Jovana Šakota Rosić
Ph.D. Student
University of Belgrade
Faculty of Mechanical Engineering

Manuel Conte
SOLEKO S.P.A, Pontecorvo
Italy

Jelena Munćan
Assistant
University of Belgrade
Faculty of Mechanical Engineering

Lidija Matija
Associate Professor
University of Belgrade
Faculty of Mechanical Engineering

Đuro Koruga
Professor
University of Belgrade
Faculty of Mechanical Engineering

Characterization of Fullerenes Thin Film Oon Glasses by UV/VIS/NIR and Opto-Magnetic Imaging Spectroscopy

UV/VIS spectroscopic characterization of glasses is a part of the standard procedure. The reasons to do it is to ensure UV eye protection and characterization of material transparency. However, we extend this research to IR domain because the quality of glasses depend not only on UV protection and their transparency but on complementarities and compatibility of eye vision with optical device, also. We characterized basic material of glasses by UV/VIS/NIR and novel method Opto-magnetic Imaging Spectroscopy (OMIS). Then we doped basic material with fullerenes, and characterized them using the same procedure. Results are presented and discussed.

Keywords: *glasses, fullerene, thin film, UV/VIS/NIR, opto-magnetic imaging spectroscopy.*

1. INTRODUCTION

People, who have perfect vision, most often use sunglasses for protection, while people with refractive anomalies use corrective glasses [1]. To achieve the desired results in vision correction, it is important to know the characteristics of materials used, because they can significantly affect the quality of visible light reaching different parts of the eye.
Current available knowledge shows that electromagnetic radiation, especially UV radiation, is potentially hazardous to the structure of the eyes, particularly the cornea, lens, and retina [2,3]. Several eye disorders are related to sun exposure. Although solar radiation comprises a broad range of wavelength, all of the eye disorders mentioned above are related to UV and short-wavelength visible light [4].

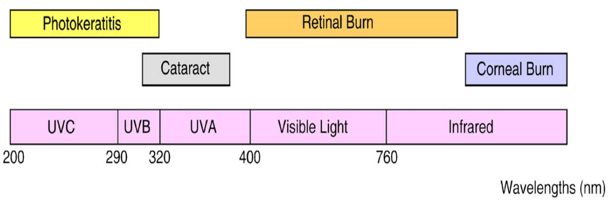

Figure 1. Adverse effects to eyes resulting from exposure to different wavelengths of electromagnetic spectrum [4]

Because of the filtration effect of ocular structures, different wavelengths within the UV and visible light ranges penetrate through different parts of the eye (cornea, lens, and retina) (Fig. 1) [4]. The cornea substantially absorbs wavelengths shorter than 295 nm. Excessive UVB exposure can cause conjunctivitis and permanent damage to the cornea. Wavelengths between 295 and 400 nm penetrate more deeply and can cause damage to the crystalline lens (ie, cataracts) [5]. Visible light and infrared transmit to the retina. Only visible light, not UV, is required for human vision. Therefore the ideal corrective glasses and sunglasses should substantially reduce UV to cornea and lens, including that from lateral directions.

Different materials have been used in spectacles glass manufacturing, but in our research we chose to use white float glass (PGO, Germany), glass with applied layer of fullerene C_{60} thin film on the surface. By adding the fullerene film we have tried to enhance protective functions of these materials. The aim of this research is to expand characterization of optical properties of regular and fulleren-modified glasses which provide UV protection and could be more compatible with human vision system.

Fullerenes are the class of carbon cluster cage molecules with 12 pentagons and different number of hexagons (C_{2n+20}, n=0, 2, 4, 6, …; n represents number of hexagons). They represent the third known crystal form of carbon, in addition to graphite and diamond. One of the most interesting fullerenes structure is molecule C_{60}. Fullerene C_{60} is a precisely defined molecule and consists of 60 carbon atoms arranged in cage that is made up of 12 pentagons and 20 hexagons by icosahedral symmetry [6]. Nanostructured materials refer to materials with dimensions less than 100 nm [7]. Fullerene C_{60} diameter is about 1 nm [6]. These materials have potential applications in areas such as electronics, magnetism, optics, energy storage, electrochemistry and biomedical sciences [7].

