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Faculty of Mechanical Engineering, Transport and Aeronautics
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**METHOD FOR REGULATION OF
POLYMETHYL METHACRYLATE EYE
PROSTHESIS WETTABILITY BY USING
ULTRAVIOLET RADIATION**

Summary of the Doctoral Thesis

Field: Mechanical engineering
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DOCTORAL THESIS
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DECLARATION OF ACADEMIC INTEGRITY

I hereby declare that the Doctoral Thesis submitted for the review to Riga Technical University for the promotion to the scientific degree of Doctor of Engineering Sciences (Telecommunications) is my own. I confirm that this Doctoral Thesis had not been submitted to any other university for the promotion to a scientific degree.

Linda Lancere(Signature)

Date:

The Doctoral Thesis has been written in the Latvian language; it consists of the Introduction, 4 Chapters, Conclusions and Bibliography with 83 reference sources. The volume of the present Doctoral Thesis is 101 pages.

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GENERAL DESCRIPTION OF THE DOCTORAL THESIS

Thesis Topic Rationale

Currently, the most common material for fabrication of ocular prostheses is a dielectric polymethyl methacrylate (PMMA). Deterioration in wettability of the prosthesis surface decreases user comfort and causes eyelid inflammation. Worldwide, around 500 million patients per year are using PMMA ocular prostheses [21]. If wettability of PMMA surface worsens, the prosthesis needs to be replaced, this costs around 1.5 billion EUR annually worldwide [14]. These expenses could be reduced significantly if patients would be able to renew wettability of the prostheses in home conditions. However, at present, this option is not possible due to the lack of appropriate technologies.

An essential component of the surface energy of a dielectric is surface electric potential. Ultraviolet (UV) radiation causes transitions of electrons to the surface localized states and therefore can be used regulating PMMA wettability in home conditions.

The above proves that the topic of the Doctoral Thesis aimed at regulation of surface electric potential and wettability of PMMA in home conditions using UV is **significant** and satisfies needs of patients.

Aim and Tasks of the Thesis

The aim of the doctoral thesis is to develop a method for wettability regulation of PMMA surface by using UV radiation for application in ocular prosthetics.

To achieve the aim of the thesis the following tasks have been put forward:

1. To develop research method for wettability regulation of PMMA surface using UV radiation (research sequence, preparation of PMMA samples, method and modes of UV exposure, selection of methods for characterization of PMMA surface).
2. To determine experimentally the influence of environmental conditions on a regulation of PMMA wettability.
3. To study experimentally the influence of UV on electric potential, chemical composition and morphology of PMMA surface that influences wettability.
4. To develop the method for regulation of PMMA wettability by using UV.
5. To evaluate the economic efficiency of the developed method of PMMA wettability regulation for application in ocular prosthetics.
6. To approbate the achieved results by determining the influence of PMMA surface properties modified by UV on microorganism adhesion and induction of surface electric potential of nanocoatings.

Scientific Novelty

1. The method of PMMA wettability regulation has been developed that induces surface electric potential by applying UV irradiation in the wavelength range 200–400 nm under atmospheric conditions (mercury-xenon UV source, 200 W). UV irradiation does not change surface morphology.
2. It has been shown that by modifying surface electric potential of PMMA using UV irradiation with exposures from 5 to 120 minutes, it is possible to obtain hydrophilic or hydrophobic surface properties, and decrease or increase in contact angle respectively.
3. It has been found that UV exposure influences polar and dispersive components of PMMA surface energy. After 45 minutes of UV irradiation, the polar component has the greatest impact on wettability. After 15 minutes of UV irradiation, the dispersive component has the greatest impact on wettability.

4. It has been shown that the induced changes of PMMA wettability are stable during 20 days after UV exposure if PMMA is stored in a closed glass container at 23 ± 3 °C temperature and 20–55 % moisture.
5. It has been found that UV exposure of PMMA longer than 60 minutes decreases microorganism adhesion to PMMA surface that will influence the interaction of the material with microorganisms.
6. It has been shown that 5minute long irradiation of PMMA reduces the surface electric potential of TiO₂ coating that is afterward deposited on PMMA (“*Atomic Layer Deposition*”).

Theses to Defend

1. It is possible to regulate PMMA wettability from hydrophilic to hydrophobic by using UV radiation in the wavelength range 200–400 nm under atmospheric conditions (mercury-xenon UV source, 200 W).
2. Surface electric potential and surface energy of PMMA depend non-linearly on UV exposure in the exposure range 0–120 minutes: decreasing after 5 and 120 minutes of UV exposure and increasing after 45 minutes of the exposure in a wavelike pattern.
3. Changes in PMMA wettability induced by UV radiation are stable for 20 days after UV exposure if PMMA is stored in a closed glass container at 23 ± 3 °C temperature and 20–55 % moisture.
4. UV exposure of PMMA longer than 120 minutes influences interaction of PMMA with microorganisms (the yeast was used as a model).

Practical Significance

1. The developed method of PMMA wettability regulation that uses UV irradiation will be used to extend exploitation time of eye prostheses. Wettability changes are stable at least for 20 days.
2. By using UV radiation, it is possible to adjust PMMA wettability from hydrophilic to hydrophobic.
3. UV-irradiation of PMMA influences interaction of the material with microorganisms. This property can be used to regulate biocompatibility of PMMA eye prostheses.
4. By regulating surface electric potential of PMMA using UV radiation, it is possible to adjust the surface electric potential of TiO₂ nanocoating afterward deposited on PMMA. For example, this can be useful for catalysis processes.
5. Exploitation costs of the developed method for one prosthesis are ~4 times less than the traditional approach.

Approbation of the Thesis

The following bachelor’s and master’s theses were developed on the research topic supervised by the author:

- Aļina Grīva. Possibilities for regulation of PMMA surface wettability. (Original title: *PMMA virsmas slapināšanas regulēšanas iespējas*), the Bachelor’s Thesis was defended in 2012.
- Evita Trušeļe. Stability of PMMA surface wettability regulated by UV in time. (Original title: *Ar UV starojumu regulētas PMMA virsmas slapināšanas īpašību stabilitāte laikā*), the Bachelor’s Thesis was defended in 2012.

- Arta Akurātere. PMMA wettability depending on the UV wavelength. (Original title: *PMMA slapināšanas īpašība atkarībā no UV starojuma viļņa garuma*), the Bachelor's Thesis was defended in 2013.
- Ansis Ventiņš. PMMA wettability in dependence on the UV wavelength in oxygen-less environment. (Original title: *PMMA slapināšanas īpašības atkarībā no UV starojuma bezskābekļa vidē*), the Bachelor's Thesis was defended in 2013.
- Aļina Grīva. PMMA surface energy depending on outer environment. (Original title: *PMMA materiāla virsmas enerģijas atkarība no ārējiem apstākļiem*), the Master's Thesis was defended in 2014.

