changes in the polymer structure. With the development of printed organic electronics there is an ever growing interest in their protection from damaging effects- e.g. photodegradation. In this study we present a method for the deposition and characterization of transparent UV-absorbing films on flexible organic substrates.

Key words: *UV-protection, flexible protective coatings, OPV, PVA, - 2-hydroxy-4–methoxy-benzophenone-5-sulfonic acid*

1. INTRODUCTION

The operational life time of every product plays an instrumental role in its successful real world application. An ever growing interest in organic photovoltaic (OPV) cells has led to the development of more effective materials (Hoppe & Sariciftci 2004), configured in various device architectures (Khan, Ray & Alam 2014), (Li et al. 2014). However their limited lifetime compared to conventional silicon-based photovoltaic technology is a major setback, hindering their large scale introduction. The short wavelength part of the solar light spectrum (UV light) has been identified as a major cause of efficiency decay in polymer solar cells. One of the methods for protection against UV-induced photodegradation of organic solar cells, proposed in some studies (Jørgensen, Norman & Krebs 2008), is the addition of a UV-filtering layer to the solar cell. These must possess specific material properties in order to be introduced in polymer solar cells. The UV-protective layers must absorb most of the damaging portion of the solar light (spectral region ranging from 400 nm to 320 nm), reaching the earth surface, whilst allowing for the visible light to reach the active layers of the underlying solar cells. Materials used in the protective coatings must be compatible with the high throughput printing technologies (e.g. roll-to-roll processes) used for the production of OPV cells.

Polyvinyl alcohol (PVA) has been shown as a polymeric vehicle for barrier films for OPV cells (Gaume et al. 2011). This environmentally friendly polymer can be easily deposited in thin transparent films with the aid of solution processing techniques (Jiang et al. 2014). It is soluble in aqueous media, easing processing and deposition by eliminating the need of expensive and potentially toxic organic solvents. PVA films have good mechanical properties (Fukumori & Nakaoki 2014), offering the potential for protective coating, deposited on flexible substrates. This presents a huge advantage for lightweight flexible OPV devices, protected from damaging atmospheric influences. PVA is a chemically stable polymeric material (Kiatkamjornwong, Rattanakasamsuk & Noguchi 2003) with excellent gas barrier properties (Morlier, Cros & Garandet 2013), that can be easily further reinforced by cross-linking in various post-processing techniques (Gohil, Bhattacharya & Ray 2006). PVA-based films have been proposed as oxygen barriers for OPV cells (Ahmad et al. 2013).

In the current study an easy low cost solution processing technique of PVA-based protective coatings with high UV-filtering properties is presented. An organic UV-absorber- 2-hydroxy-4–methoxy-benzophenone-5-sulfonic acid has been added to PVA solutions, in order to produce UV-filtering transparent polymeric films. These were used in the deposition of thin films, dried at various thermal conditions, influencing changes in the surface and spectral properties. The surface morphology of the UV-filtering PVA films was analyzed by means of AFM microscopy. Wettability and the hydrophobic/hydrophilic nature of the film surfaces were characterized by a sessile drop test with an optical tensiometer with a high speed camera. Spectral properties of the deposited films were studied though UV-vis absorption spectra.

2. MATERIALS AND METHODS

2.1. Chemicals

PVA with molecular weight of 72000 and an alcoholysis degree of 98-99% was used as received. 2-hydroxy-4–methoxy-benzophenone-5-sulfonic acid (CAS 4065-45-6), molecular weight 308,3 g/mol with 99% purity was purchased from Elton, Bulgaria under the trade name Escalol 577..

2.2. Preparation of PVA stock solutions

First a 10 w/w % aqueous PVA stock solution was prepared in distilled water in closed vials, immersed in 80°C water bath under constant agitation. After 2h dissolution of the PVA, no solid polymer was observable. The solution was then mixed in an ultrasonic bath, heated to 80°C, for further 30 min to ensure complete dissolution of the polymer. The aqueous PVA stock solution was left to cool to room temperature. 1,542 g of Escalol 577 were added to 20 mL of 10 % aq. PVA solution under constant magnetic stirring at room temperature to obtain a 0.25 M concentration with respect to the stock solution. The Escalol 577 containing solution was ultrasonically mixed for further 10 min before deposition to ensure complete dissolution of the UV-absorber. The final solution was kept at room temperature in air-tight opaque vials. The solution remained unchanged at these conditions with precipitate formation.