Characterization and comparison of materials for spectacles glass with and without the fullerene was made. Unlike previous research which focused only on the UV/VIS characterization of materials which provide information about the permeability of materials, we have expanded our research to the Infrared spectroscopy (IR) and the Opto-magnetic Imaging Spectroscopy (OMIS), because it is necessary to characterize the material in terms of biocompatibility and biotoxicity for those materials that come in contact with the tissue. This paper presents the results of this characterization.

Received: February 2014, Accepted: March 2014
Correspondence to: Jovana Šakota Rosić, M.Sc.
Faculty of Mechanical Engineering,
Kraljice Marije 16, 11120 Belgrade 35, Serbia
E-mail: jsakota@mas.bg.ac.rs
doi:10.5937/fmet1402172S

2. MATERIALS

For purposes of this research, we used two types of materials: white float glass and white float glass+C_{60}.

Transparent white float glass (PGO, Germany) has following characteristics: 1.1 mm thickness, refractive index 1.52 on 587.6 nm, coefficient of thermal expansion $84x10^{-7}$ in range of 0-100°C, dielectric constant 7.75 on 25°C and 1 MHz, specific resistivity 9.7 [log R (Ωcm)] and transparence of 92%in range of wavelength 380-2500 nm [8, 9].

We use this type of glass to deposit fullerene (C_{60}) thin film. The thickness of applied film layer was 100 nm. All measurements were performed in air at room temperature.

Spectroscopic properties of fullerenes are closely related to their symmetry [10]. Structural information can be obtained from the number of connections, for example in the IR spectrum. It is considered that fullerene is responsible for better electromagnetic properties of transmitted light [11] that are convenient to the human eye. C_{60} has a very low solubility and high crystallinity. Also, the C_{60} fullerene and its derivatives show different excellent electronic, conductive, magnetic and photochemical properties.

3. METHODS

1. Physical Vapor Deposition (PVD):

Physical Vapor Deposition processes (often just called thin film processes) are atomistic deposition processes in which material is vaporized from a solid or liquid source in the form of atoms or molecules, transported in the form of a vapor through a vacuum or low pressure gaseous (or plasma) environment to the substrate where it condenses. Typically, PVD processes are used to deposit films with thicknesses in the range of a few nanometers to thousands of nanometers [7].

PVD techniques include all techniques based on evaporative deposition, such as e-beam or hot-boat evaporation, reactive evaporation and ion plating [12].

Physical Vapor Deposition is a process by which a thin film of material is deposited on a substrate according to the following sequence of steps: 1) the material to be deposited is converted into vapor by physical means; 2) the vapor is transported across a region of low pressure from its source to the substrate; and 3) the vapor undergoes condensation on the substrate to form the thin film.

One advantage of the technique is that the evaporation can be carried out in an ultra-high vacuum (UHV) chamber, so that contamination of the substrate, by residual gases, is minimal [13].

To make fullerenes thin film vacuum deposition technique apparatus Vacuum Evaporator JEE-400 (JEOL, Japan) with vacuum about 10^{-5} Pa in the bell-jar with diameter 240 nm and h=270 mm has been used. The bell-jar houses are the two pairs of electrodes: one is fitted with a pair of heater holders and the other with a pair of fullerene holder. Vacuum pressure is accurately measured by a built-in Penning and Pirani gauge [8].

Figure 2. Vacuum deposition technique (NanoLab 1, Faculty of Mechanical Engineering, University of Belgrade)

2. UV/VIS:

Safas Monaco spectrophotometer was used for UV/VIS characterization utilizes ultraviolet-visible spectroscopy (UV-Vis) in the 50-1050 nm wavelengths range with a 2 nm resolution. This means it uses light in the visible and adjacent (near-UV and near-infrared range).

Since the UV-Vis range spans the range of human visual acuity of approximately 400 - 700 nm, UV-Vis spectroscopy is useful to characterize the absorption, transmission, and reflectivity of a variety of technologically important materials, such as pigments, coatings and filters. This more qualitative application usually requires recording at least a portion of the UV-Vis spectrum for characterization of the optical or electronic properties of materials.