Publications

The main results of the thesis are published (listed by year of publishing, authors indicated in alphabetic order):

I. Publication in the scientific journal indexed by SCOPUS database:

1. Dekhtyar Y., Lancere L., Polyaka N., Sudnikovich A., Tyulkin F., Valters V. PMMA wettability caused by ultraviolet radiation// *Advanced Materials Research* 222 – 2011 – pp.322–325.

II. Conference proceedings indexed by SCOPUS database:

1. Dekhtyar Yu., Lancere L. UV Radiation Influence on Prosthetic PMMA Surface Charge// *IFMBE (International Federation for Medical and Biological Engineering) Proceedings* 39 – 2013 – pp. 2302–2304.
2. Andersons B., Dekhtyar Yu., Griva A., Lancere L., Sansonetti E. Wettability of the PMMA surface caused by its polarization due to UV radiation// *Proceedings of 2012 21st IEEE Int. Symp. on Applications of Ferroelectrics held jointly with 11th IEEE European Conference on the Applications of Polar Dielectrics and IEEE PFM, ISAF/ECAPD/PFM 2012 – 2012 – pp.146–148.*
3. Dekhtyar Yu., Lancere L., Polyaka N., Sudnikovich A., Tyulkin F., Valters V. Surface properties of ocular prostheses material change under UV influence// *IFMBE Proceedings* 37 – 2011 – pp.1047–1049.

III. Full-text conference proceedings:

1. Dekhtyar Yu., Lancere L. Surface wettability regulation for prosthetic applications// *Biomedical Engineering – 2011. Proceedings of International conference, Kaunas University of Technology – 2011 – pp.215–218.*
2. Dekhtyar Yu., Lancere L., Polyaka N., Sudnikovich A., Tyulkin F. Ultra Violet radiation regulates wettability of prosthetic PMMA// *International Conference on Nanotechnologies and Biomedical Engineering Proceedings – 2011 - pp.255–256.*
3. Dekhtyar Yu., Lancere L., Polyaka N., Sudnikovich A., Tyulkin F., Valters V. Ultraviolet radiation influences wettability and biological properties of PMMA surface// *Biomedical Engineering conference, Kaunas, Lithuania – 2009 – pp.69–71.*
4. Dehtjars, J., Lancere L., Poļaka, N., Rapoport, A., Rusakova, T., Soudnikovich, A., Valters, V. Wettability and Bioproperties of PMMA Used for Eye Prostheses in Dependence on Ultraviolet Radiation// *Biomedical Engineering: Proceedings of the 13th International Conference, Lietuva – 2009 – pp.179–182.*

IV. Peer-reviewed conference abstracts:

1. Dekhtyar Yu., Griva A., Lancere L. Commercial and prosthetic PMMA surface wettability regulation// FMNT Book of Abstracts - Riga, Latvia – 2011 – p.76.
2. Dehtjars J., Lancere L. *UV ietekme uz PMMA virsmas lādīņu*// Apvienotais Pasaules latviešu zinātnieku III kongress un Letonikas IV kongress „Zinātne, sabiedrība un nacionālā identitāte” - Rīga, Latvija – 2011 – 86. lpp.
3. Dekhtyar Yu., Lancere L., Polyaka N., Sudnikovich A., Tyulkin F. UV treatment for PMMA ocular prosthesis// 9th ScanBalt Forum 2010 Proceedings - Tallinn, Estonia – 2010 – p. 100.1

1. REVIEW OF LITERATURE

1.1. Application of PMMA in Ocular Prosthetics and Problems Related to Surface Wettability

PMMA is a thermoplastic, colourless polymer that is transparent to visible and UV radiation and has chemical, mechanical, dielectric and optical properties due to which it is used in ocular prosthetics. The structural formula of PMMA is shown in Fig. 1.1. The material is biocompatible which is the most important property in medicine meaning that the material can get into contact with body tissue and blood [2] [39]. The material is an atactic acrylate that can be processed repeatedly (heated and cooled) without degradation [21].

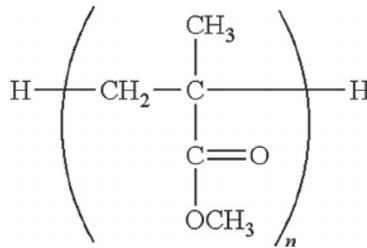


Fig. 1.1. Structural formula of PMMA [54].

One of the widest applications of PMMA in medicine is the manufacturing of artificial bones and prostheses such as dental and jaw implants, facial prostheses (intra-ocular and orbital – Fig. 1.2), nose and cranial prostheses, nasal stents and others [64]. Good optical properties of the material allow to use it for fabrication of implantable ophthalmic lenses and hard contact lenses.

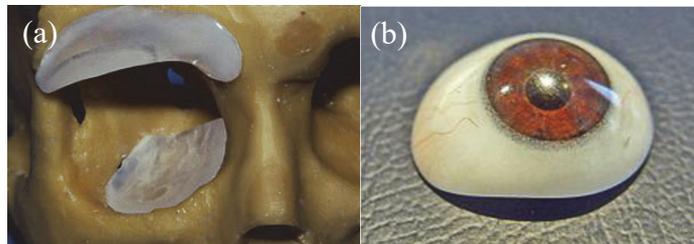


Fig. 1.2. PMMA facial (a) and ocular implants (b) [32] [35].

Two materials are usually used for fabrication of ocular implants – PMMA and cryolite glass. However, PMMA prostheses have superior mechanical properties so they are used for a majority of patients.

Both materials require maintenance inspection and treatment (polishing) once per year. Based on opinions of prosthetists, it was concluded that PMMA surface wettability deteriorates over time resulting in friction increase between the prosthesis and eye lid and leading to mechanical degradation of PMMA surface. The patients experience discomfort, frequent blinking results in corneal abrasion and, consequently, inflammation. To avoid these problems, the prosthesis must be replaced every three years. PMMA wettability depends on surface energy. The surface energy can be modified by inducing electron transitions to the surface localized states and thus changing the surface charge density. Therefore, the wettability of PMMA can be regulated.

Surface energy also defines adhesion or repulsion of microorganisms to a surface. This influences significantly biocompatibility of the prosthesis and interaction with the environment. Wettability is also a decisive comfort factor for patients who use PMMA lenses [71]. The patients with intraocular lenses are blinking around 11 000 times per 24 hours, therefore it is necessary to maintain appropriate wettability throughout the day. Even special solutions for storage of contact lenses and eye drops that act for a short period of time do not help to solve this problem. To address this problem, PMMA surface can be modified and its properties can be improved using physical or chemical methods that increase surface energy and make the surface more hydrophilic [63]. Problems of PMMA surface wettability are important not only in medicine. For example, PMMA substrates are used in microelectronics, other components are bonded to the substrate, and therefore good adhesion between the surfaces is particularly important. PMMA surface is characterized by poor adhesion of water (hydrophobicity) and low values of surface energy. Therefore, PMMA surface needs to be modified in order to improve its hydrophilic properties.