2.3. Pre-cleaning of flexible organic substrates

Acetate based transparencies for overhead projectors were used as flexible transparent substrates for the PVA films, containing UV-absorber. The substrates were pre-cleaned before each deposition by successive immersion in ultrasonic baths filled with distilled water and a 1:1 ethanol-ether solution respectively. The substrate was then dried under a stream of dry nitrogen in room temperature.

2.4. Deposition via spring loaded hand proofer

The prepared liquid stock solutions were deposited on a flexible polymeric substrate with the help of a spring loaded hand proofer (Early Manufacturing Inc., USA), made up an anilox and a rubber roller. The constant contact pressure between the two rollers was ensured by a uniform spring load. A mechanically engraved stainless steel anilox drum with a 180 pyramidal cell count per line and a volume of 11.8 BCM (Billion Cubic Microns per square inch) was utilized. Before each deposition both rollers were pre-cleaned successively with distilled water, a 1:1 ethanol: ether solution and dried at room temperature under a stream of dry compressed nitrogen.

All films were deposited at room temperature. Films dried at elevated temperature (40 °C, 60 °C and 80 °C) were placed horizontally in a preheated laboratory oven, preset at the desired temperature. All films were left to dry for 1 h, regardless of curing temperature. In order to achieve complete covering of the surface, films were deposited in 4 successive depositions. A simplified scheme of the deposition process is shown in Figure 1.

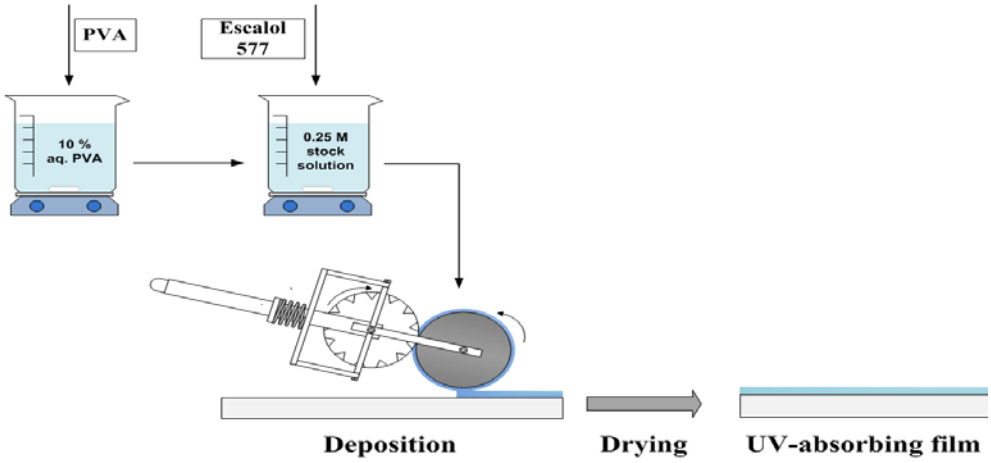


Figure 1 Preparation of aqueous solution and coating technique

2.5. Atom Force Microscopy analysis

The surface morphology of deposited films was characterized through AFM using an Easyscan 2 atomic force microscope (NanoSurf, Switzerland) set in dynamic force mode. An Al-coated silicon tip (Budget Sensors, Bulgaria) with a resonance frequency of 190 kHz and a force constant of 48 N/m was utilized. AFM images were recorded and analyzed with the aid of provided firmware. For each site the analyzed area was set at 49x49 μm, with a scanning rate of 2 seconds per line and a resolution of 256 recorded points per line. The surface roughness of the deposited films was described by a root mean square (Sq) roughness, calculated over the whole analyzed area. It represents the average sum of the distances of all points from the measured surface, in direction-perpendicular to the conditional plane (parallel to the surface). The Sq values were calculated according to equation (1):

$$S_q = \sqrt{\frac{1}{MN}\sum_{k=0}^{M-1}\sum_{l=0}^{N-1} z(x_k, y_l)}^{2} \quad \textbf{(1)}$$

2.6. Contact angle measurement

The contact angles were measured by a sessile drop test using a Theta Light optical tensiometer at room temperature. Distilled water droplets with similar volume (around 3μL) were dropped on the sample surface on 5 different sites. For every measurement 240 separate images were recorded by a high speed camera (set-up at a recording speed of 60 frames per second) and analyzed though the OneAttention firmware. Every recorded image was analyzed via curve fitting according to the Young-Laplace equation to the shape of the drop. For every test site a mean contact angle was calculated. The contact angle of each deposited film was calculated as a mean value of all mean values for the 5 measurement sites.