3. IR:

For investigation in IR part of the spectra, FTIR-620, JASCO, Japan instrument was used. It was used in transmission and reflection mode, in the 5000-600 cm^{-1} wavelengths range with a resolution from 0.25 to 16 cm^{-1}

4. Opto-magnetic Imaging Spectroscopy (OMIS):

In this method the basic tool is the light (polarized light and white light), wavelength range from 400-700 nm. Each type of matter has special, different, angle value of light polarization.

If we point a beam of light on a sample surface at a right angle then the reflected light contains information about the electromagnetic properties of the sample. However, if we point a beam of light on a sample of given material under a certain angle, than the sample will make the polarized pattern of light. This angle is called Brewster's angle and it represents the magnitude of the angle of incidence under which the sample polarizes the incident light (Fig. 3). Reflected light will have only electrical component and the properties of the sample based on the electric surface conditions. In this way, on the based on light we can get to materials electrical properties. But if the surfaces are the same in both cases, then we can deduce first reflection from the second reflection and get magnetic properties of the sample (opto-magnetic fingerprint – OMF) [8, 14,15].

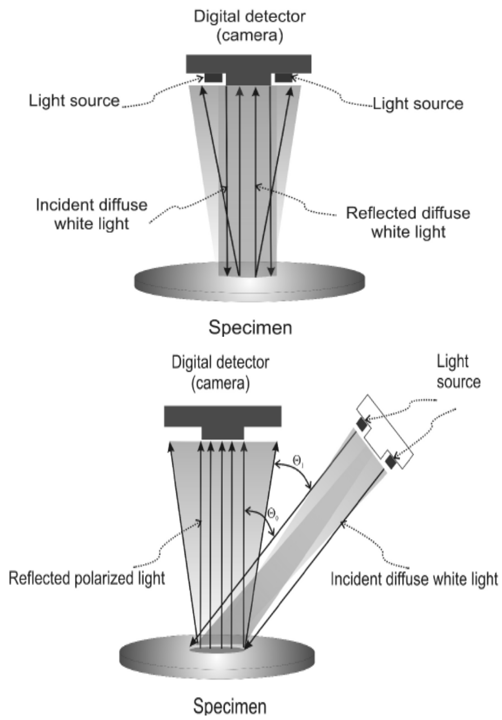

Figure 3. Incident white light can give different information about sample surface properties depending on the angle of light incidence

Taking the difference between white light (electromagnetic) and reflected polarized light (electrical) yields magnetic properties of matter based on light-matter interaction [16]. Digital images in RGB (R-red, G-green, B-blue) system were used, therefore basic pixel data in red and blue channels for white diffused light (W) and reflected polarized white light (P) were chosen. Algorithm for data analysis is based on chromaticity diagram called "Maxwell's triangle" and spectral convolution operation according to ratio of (R-B) & (W-P) [9]. The abbreviations means that Red minus Blue wavelength of White light and reflected polarized light are used in spectral convolution algorithm to calculate data for opto-magnetic spectroscopy of matter [17].

We have taken 10 pairs of white and polarized images of glass surfaces. Polarized white light is obtained by reflection from the sample under Brewster's angle. Digital images are obtained with a standard digital camera. The equipment used is Canon brand, model IXUS 105, 12.1 MP. Ilumination of the sample is provided by two light systems: white diffuse light is provided with a system of 3 LED diodes, while the other system of 3 LED diodes is placed at an angle of 53° relative to the vertical axis. Digital images of the samples lover the area of the glass surface 25 mm diameter in size. The obtained images were cropped in Photoshop, to size 250x250 pixels. New images obtained by cropping, were processed using code written in MATLAB. The results are presented in a form of diagrams which features characteristic values of wavelengths and intensities.

4. RESULTS AND DISCUSSION

The first picture of basic material is taken under diffuse light, and the second with light under angle of 53°. The obtained images were cropped in Photoshop, and were processed using code written in MATLAB. The result is the Intensity-Wavelength diagram, where we can see four peak values, the positive ones at approximately 115.87 nm (intensity of 79.18) and 118.46 nm (intensity of 47.74), and the negative ones at approximately 117.53 nm (intensity of -138.94) and 119.74 nm (intensity of -18.02). Also we can notice that the intensitis are zero at these wavelengths: 116.64 nm, 117.98 nm and 119.22 nm.