1.2. Existing Methods of Wettability Regulation

The following methods are used to modify the surface of polymers [32][68]

1. Physical methods:
 - 1.1. Corona discharge;
 - 1.2. Treatment with gases (plasma, etching, oxidation, and others);
 - 1.3. Treatment with electromagnetic radiation (UV, lasers, ionizing radiation (e.g. X-ray, gamma), and others).
2. Chemical Methods:
 - 2.1. Coatings;
 - 2.2. Treatment with chemical solutions, active substances;
 - 2.3. Desorption of chemically active groups to the surface, and others.
3. Physico-chemical methods:
 - 3.1. Microlithography;
 - 3.2. Grafting, and others.
4. Mechanical methods:
 - 4.1. Polishing;
 - 4.2. Abrasive blasting;
 - 4.3. Micromanipulation techniques, using, for example, atomic force microscopy, and others.
5. Biological methods:
 - 5.1. Physical adsorption of biomolecules;
 - 5.2. Chemical adsorption of biomolecules, and others.

Most of the methods are too complicated to apply them in home conditions (corona discharge, treatment with plasma, irradiation in vacuum, all chemical and biological methods). Mechanical treatment of the surface is not used in ocular prosthetics because it changes surface roughness. In general, the aim of all methods is to form or attach functional groups that change surface wettability. In ocular prosthetics PMMA surface requires polar groups to become more hydrophilic. Literature data about physical and chemical methods of surface wettability regulation are summarized in Table 1.1.

Table 1.1.

Comparison of the most common surface modification methods [9], [31], [63], [64], [65], [68],[71], [82].

No.	Method	Processing method	Contact angle, °
1		Untreated PMMA	81±2
2	Chemical	Treatment with 3M H ₂ SO ₄	77±3
3		Treatment with 3M H ₂ SO ₄ 2 times	77±3
4		Treatment with 1M NaOH (water solution)	80±2
5		Treatment with 1M NaOH (hydroalcoholic solution)	65±3
6		Treatment with lithium aluminium hydride	37,2±0,3
7	Physical	Treatment with O ₂ plasma for 1 min	40±2
8		Treatment with O ₂ plasma for 1.5 min	37,2±3
9		Treatment with UV radiation for 15 min (250–350 nm)	73±3
10		Treatment with UV radiation for 60 min (250–350 nm)	78±2
11		Treatment with CO ₂ laser, 193 nm, 250 shots	65±3

The values of contact angles listed in Table 1.1 show that the most effective surface modification method is treatment with plasma. The changes of the contact angle are greater than 50 %, the hydrophilic surface is obtained. However, plasma influences not only the chemical composition of the surface but also surface morphology. Defects are formed on the surface as seen in Fig. 1.3, therefore, the method cannot be applied in ocular prosthetics.

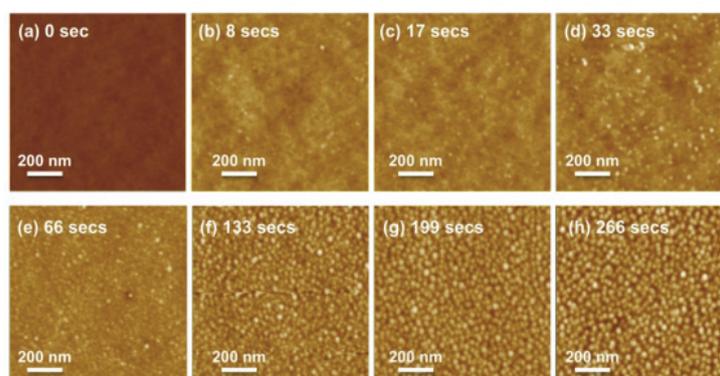


Fig. 1.3. PMMA surface morphology after treatment with O₂ plasma [9].

Physical and chemical surface modification methods have their advantages and disadvantages. For example, chemically active substances and chemical surface treatment are complicated and expensive, specialists with specific knowledge are required. Besides, harmful chemical compounds are formed, changes occur not only on the surface of the material but also in its depth, relaxation time of the contact angle changes is shorter than exploitation time of the prosthesis. Plasma and laser treatment also increase the surface roughness of the material, as well as the methods are quite complex. This makes them unsuitable for independent use by patients in home conditions.

Conclusions. By exposing the surface to UV light (200–400 nm wavelengths), it is possible to regulate the surface electric potential and, correspondingly, surface energy and wettability. At the same time, an atomic/molecular composition of the material remains

unchanged. UV-irradiation of the material in room conditions rather than in vacuum allows to realize the method which can be implemented by a user of the prosthesis in home conditions. By performing UV-irradiation under atmospheric conditions rather than in vacuum it is possible to obtain the method which can be implemented by a prosthetist in its office.

1.3. Modification of Surface Properties Using UV Radiation

The absorbance of radiation is more likely to occur when the energy of a photon is equal to the difference between the energy of quantum states (ground and excited quantum states). Light with a wavelength λ is absorbed only if:

$$\lambda = \frac{hc}{E_2 - E_1}, \quad (1.1) [1]$$

where E_1 – the energy level of a molecule before absorption,
 E_2 – the energy level of a molecule resulting from absorption,
 h – the Plank constant, $h \approx 6.626 \cdot 10^{-34}$ J·s,
 c – the speed of light in vacuum, $c \approx 3 \cdot 10^8$ m/s.

The bandgap of PMMA is ~ 4 eV [36]. Therefore, the UV energy greater than 4 eV is required to transfer an electron from ground to excited state. UV radiation can cause both electron transitions (Fig. 1.4) and changes at the molecular level (Fig. 1.5) depending on the wavelength and received exposure. According to the Landau theory [72], electrons are excited from to the surface where 1) the electrons can fall to free surface states, or 2) relax back to the valence band located in the volume of the material. In the case of ocular prostheses only surface properties have to be modified, therefore, 200–400 nm or 6.2–3.1 eV UV light was selected that allows to detect possible transitions of electrons between surface states. The described processes influence surface wettability and surface energy as described in Section 1.4.

Possible transitions of electrons, as well as possible structural changes of PMMA under influence of 200–400 nm UV, are described below.

Molecular orbitals have σ and π type bonds, both types of the orbitals can be bonding and antibonding, n – the functional group with a lone pair of electrons. Light absorption results in transition from the bonding σ or π orbital to the antibonding σ^* or π^* one (σ - σ^* or π - π^* transitions, Fig. 1.4).

In the ground state σ , π and n orbitals are occupied with electrons, σ^* and π^* orbitals are empty. Light absorption results in transitions of electrons from occupied to empty orbitals. π - π^* transitions occur in aromatic molecules, n - σ^* and n - π^* transitions in molecules containing N, O and S atoms. By exposing PMMA to UV in the range of 200-400 nm, n - σ^* (150–200 nm), n - π^* (around 300 nm) and π - π^* transitions can occur, consequently, C-O and C = O bonds can be excited.