2.7. Spectral characterization

Spectral characteristics of the deposited UV-absorbing PVA-films were recorded by an Agilent Carry 100 UV-Vis spectrophotometer in absorption mode with a data interval of 1 nm. Absorbance spectra were recorded in double beam mode against a polymer substrate, pre-cleaned as previously described.

3. RESULTS AND DISCUSSION

3.1. Surface characterization of UV-absorbing PVA films

It has been already shown, that changes in the surface structure influence strongly other surface properties of polymeric materials (e.g. wettability and adhesion). In the present study we prepared thin polymer films from liquid precursor solutions with constant composition dried at different temperatures ranging from 20 °C to 80 °C. As a result some changes in the surface characteristics- mean surface roughness and wettability, of the obtained films are observed. The temperature dependence of the root mean square of the surface roughness of four PVA films is shown in Figure 2. There is a significant decrease in the surface roughness for films, dried at higher temperature. As no other deposition parameters (solution composition, coating technique and set-up or the duration of the drying step) it is concluded, that the drying temperature has an impact on the surface characteristics. We suggest that by varying the thermal conditions during drying, a control over the rate of evaporation was achieved.

Results from the AFM study indicate that the increase of the drying temperature leads to smoothing of the film surface. Films, dried at room temperature possess a very distinct surface topology with a multitude of sharp ridges and grooves, illustrated in the 3D AFM image in Figure 3 (left). These surface features are also present in films dried at higher temperatures- Figure 3 (right) and Figure 4, but have a significantly decreasing relative height in respect to overall surface. As it is shown in Figure 4 (right) the surface of a UV-absorbing PVA film, dried at 80 °C, is much smoother with individual features rising above the mean conditional surface. It must be noted that all substrates were handled and pre-cleaned in a similar fashion as to avoid patterning of the film surface by the underlying substrate. Due to the high thermal stability of PVA in the temperature range, selected in the present study (Zheng & Kong 2007), chemical changes in the composition of the films due to thermal oxidation should not be considered. As all films were deposited via the same coating technique, with cutting conditions as the only varied parameter, we attribute the changes in the surface roughness as a result only of changes in the conformation of the PVA matrix during the drying step of the deposition.

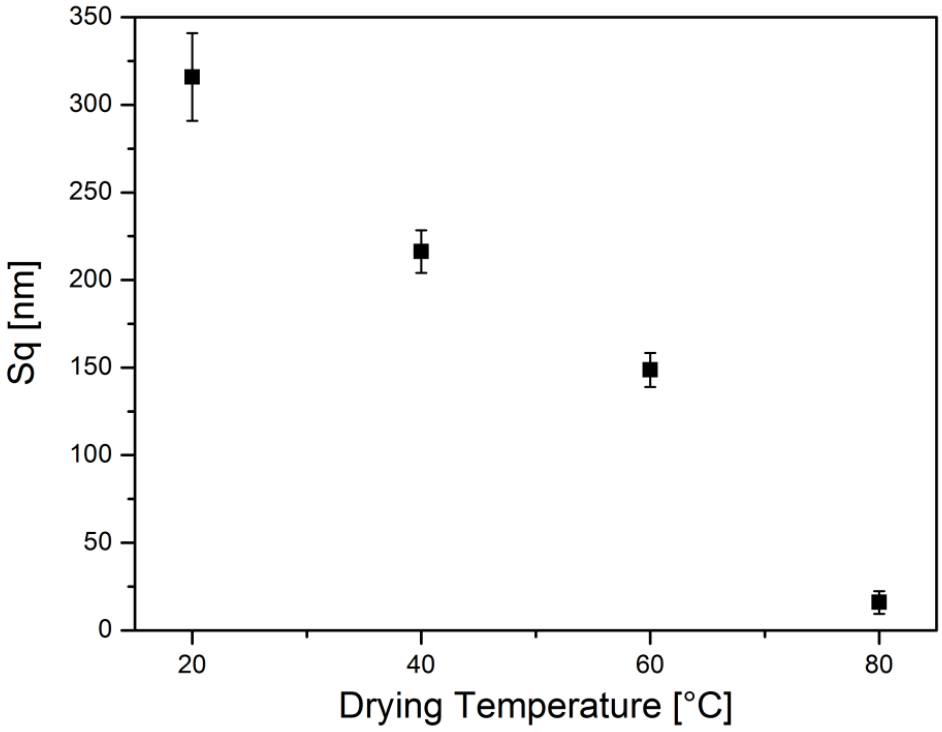


Figure 2 – Mean square roughness of deposited films, dried at ascending temperature from 20 °C to 80 °C