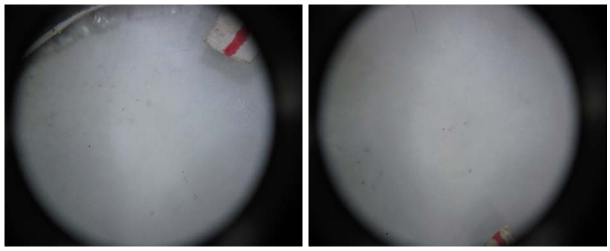

Figure 4. Digital image of basic material (glass) taken with opto-magnetic imaging spectroscopy method (OMIS): a) diffuse white light (left), b) reflected polarized light (right).

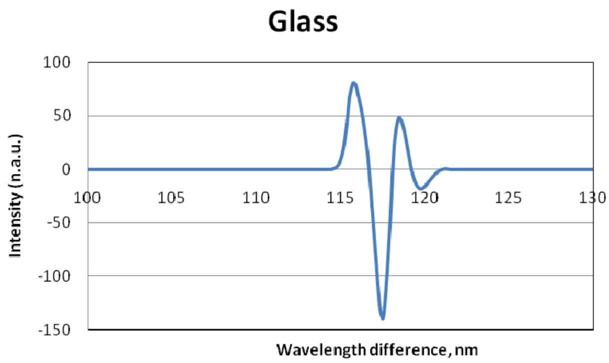

Figure 5. OMIS diagram of basic material (glass) taken with opto-magnetic imaging spectroscopy method obtained from images 4a, b.

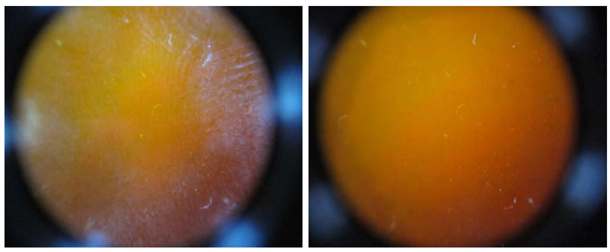

Figure 6. Digital image of photonic material (glass and C_{60}) taken with opto-magnetic imaging spectroscopy method (OMIS): a) diffuse white light (left), b) reflected polarized light (right).

For the diagram of glass+C_{60} we can see two peak values, the positive one at approximately 116.04 nm (intensity of 18.88), and the negative one at approximately 112.65 nm (intensity of -18.21). Comparing to the base material, here we can notice that the amplitudes have zero values at one wavelength: 114.76 nm.

Here we can see the difference between values on Intensity-Wavelength diagrams for basic and basic+C_{60} material, and also we can see the difference in the number of peaks between these two diagrams. Based on this we can conclude that there is a significant difference between the two samples of glass materials. The differences in wavelengths are approximately 3 nm for positive peak, and approximately 7 nm for the negative one, and for intensities approximately 120 units for the negative peak and 61 units for the positive one.

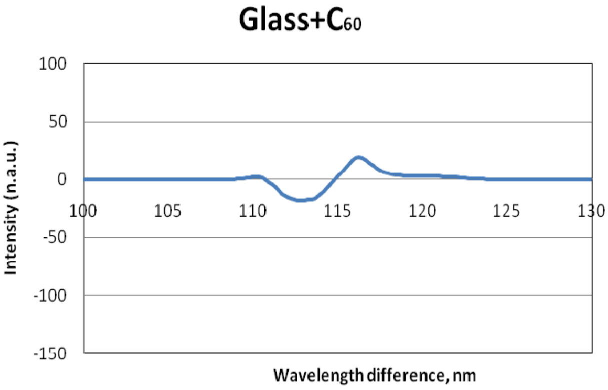

Figure 7. OMIS diagram of photonic material (glass and C_{60}) taken with opto-magnetic imaging spectroscopy method obtained from images 6a, b.