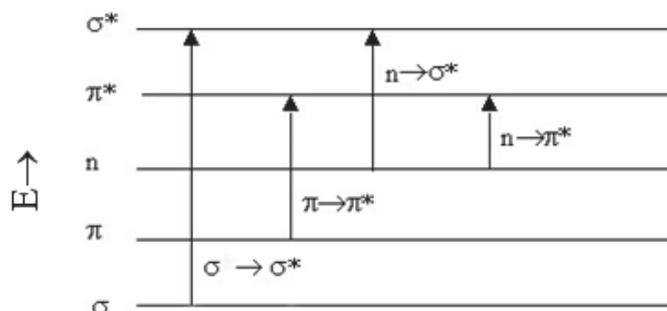


Fig. 1.4. Energy levels of a molecule and transitions of electrons.

Carbonyl groups (the chromophore group of PMMA) easily enter excited state after irradiation with 270–330 nm UV. After that Norrish type I or II photochemical processes take place (Fig. 1.5) [81]

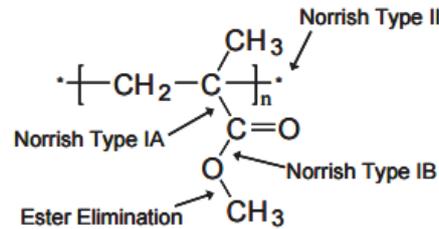


Fig. 1.5. Photochemical processes taking place in PMMA [12].

Light with 400 nm and 300 nm wavelength has 300 kJ/mol and 390 kJ/mol energy respectively. For example, the energy of C–C and C–H bonds is equal to 420 kJ/mol and 340 kJ/mol, sometimes the energy of these bonds is even less in PMMA which depends on the presence of unsaturated compound in the molecule.

It means that UV light, and sometimes the visible light as well, has sufficient energy to break chemical bonds. The shorter the wavelength the more efficient bond destruction process.

When PMMA surface is exposed to UV, photochemical reactions take place on the surface due to the presence of UV-absorbing chromophore group and dopants (additives and others compound added by a manufacturer of the material). Upon the absorption of UV, breaking of the main polymer chain of PMMA can occur and free radicals can form.

The influence of light on polymers takes place in the following order:

1. Absorption of the light photon.
2. Relaxation of the excited state.
3. Primary photochemical reactions that result from the excited state of electrons.
4. Secondary dark and photochemical reactions that consume microradicals and other substances that were formed in the primary reaction.

The absorbance of radiation is important in the first stage of photodestruction. The intensity of UV light decays rapidly as the light passes through the depth of the polymer, therefore chemical reactions mostly occur on the surface. The first stage of the photodestruction process is homolytic bond fission and formation of free radicals. These radicals interact with the ambient oxygen leading to effective oxidation processes [43] [59] [79] [81]. When the excitation of the bonds (photochemical processes) occur, transitions of electrons (can be detected by ultraviolet–visible (UV-Vis) spectrophotometry) or changes in charge density distribution (can be detected by infrared (IR) spectrometry) take place [49].

1.4. Surface Energy and Wettability

Wettability is characterized by adhesion and cohesion forces (Fig. 1.6) that act on the interface between the substrate (PMMA) and the liquid. When adhesion forces are reduced and cohesion forces are increased, eye prosthesis wettability worsens. This means that the contact angle increases and becomes greater than 90°. The adhesion influences friction force for surfaces that are in contact, for example the eye lid and PMMA prosthesis. The friction is minimal for surfaces with high adhesion of the liquid.

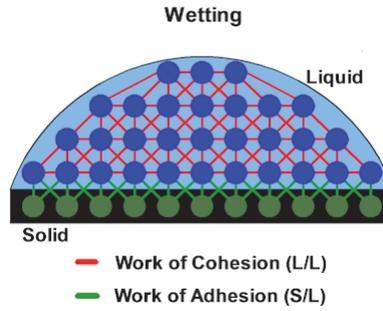


Fig. 1.6. Schematic illustration of cohesion and adhesion forces acting at the interface between solid and liquid.

The adhesion is determined by molecular interactions in surface layers and is characterized with the work of adhesion which must be done to separate two adjacent surfaces. The work of adhesion can be calculated using Young-Dupré equation (Fig. 1.7):

$$W^a = 2\Phi(\gamma_1\gamma_2)^{1/2} = \gamma_1(1 + \cos\theta), \quad (1.2)$$

where γ_1 – the liquid/vapor interfacial energy, mN/m;
 γ_2 – the solid/vapor interfacial energy, mN/m;
 γ_{12} – the solid/liquid interfacial energy, mN/m;
 θ – the contact angle, ° [76];
 Φ – the interaction parameter, $0.5 < \Phi < 1.15$, [22], [30].

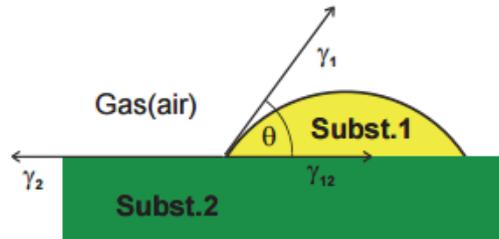


Fig. 1.7. Schematic illustration of a liquid on a solid surface with energy vectors γ and contact angle θ .

Φ is the function of the molar volumes of the substances 1 and 2:

$$\Phi = \frac{4r_1r_2}{(r_1 + r_2)^2} \cdot \frac{\sum A_{12}}{(\sum A_{11} + \sum A_{22})^{1/2}}, \quad (1.3)$$

where r_1, r_2 – the molecular radii,
 $\sum A$ – the sum of all kinds of intermolecular forces (dispersive, polar, Van der Waals, etc.) [30].

The interaction coefficient can also be expressed by Equation (1.4), its simplified visualization is shown in Fig. 1.8. Expanded explanation of the Equation can be found in Section 1.4 of the Doctoral thesis [74].

$$\Phi = \Phi_A + \Phi_B, \quad (1.4)$$

where Φ_A – Van der Waals attraction potential, kT;
 Φ_B – electrostatic repulsion potential, kT.

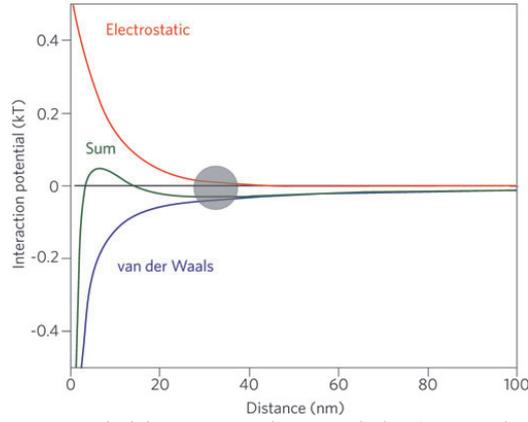


Fig. 1.8. Interaction potential between the particle (grey circle) and the surface.