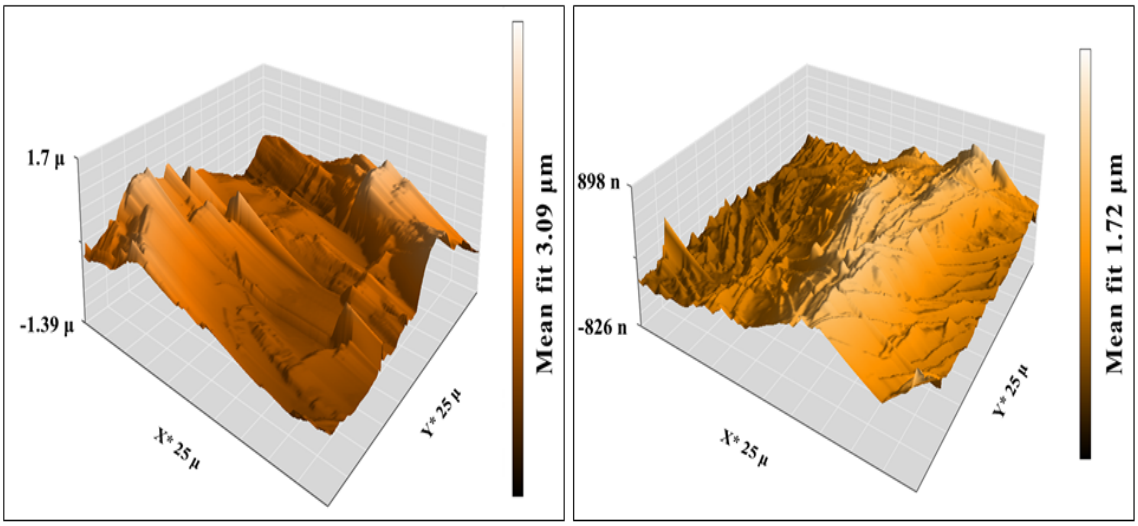


Figure 3 – AFM images of surfaces of deposited films dried at 20 °C (left) and 40 °C (right)

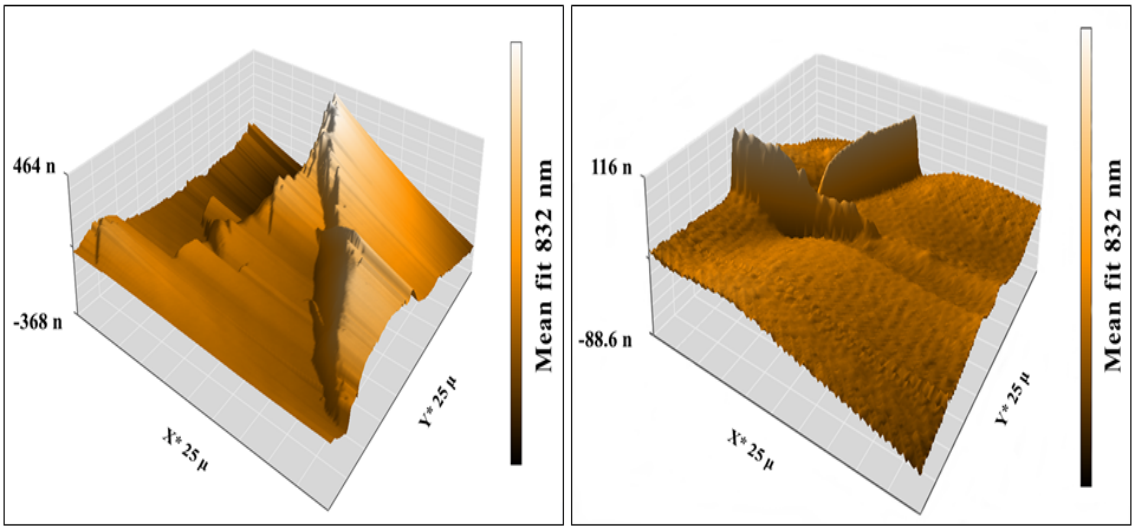


Figure 4 – AFM images of surfaces of films dried at 60 °C (left) and 80 °C (right)

It has already been demonstrated, that conditions during water evaporation of the PVA-water solution, can significantly alter the structure of the final film. When the evaporation is accelerated (e.g. by treating the liquid film at higher temperature) the polymer chain of PVA flexes in such a way, causing acetoxyl groups to dominate the surface. These changes in the ordering the different groups, may cause different ordering of the polymer chain. These effects have been discussed by (Zhang, Zhang & Wang 2009) and attributed to a conformation of the surface molecules. The authors suggest that the rate of evaporation (set by drying temperature) influences whether hydroxyl or acetoxyl groups dominate the surface of the final PVA film. These conformations during water evaporation and polymerization of the PVA matrix, in a connection to covalent ester links between the UV-absorber and the PVA molecules could lead to the evolution of surface cracks.