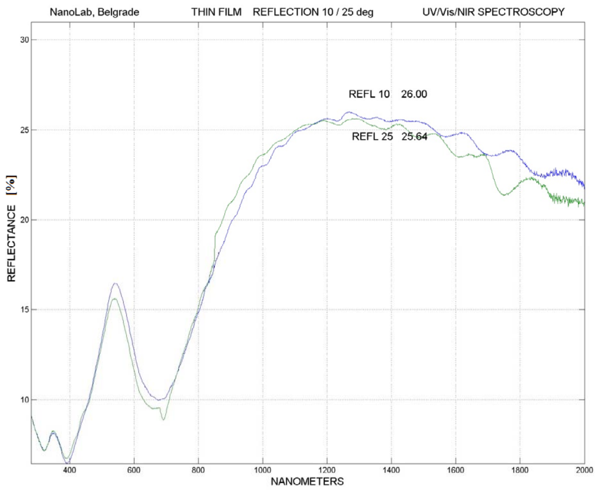

Figure 8. The results acquired using UV/VIS/NIR (300-2500 nm)

The spectra of the sample presented in Fig. 8 represents results acquired using Safas Monaco spectrophotometer for the thin film layer thickness of 100 nm. Two beams of light were directed towards the glass, first ray of light under angle of 10 degrees, and the second under angle of 25 degrees. Based on these results we can see that the glass shows almost the same characteristics regardless of the angle of light beam. Reflectance characteristics presented, show that film-coated glasses reflect about 3-8% UV-B (290-320 nm) and 0-5% UV-A (320-400 nm). The reflectance is zero at 400 nm, but then it increases up to 17% in the visible region (400-760 nm), and is even more increased in the infrared region with maximum 26% reflectance around 1300 nm.

Absorbance spectra presented in Fig. 9 shows that film coated glasses absorb UV radiation better than uncoated one, while absorbance is almost zero for both types of glasses in visible and NIR region.

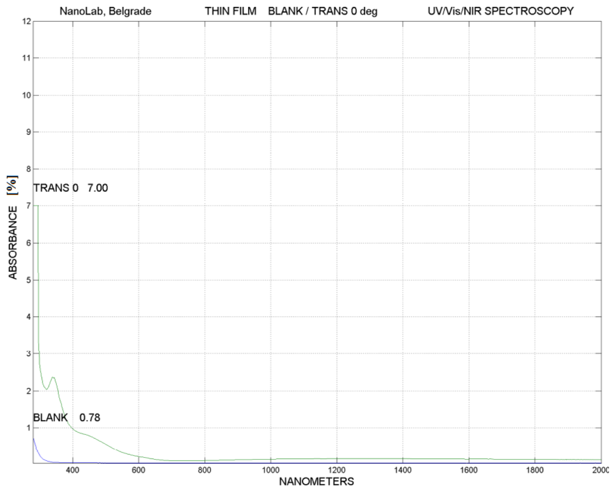

Figure 9. Absorbance spectra of the glasses with thin film

5. CONCLUSION

The aim of this research was to characterize and compare two materials, standard glasses material and standard glasses material with C_{60} thin film layer. According to opto-magnetic imaging spectroscopy results shown on diagrams, we can conclude that there is a dramatic difference in the values of the positive and negative peaks on Wavelength difference (nm)-Intensity (n.a.u.). The nano film glass has lower intensities at approximately the same wavelengths comparing to the standard glass material, which is of great importance for the further course of this experiment.

Reflectance and absorbance spectra show that better characteristics form the aspect of eye protection show glasses with thin film of fullerene.

It is also remarkable that the new material is absorbing a much greater deal of UV A and UV B part of the spectrum therefore acting as a better UV blocker then the standard material. The new photonic nanomaterial based on glass and C_{60} molecule compared to the standard material, has much better absorption characteristics of UV A and UV B radiation, because the radiation in this range effects badly on skin cells, as well as retina cells. Also, this photonic nanomaterial is a better fit considering the wavelengths for which the eye is the most sensitive.

Based on the results, it is possible to detect the differences in the characteristics between nanophotonic glasses material and basic glasses material with opto-magnetic imaging spectroscopy method.

ACKNOWLEDGMENT

This research has been partially funded by Ministry of Science and Technological Development of Republic of Serbia, through Project III 45009, “Functionalization of nanomaterials for manufacturing new sort of contact lenses and early diagnostics of diabetes’’.

REFERENCES

[1] Sokol, J.L., Mier, M.G., Bloom, S. and Asbell, P.A.:A study of patient compliance in a contact lens-wearing population, The CLAO journal:

official publication of the Contact Lens Association of Ophthalmologists, Inc 16 (3), 1990.