The surface energy consists of the polar and dispersive components (Young Equation (1.5) written using OWRK (Owens, Wendt, Rabel and Kaelble) method [38]):

$$\sqrt{\gamma_{sv}^d \gamma_{lv}^d} + \sqrt{\gamma_{sv}^p \gamma_{lv}^p} = 0.5\gamma_{lv} (1 + \cos \theta_\gamma), \quad (1.5)$$

- where γ^d – the dispersive component of the energy, mN/m;
 γ^p – the polar component of the energy, mN/m;
 θ_γ – Young contact angle, °;
the indices sv – the solid/vapor interface;
 lv – the liquid/vapor interface;
 sl – the solid/liquid interface.

When a molecule of the surface leaves its optimum state, meaning that the molecule is no longer in contact with the other molecules, it gains the internal energy which is based on imbalance of intermolecular forces. The described component of the energy is called the dispersive component.

For the remaining part of the surface energy the electrostatic forces are responsible – the polar component [37] which can be regulated by adjusting surface electric potential. The Doctoral thesis is focused on this study.

2. EXPERIMENTAL PART

This Section describes the implementation of the aim of the Doctoral thesis, namely, the development of the method for PMMA wettability regulation using UV.

In Sections 2.1–2.4 the research implemented according to Task 1 is described, in Section 2.5 according to Task 2.

2.1. Research Methodology

In order to develop the method of wettability regulation that could be applied by the user of eye prosthesis in home condition, the research sequence was planned as well as the noncontact method, i.e. non-ionizing UV radiation was selected for charging of a material surface.

To determine experimentally the possibility to implement UV, the first step was a selection of the most suitable material, irradiation method and conditions, as well as the selection of appropriate methods for characterization of the material surface. The methods had to be non-destructive and sensitive enough to detect changes in surface charge.

After the theoretical planning, environmental conditions for PMMA irradiation were determined experimentally such as a presence of atmospheric air during the irradiation, influence of humidity and temperature on wettability. In addition, it was important to determine stable conditions of PMMA storage throughout the research. In order to provide comparable conditions for wettability studies, all samples were irradiated using the unified approach: PMMA material (the main parameters 1.19 g/cm³ density, 92 % light transparency, and 5 mm thickness) was exposed to UV in 200–400 nm range under room conditions with exposures 5–120 minutes (described in detail in Section 2.3).

Influence of UV on PMMA surface electric potential, wettability, chemical composition and morphology was studied experimentally, based on the determined parameters of humidity, temperature, storage conditions and selected surface characterization methods such as photoelectron emission spectroscopy (measurements of surface electric potential), axisymmetric drop shape analysis method (contact angle, wettability), atomic force microscopy.

For all methods, the surface of a non-irradiated sample was measured at first. Then the irradiation of the sample followed and surface measurements were repeated. After that the same sample was irradiated and measured again, and the process was repeated several times (Fig. 2.1). This means that the sample was receiving cumulative dose of UV irradiation. The results obtained for the non-irradiated and irradiated samples were compared.

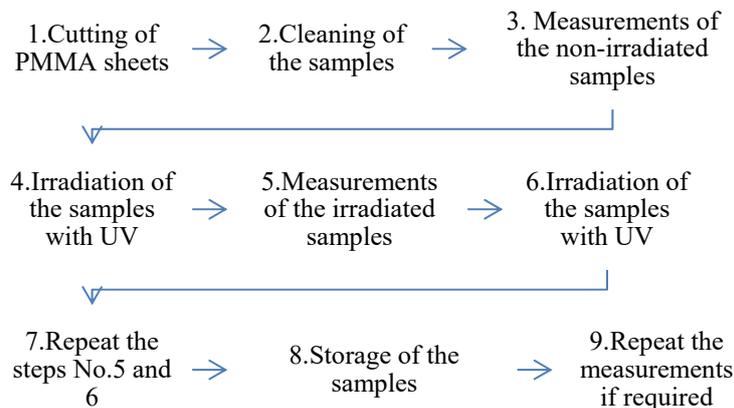


Fig. 2.1. General scheme of PMMA surface modification and measurements for all surface characterization methods.

Based on the obtained experimental results, the method of PMMA wettability regulation was developed, described in Section 4.

In order to appropiate the method in biological environment, experiments on yeast cell adhesion to the UV-irradiated PMMA substrate were performed. TiO₂ coating is widely used in medicine due to its high mechanical durability. The approbation of the method was performed by depositing TiO₂ coating onto UV-irradiated PMMA.

2.2. Preparation of PMMA Samples

The samples were cut from PMMA sheets (Fig. 2.2 (a)). PMMA sheets produced by “NUDEC” company were used since the UV-Vis spectrum of this material corresponds to the theoretical spectrum of PMMA [83] and to PMMA used in ocular prosthetics.

The main parameters of the material according to ISO 1183, ASTM D-1003, ASTM D-52 standards [55]: density 1.20 g/cm³, light transmittance 92%, thickness 3.00±0.05 mm, refractive index 1.489. The sheets were cut into 1 cm x 1 cm samples. The size of samples was adjusted if demanded by the measurement method used.

To protect the material from dust, scratches and other damage, it is sold covered with a protective tape. To clean the samples from the residues of the protective tape and other contaminants, the samples were ultrasonicated for 5 minutes in a distilled water using “Bandelin Sonorex RK3” ultrasonic bath. The distilled water was used because PMMA surface degrades when treated with alcohol, acetone and other fat solvents [3]. After ultrasonication the samples were cleaned with a lint-free cloth and blown dry with compressed air.

To determine whether additional mechanical treatment of PMMA surface is required (polishing), surface roughness was measured using “NT-MDT Solver PRO-47” atomic force microscope in a tapping mode (Fig. 2.2).

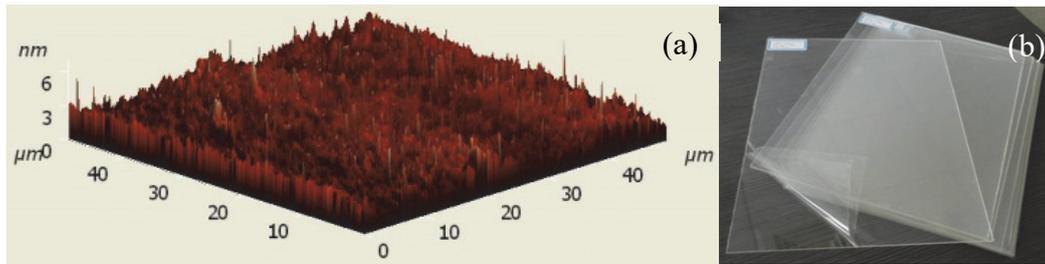


Fig. 2.2. Surface roughness of the non-irradiated PMMA measured by AFM(a); PMMA Nudac sheets before cutting (b) [32], [35].