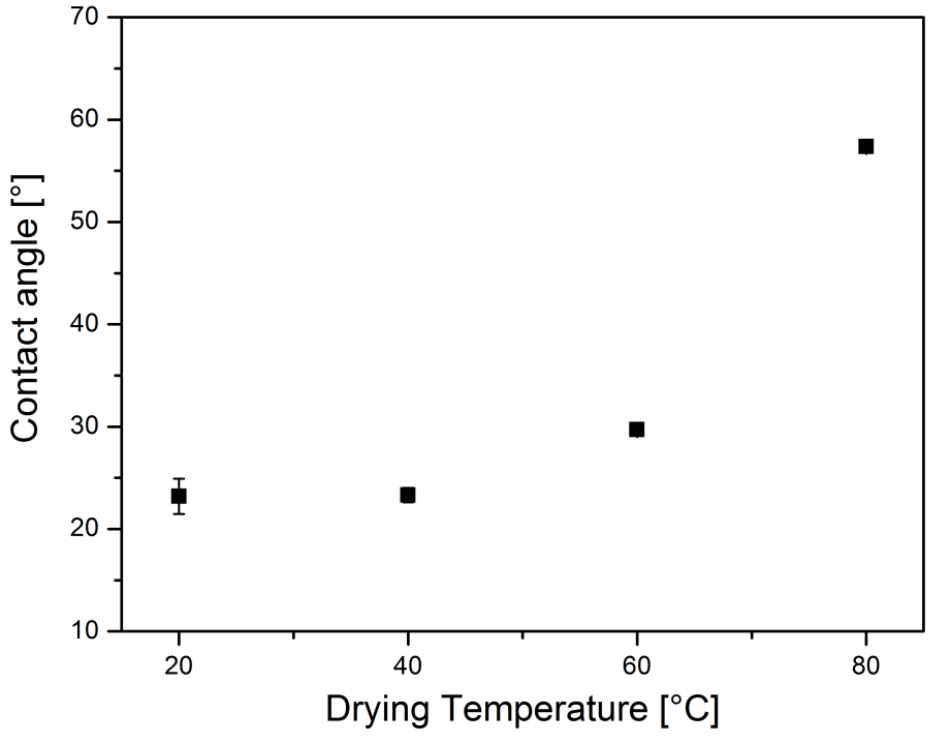


Figure 5 – Contact angle of film surfaces, dried at temperatures from 20 °C to 80 °C

The wettability of the surface of the films is also affected by the different evaporation rate during drying of the liquid PVA film. This is demonstrated from results of the contact angle measurement shown in Figure 5. Films dried at low temperatures- 20 and 40 °C have a low contact angle, indicating their hydrophilic nature. With the rise of the applied drying temperature there is a very distinct steep rise in the contact angle of the surface. It has been demonstrated that the contact angle is both dependent on surface roughness (Wenzel 1936) and on the chemical composition on the interphase (Guo et al. 2007). This abrupt change in the contact angle could be induced of both the orientation of hydrophobic groups and the smoother surface of the film. As demonstrated above films, dried at 80 °C have a significantly lower mean surface roughness. However the change to a more hydrophobic nature of the surface should also be explained by conformation changes in the polymeric chains on the surface. In the case of rapidly dried films at 80 °C, we suspect that the hydrophobic acetoxyl groups remain on the surface. It should be assumed that some of the 2-hydroxy-4–methoxy-benzophenone-5-sulfonic acid present in the liquid PVA solution has formed ester bonds with the hydroxyl groups of the PVA or they are oriented to the molecules of the UV-absorber by hydrogen bonds. In both cases the ability of PVA to flex and orient hydroxyl groups to the surface, in order to minimize the free energy should be limited. These effects are manifested by changes observed in the wettability and the surface roughness.