[2] Fishman, G.A.: Ocular phototoxicity: guidelines for selecting sunglasses. Surv Ophthalmol, 31:119-24, 1986.

[3] Javitt, J.C., Taylor, H.R.: Cataract and latitude. Doc Ophthalmol, 88:307-25, 1994.

[4] Tuchinda, C., Srivannaboon, S., and Lim, H.W.: Photoprotection by window glass, automobile glass, and sunglasses, American Academy of Dermatology, 2006.

[5] Weale, R.A.: Age and the transmittance of the human crystalline lens, J Physiol. 395:577-87, 1988.

[6] Giacalone, F. and Martin, N.: Fullerene Polymers: Synthesis and Properties (Chem. Rev. 106, 5136-5190), 2006.

[7] Mattox, D.M.: Film Formation, Adhesion, Surface Preparation and Contamination Control, Handbook of physical vapor deposition (PVD) processing, Noyes publications, Westwood, New Jersey, U.S.A, 1998.

[8] Koruga, Đ.: Apparatures for harmonizing light, Patent Application Publication, US 20008/0286453 A1, Publication Date: November 20, 2008.

[9] Koruga, Đ. and Tomić, A.: Method and algorithm for analysis of light-matter interaction based on spectral convolution, US Pat. App. No.61/061,852, 2008.

[10] Koruga, Đ. and Tomić, A.: Optomagnetic fingerprint, Nanotechnology handout, lesson 8, Faculty of mechanical engineering University of Belgrade, 2010.

[11] Matija, L., Nanotechnology-Artificial Versus Natural Self-Assembly – FME Transactions, Vol. 32, No. 1, pp. 1-14, 2004.

[12] Rossnagel, S.M.,: *Physical vapor deposition, Handbook of Semiconductor Manufacturing Technology*, Chapter 14 New York, USA, 2000.

[13] Colligon, J.S.,: Physical vapor deposition, Pergamon Materials Series**,** Chapter 9, Volume 2, Pages 225–253, 1999.

[14] Koruga, Đ., Miljković, S., Ribar, S., Matija, L. and Kojić, D.: Water Hydrogen Bonds Study by Opto-Magnetic Fingerprint Technique, Selected papers presented at the Eleventh Annual Conference of the Materials Research Society of Serbia, Vol. 117, 2010.

[15] Papić-Obradović, M., Kojić, D. and Matija, L., Opto–Magnetic Method for Epstein — Barr Virus and Cytomegalovirus Detection in Blood Plasma Samples, Selected papers presented at the Eleventh Annual Conference of the Materials Research Society of Serbia, Vol. 117, 2010.

[16] Koruga, Đ. and Tomić, A., System and method for analysis of light - mater interaction based on spectral convolution in MATLAB, US Pat. App. No. 0245603, 2009.

[17] Matija, L., Kojić, D., Vasić, A., Jovanović, T. and Koruga, Đ., *Uvod u nanotehnologije*, Nauka-DonVas, edited by Nikola Dončev, pp. 242-254, Beograd, 2011.

КАРАКТЕРИЗАЦИЈА ТАНКОГ ФИЛМА ФУЛЕРЕНА НА СТАКЛИМА ЗА НАОЧАРЕ ПРИМЕНОМ УВ/ВИС/НИР И ОПТО-МАГНЕТНЕ ИМИЏИНГ СПЕКТРОСКОПИЈЕ

Јована Шакота Росић, Мануел Конте, Јелена Мунћан, Лидија Матија, Ђуро Коруга

УВ/ВИС испитивање стакала за наочаре је део стандардне процедуре. Разлог за то јесте да се осигура УВ заштита ока, као и карактеризација транспарентности материјала. Међутим, ми смо проширити ово истраживање у ИР домену из разлога што квалитет стакала не зависи само од УВ заштите и њихове транспарентности, већ такође и од комплементарности и компатибилности ока са оптичким помагалом. Извршена је карактеризација основног материјала за наочаре помоћу УВ/ВИС/НИР и нове методе опто-магнетне имиџинг спектроскопије. Након тога основни материјал допиран је фулереном, и извршена је карактеризација применом истих метода. Резултати су представљени и дискутовани.