It was found that the surface roughness was 2 ± 1 nm. This means that additional polishing of the samples is not required because the surface roughness of PMMA applied for fabrication of intraocular lenses is 7.0 ± 0.6 nm [47].

2.3. Irradiation of PMMA with UV Radiation

2.3.1. Irradiation Technique

During the development of the irradiation method, optimal distance between the sample surface and UV light source was determined that does not cause thermal degradation of PMMA surface. Also, the position of the sample within the light distribution field was determined, and the irradiation time was corrected taking into account UV lamp operating time. The correction was made using data from UV lamp technical datasheet.

Hamamatsu Lightningcure L8222-04 mercury-xenon UV lamp with A2873 light guide was used. Mercury-xenon lamp combines the best characteristics of xenon and high-pressure mercury lamps – the spectral distribution includes a continuous spectrum from ultraviolet to infrared (Fig. 2.4) [27].

By placing the sample at different distances from the UV light guide output (10–65 cm) in the vertical position, the distance 40 cm was selected. This distance does not cause thermal degradation of PMMA and it is possible to position the whole area of the sample within the UV incidence area (Fig. 2.3).

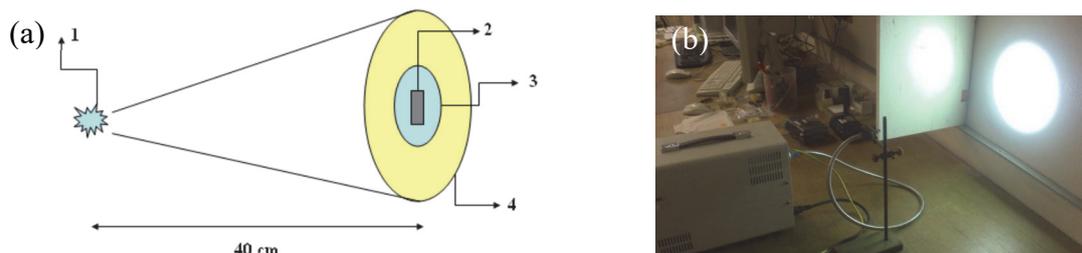


Fig. 2.3. PMMA irradiation scheme (a) theoretical, (b) experimental: 1 – UV source, 2 – firmly positioned PMMA sample, 3 – UV light incidence area, 4 – visible light incidence area.

2.3.2. Optimization of UV Exposure

Intensity and distribution of UV radiation on the irradiated surface depend on the distance from the light guide output. The larger the distance the lower the intensity and the larger light incidence area (Fig. 2.4).

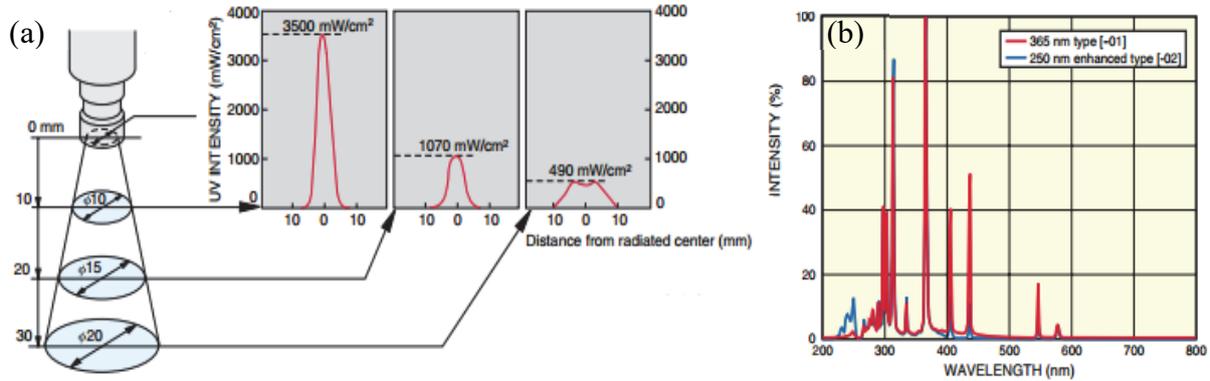


Fig. 2.4. (a) Distribution of UV intensity on the sample surface depending on the distance from the light guide output; (b) spectral distribution of the UV lamp [27].

UV light has the maximum intensity at 365 nm. The intensity at 365 nm is equal to $I_0 = 35\,000\text{ W/m}^2$ at 10 mm distance from the light guide output (Fig.2.4). The intensity decreases when operating time of the lamp increases (Fig. 2.5) [27].

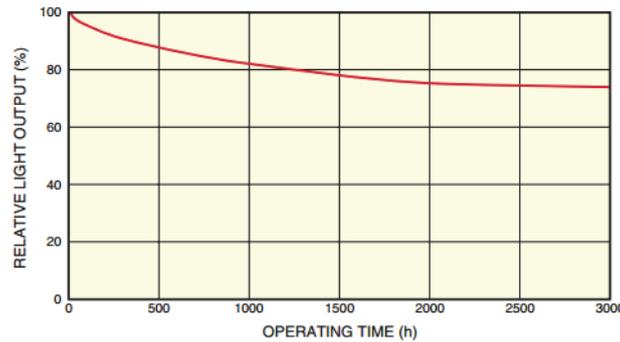


Fig. 2.5. UV intensity at 365 nm depending on UV lamp operating time.

If UV light intensity is constant during the irradiation, the UV dose received by the sample can be calculated as the product of light intensity and irradiation time [12]:

$$\text{Dose} = I \cdot t, \text{ J/m}^2, \quad (2.1)$$

where I – the intensity of UV radiation, W/m^2 ;
 t – the irradiation time, sec.

Taking into account the decrease in UV intensity over time (Fig. 2.5), irradiation time has to be corrected so that all samples with the same nominal irradiation time would receive the same dose:

$$t_c = t_{100\%} + t_{100\%} \cdot \frac{I_{100\%} - I_c}{100\%} \quad (2.2)$$

where t_c – corrected irradiation time, min;
 $t_{100\%}$ – nominal irradiation time at 100% of UV intensity, min;
 $I_{100\%}$ - 100% UV intensity, %;
 I_c – reduced UV intensity (the data from Fig. 2.5), %.

Table 2.1 summarizes corrected exposure time that was used for PMMA irradiation depending on the decrease in UV lamp intensity.

Table 2.1

Dependence of PMMA irradiation time on intensity of UV lamp

Percentage from maximum UV intensity, %	100	95	90	85	80	75	70
UV exposure, min	Nominal time	Corrected time					
	120	126	133	141	150	160	171
	45	47	50	53	56	60	64
	5	5	6	6	6	7	7

UV intensity incident on the sample surface depending on the distance from the light guide output was calculated using the data from Fig. 2.5 and the law of inverse squares:

$$I \propto \frac{1}{x^2}, \quad (2.3)$$

where x – the distance from the light guide output, m.