3.2. *Spectral characteristics of UV-absorbing films*

The spectral characteristics of the deposited PVA films are the most important properties for their possible use in flexible photovoltaic cells. In order to achieve the desired UV-filtering property of the thin polymer films an organic UV-absorber- 2-hydroxy-4–methoxy-benzophenone-5-sulfonic acid (referred to in the present article under the trade name Escalol 577) was added to the PVA solution. This compound as a part of the benzophenone class is a good UV-absorber with a high absorbance capacity in the UVA and UVB ranges (320-400 nm and 290-320 nm, respectively) (Orisi, Giannini & Gagliardi 2006). It is soluble in aqueous media (Giokas, Salvador & Chrisvert 2007), making it easily adoptable for PVA protective films. Escalol 577 has a significant stability upon light exposure (Santos, Miranda & Esteves da Silva 2012), guaranteeing the longevity of the final protective film. An essential property of the UV-filtering film is its high transparency in the visible light range. Protective coatings should provide no light shading for underlying layers. These properties of the UV-absorbing PVA films were studied by means of UV-vis spectroscopy.

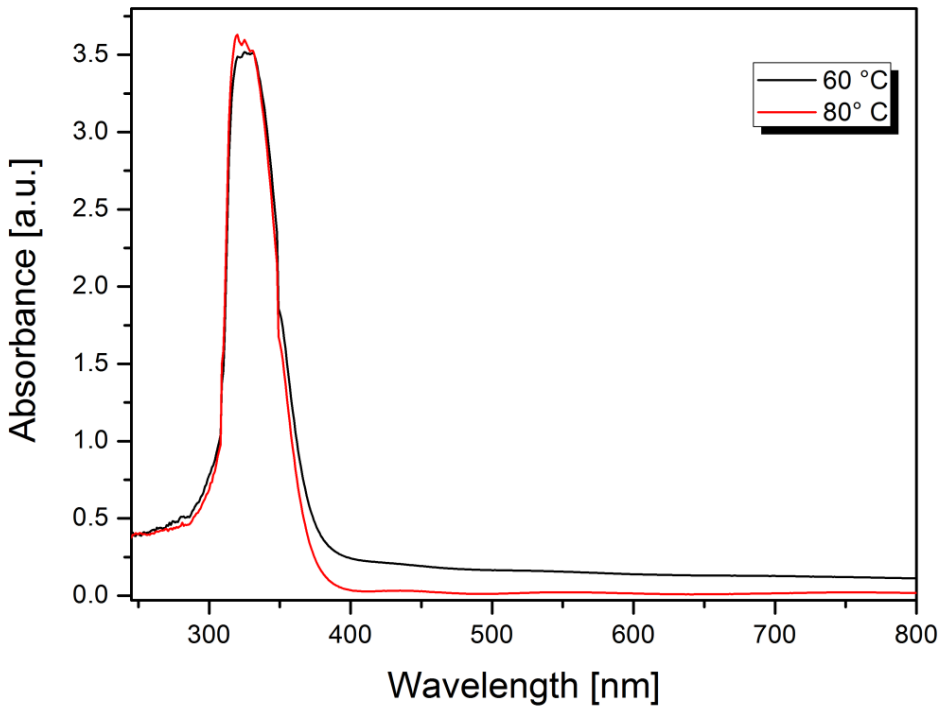


Figure 6– Absorbance spectra of Escalol 577 containing PVA films

As shown in Figure 6 Escalol 577 containing PVA films deposited by the laboratory flexographic method retain the UV absorbing capability of the pristine organic UV-absorber. There is a very strong peak in the light absorption on 325 nm for both demonstrated films, regardless of the drying temperature selected. The intensity of the light absorption, indicative of the high UV-filtering capability, is also independent of this parameter during the deposition.

The absorbance spectra in the visible (>400 nm) range (**Error! Reference source not found.**) shows that thermal conditions during drying strongly influence the transparency of the deposited films. The increase in the drying temperature leads to a significant reduction of the absorbed light. Films dried at room temperature are more opaque and have limited visible light transmittance, as opposed to films dried at higher temperature.

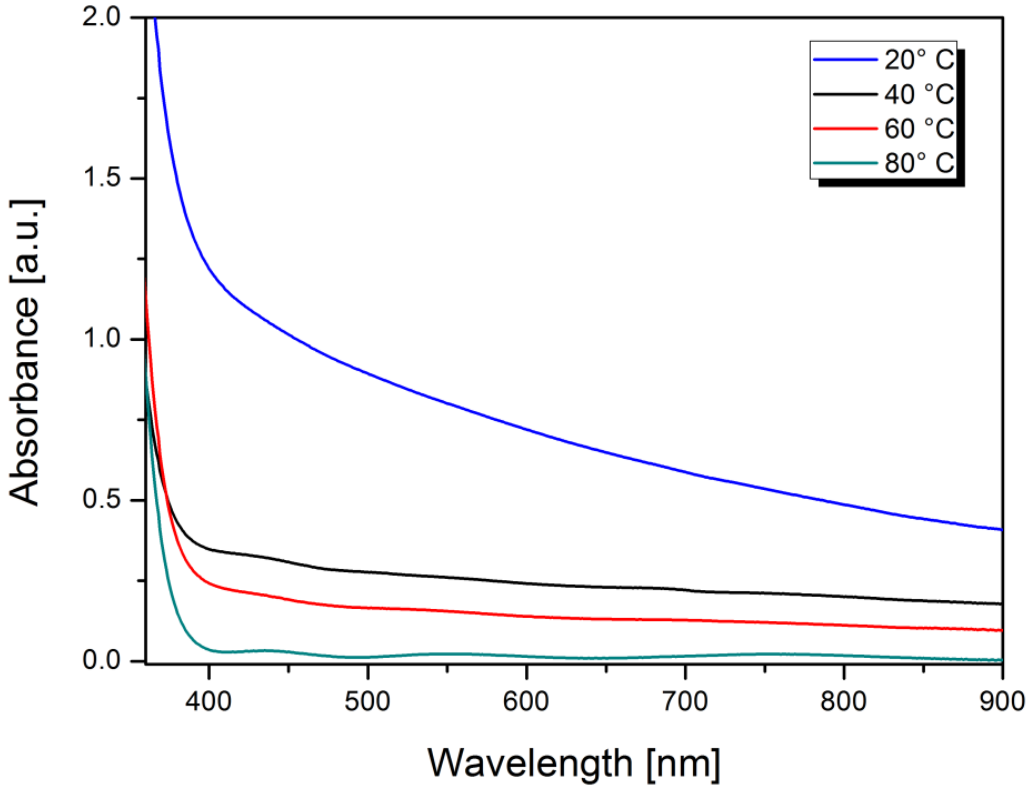


Figure 7 – Absorbance spectra of film dried at various temperatures in the visible light region (>400 nm)

UV-absorbing PVA films treated at 80 °C are almost transparent to visible light. This would allow for a maximal light flux, reaching underlying polymers, and ultimately translating in a minimized efficiency loss of the photovoltaic devices due to shading. The light transparency of the films deposited at low temperatures should be attributed to changes in the structure of the polymeric PVA matrix. Lower drying temperatures could allow for different chemical groups in the liquid solution to arrange in such a way, that causes internal stresses and the development of cracks on the film surface. These lead to a light scattering ultimately manifested by an undesired opacity in the visible light region. On the basis of absorbance spectra, recorded in the visible light range (from 400 nm to 800 nm), it can be outlined, that films processed at 80 °C possess superior spectral properties. These have demonstrated a better transparency in the visible light range, whilst having equal UV-filtering properties.

4. SUMMARY

The surface structure of thin UV-absorbing PVA films, prepared at different drying temperatures has been investigated using AFM, and contact angle measurements. The spectral characteristics of the PVA films have been studied through UV-vis spectroscopy. The AFM study revealed a decrease in the mean surface roughness for films dried at higher temperatures. Increasing the drying temperature led to smoothing of the surface. It was

shown that the contact angle of the PVA films increases as the drying temperature during the deposition is increased. This effect was attributed to changes of the surface roughness to some extent, but primarily to conformation changes of the polymer. The deposited UV-filtering PVA films exhibited a more hydrophobic nature with ascending drying temperature.

All PVA films, containing an organic UV-absorber exhibited high absorption in the region below 400 nm. The increase in the drying temperature led to smoothing of defects and cracks on surface of the film, making it more transparent in the visible light region. Films dried at 80 °C were almost completely transparent to visible light, yet still possessing a characteristic high UV-filtering capability. They can be deposited on flexible polymeric substrates via facile methods like flexographic printing. These properties allow for the future employment of the UV-absorbing PVA films described in this study as the protection of flexible polymer solar cells.