Taking into account UV lamp operating time, it was calculated that the maximum UV intensity was around 29167 W/m² (at 10 mm distance from the light guide output). The graph in Fig. 2.6 shows the calculated dependence of UV intensity on the distance from the light guide output.

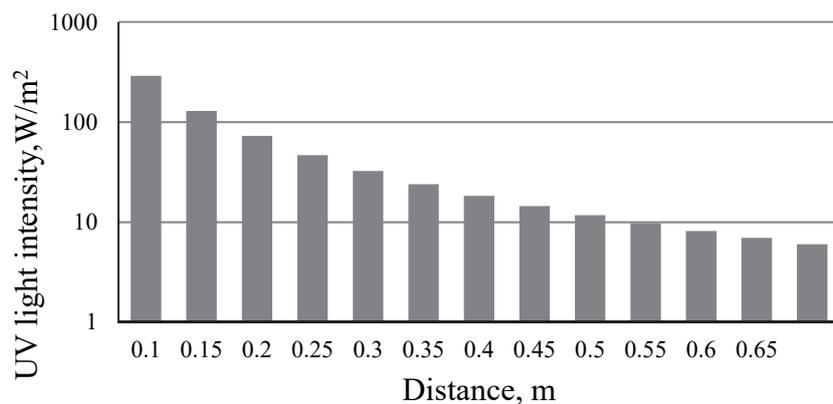


Fig. 2.6. UV intensity depending on the distance between the irradiated surface and the light guide output.

As the result of the studies described above, it was found that the irradiation distance has to be 40 cm, and the calculated maximum intensity of UV radiation incident on the sample surface is 17.5 W/m². This distance was selected as it does not result in thermal degradation of the sample and it is possible to position the whole sample within the UV light incidence area. In experimental research, the UV exposure has to be corrected using data from Table 2.1 according to operating hours of the UV lamp. For example, if the UV light intensity according to the lamp operating time is 85 %, it is necessary to irradiate the sample 53 minutes rather than 45 minutes as in the case of 100 % lamp intensity.

2.4. PMMA Surface Characterization Methods

The surface characterization methods [10] were analysed in order to identify the methods that describe changes in surface properties as well as methods that can detect changes in chemical composition generated under influence of UV.

The most significant criterion for selection of the methods is an ability of a method to register minimum changes in PMMA surface because UV radiation in the range of 200–400 nm has little energy (<6.2 eV) under room conditions in order to create defects in a material with high probability.

Taking into account the ability of UV radiation in a 200–400 nm range to cause changes in the distribution of the centers related to surface electric potential, as well as in chemical bonds and surface morphology, the following methods were selected (listed in priority order) in order to study the influence of UV on PMMA surface:

1. Photoelectron emission spectroscopy – the method that has high sensitivity to study changes in surface electric potential. The wettability of eye prosthesis surface is directly related to surface potential. When the wettability worsens (the surface becomes more hydrophobic), the patient has complications [71].
2. Axisymmetric drop shape analysis to study changes in wettability. The method has high sensitivity to changes in wettability (contact angle) and surface energy.
3. UV-Vis spectrophotometry to study changes in chemical composition. The method characterizes transition of electrons induced by UV.
4. Fourier transform infrared spectroscopy, attenuated total reflection technique (FTIR-ATR), to detect changes in chemical composition. The method characterizes possible induced vibration energies of molecules, excited molecular bonds.
5. X-ray photoelectron spectroscopy (XPS) to study changes in chemical composition.
6. Atomic force microscopy (AFM) to detect changes in surface roughness at micro and nano scale. If roughness of PMMA surface increases as the result of the irradiation, the method cannot be used for eye prostheses.
7. Optical microscopy to study interaction with microorganisms that characterizes adhesion of microorganisms to PMMA surface.

In order to study influence of environmental conditions on wettability changes, the methods 1–3 are used.

2.5. Influence of Environmental Conditions on Wettability Regulation

UV radiation together with the environmental factors such as temperature, humidity, and increased content of oxygen can accelerate destruction and aging of polymers. It is possible that for certain values of humidity and temperature the processes, including the influence of UV radiation, occur at a higher rate. Therefore, temperature and humidity are important for the PMMA surface modification process [44].

2.5.1. Temperature, Humidity and Storage Conditions

At elevated temperatures molecular mobility increases resulting in increased diffusion of oxygen and formation of free radicals. The reactions may occur which do not take place at lower temperatures [15]. During storage and exploitation of polymers changes in physical properties occur gradually under influence of environmental conditions – flexibility and strength reduce, the material becomes brittle. The aging process is associated with significant changes in the polymer structure. Under the influence of moisture splitting of molecules takes place [41].

The results obtained in Fig. 2.7 demonstrate that humidity influences wettability depending on the exposure time. The greatest changes in the contact angle appear after 45 minutes of the irradiation at the relative humidity of 20 % and room temperature. Taking the scattering into account, the recommended humidity is 20–55 % and exposure 45 minutes, because the surface becomes more hydrophilic under these conditions which are desirable for ocular prostheses.

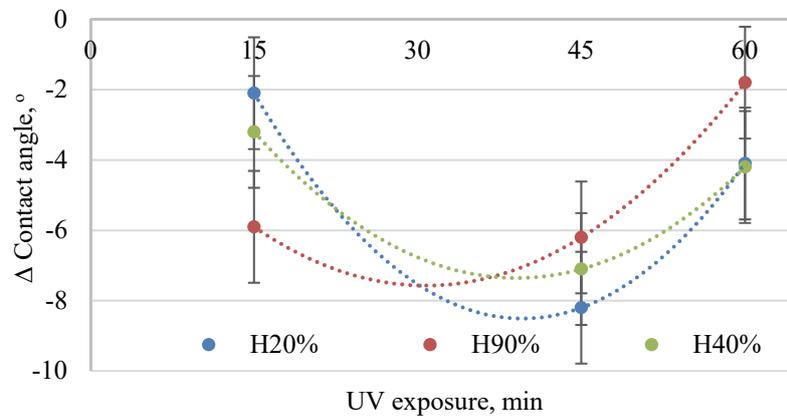


Fig. 2.7. Influence of relative humidity on changes in contact angle after 15, 45 and 60 minutes of UV exposure at 23 °C.

Fig. 2.8 shows how temperature influences wettability depending on UV exposure. Taking the scattering into account, the recommended temperature is 23 ± 3 °C and 45 minutes of UV exposure. The data about the influence of temperature on the contact angle at 80 and 90 % relative humidity can be found in the Doctoral Thesis.