5. ACKNOWLEDGMENTS

This material (presentation, paper, report) has been produced with the financial assistance of the European Social Fund, project number BG051PO001-3.3.06-0014. The author is responsible for the content of this material, and under no circumstances can be considered as an official position of the European Union and the Ministry of Education and Science of Bulgaria

REFERENCES

Ahmad, J, Bazaka, K, Anderson, J, White, RD & Jacob, MV 2013, 'Materials and methods for encapsulation of OPV: A review', *Renewable and Sustainable Energy Reviews*, vol 27, pp. 104-117.

Fukumori, T & Nakaoki, T 2014, 'High-tensile-strength polyvinyl alcohol films prepared from freeze/thaw cycled gels', *Journal of Applied Polymer Science*.

Gaume, J, Wong-Wah-Chung, P, Rivaton, A, Thérias, S & Gardette, J-L 2011, 'Photochemical behavior of PVA as an oxygen-barrier polymer for solar cell encapsulation', *RSC Adv. (RSC Advances)*, vol 7, no. 8, p. 1471.

Giokas, DL, Salvador, A & Chrisvert, A 2007, 'UV filters: From sunscreens to human body and the environment', *TrAC Trends in Analytical Chemistry*, vol 26, no. 5, pp. 360-374.

Gohil, MJ, Bhattacharya, A & Ray, P 2006, 'Studies On The Crosslinking Of Poly (Vinyl Alcohol)', *J Polym Res (Journal of Polymer Research)*, vol 13, no. 2, pp. 161-169.

Guo, R, Ma, X, Hu, C & jiang, Z 2007, 'Novel PVA–silica nanocomposite membrane for pervaporative dehydration of ethylene glycol aqueous solution', *Polymer*, vol 48, no. 10, pp. 2939-2945.

Hoppe, H & Sariciftci, NS 2004, 'Organic solar cells: An overview', *Journal of Materials Research*, vol 19, no. 07, pp. 1924-1945.

Jiang, H, Zuo, Y, Zhang, L, Li, J, Zhang, A, Li, Y & Yang, X 2014, 'Property-based design: optimization and characterization of polyvinyl alcohol (PVA) hydrogel and PVA-matrix composite for artificial cornea', *Journal of Materials Science: Materials in Medicine*, vol 25, no. 3, pp. 941-952.

Jørgensen, M, Norman, K & Krebs, FC 2008, 'Stability/degradation of polymer solar cells', *Solar Energy Materials and Solar Cells*, vol 92, no. 7, pp. 686-714.

Khan, MR, Ray, B & Alam, MA 2014, 'Prospects of layer-split tandem cells for high-efficiency OPV', *Solar Energy Materials and Solar Cells*, vol 120, pp. 716-723.

Kiatkamjornwong, S, Rattanakasamsuk, K & Noguchi, H 2003, 'Evaluation of Some Strategies to Control Fading of Prints from Dye-Based Ink Jet', *Journal of Imaging Science*, vol 47, no. 2, pp. 149-154.

Li, N, Baran, D, Spyrioulos, GD & Zhang, H 2014, 'Environmentally Printing Efficient Organic Tandem Solar Cells with High Fill Factors: A Guideline Towards 20% Power Conversion Efficiency', *Advanced Energy Materials*.

Morlier, A, Cros, S & Garandet, J-P 2013, 'Gas barrier properties of solution processed composite multilayer structures for organic solar', *Solar Energy Materials and Solar Cells*, vol 115, pp. 93-99.

Orisi, D, Giannini, G & Gagliardi, L 2006, 'Simple Extraction and HPLC Determination of UV-A and UV-B Filters in Sunscreen Products', *Chroma (Chromatographia)*, vol 64, no. 9-10, pp. 509-515.

Santos, AJM, Miranda, S & Esteves da Silva, JCG 2012, 'The degradation products of UV filters in aqueous and chlorinated aqueous solutions', *Water Research*, vol 46, no. 10, pp. 3167-3176.

Wenzel, RN 1936, 'RESISTANCE OF SOLID SURFACES TO WETTING BY WATER', *Industrial & Engineering Chemistry*, vol 28, no. 8, pp. 988-944.

Zhang, W, Zhang, Z & Wang, X 2009, 'Investigation on surface molecular conformations and pervaporation performance of the poly(vinyl alcohol) (PVA) membrane', *Journal of Colloid and Interface Science*, vol 333, no. 1, pp. 346–353.

Zheng, P & Kong, LX 2007, 'A thermal degradation mechanism of polivinyl alcohol/silica nanocomposites', *Polymer Degradation and Stability*, vol 92, no. 6, pp. 1061-1071.