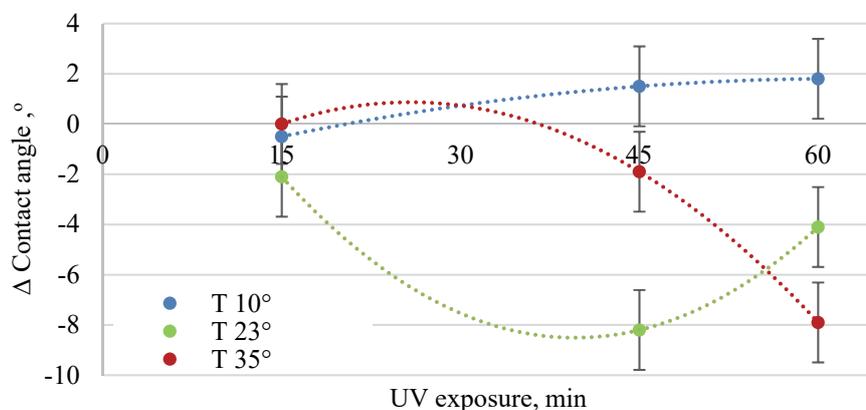


Fig. 2.8. Influence of temperature on contact angle changes after 15, 45 and 60 minutes of UV exposure at 40 % relative humidity.

The influence of storage container on PMMA wettability was studied. Changes in contact angle were compared between samples that were stored under atmospheric conditions in an unclosed environment, filter paper, plastic and glass Petri dish (Fig. 2.9). The detailed information can be found in the Doctoral Thesis.

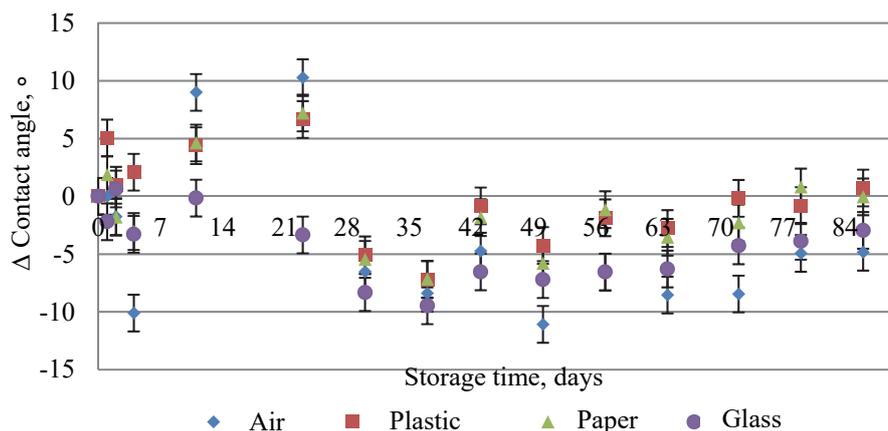


Fig. 2.9. Changes of contact angle of PMMA exposed to UV 45 minutes depending on the storage container.

The most stable behaviour of the contact angle is observed when PMMA sample is stored in the glass container for 21 days. After 20 days repeated irradiation must be performed.

2.5.2. Influence of Atmospheric Air

When oxygen is present in the environment where PMMA is irradiated, breaking of chemical bonds as the result of photodestruction can take place, free radicals can form, and the reactions can vary greatly in the presence of oxygen [7].

During photooxidation of PMMA, OH group which has hydrophilic properties can be formed on the surface. This changes polymer surface energy. The concentration of other side groups on the polymer chain can change as well [7].

The measurements were made after PMMA irradiation in vacuum and in atmospheric air (in room conditions). To obtain comparable results, the irradiation in vacuum and air was performed using the same Hamamatsu UV source and equal UV exposures. One sample was placed in vacuum, the second was in room conditions. Wettability changed only when the irradiation was performed in the air (Fig. 2.10). In vacuum polymer reactions could take place only using different mechanisms – without formation of the OH or other polar group. It is seen that the contact angle does not change after irradiation with UV (200–400 nm) in the vacuum.

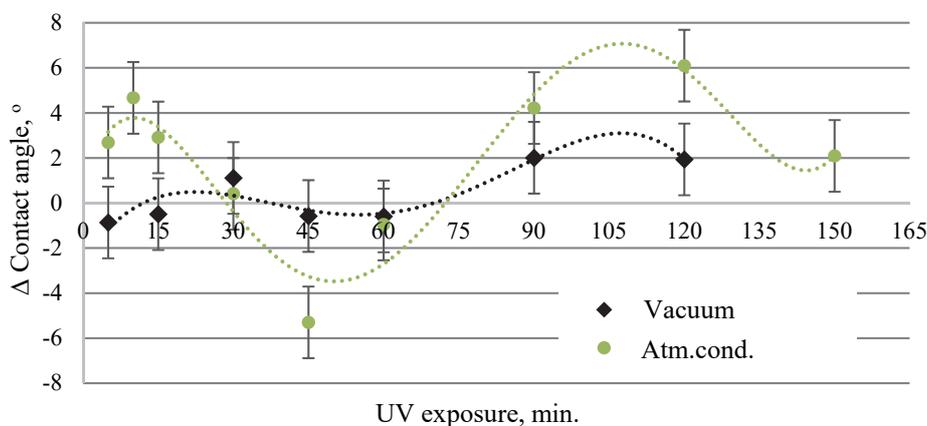


Fig. 2.10. Changes in contact angle depending on UV exposure in room conditions and in the vacuum.

Fig. 2.10 demonstrates that the changes in the contact angle are different after irradiation in the vacuum and in the air. As the result of the experiment, it was concluded that further research has to be carried out under room conditions since the contact angle changes in the vacuum could not be considered significant (the results are constant within the error bars). The room conditions have to be constant (23 ± 3 °C temperature and 20–55 % relative humidity).

3. RESULTS. INFLUENCE OF UV ON PMMA SURFACE PROPERTIES

In accordance with the third task, the influence of UV on PMMA surface was determined experimentally.

Task No.3: To study experimentally the influence of UV on electric potential, chemical composition and morphology of PMMA surface that influences wettability.

For all surface characterization methods described in Sections 3.1, 3.2 and 4.1, except the XPS method, changes Δx in PMMA surface properties before and after UV irradiation was calculated as:

$$\Delta x = x_i - x_0, \quad (3.1)$$

where x_i – the measurement of PMMA surface after UV irradiation;
 x_0 – the measurement of the non-irradiated PMMA.

3.1. Photoelectron Emission from PMMA, Wettability and Surface Energy

Fig. 3.1 shows how the work function (minimum energy that an electron requires to escape from the surface) depends on the UV exposure.

To calculate the work function, the formula that describes photoemission current was used:

$$I = A(h\nu - \varphi)^m, \quad (3.2)$$

where I – the photoelectron emission current, eI/sec;
 A – the coefficient that describes the density of electronic states;
 m – the index that describes transitions of electrons;
 φ – the photoelectron work function, eV;
 $h\nu$ – the photon energy, eV, ($h\nu > \varphi$).

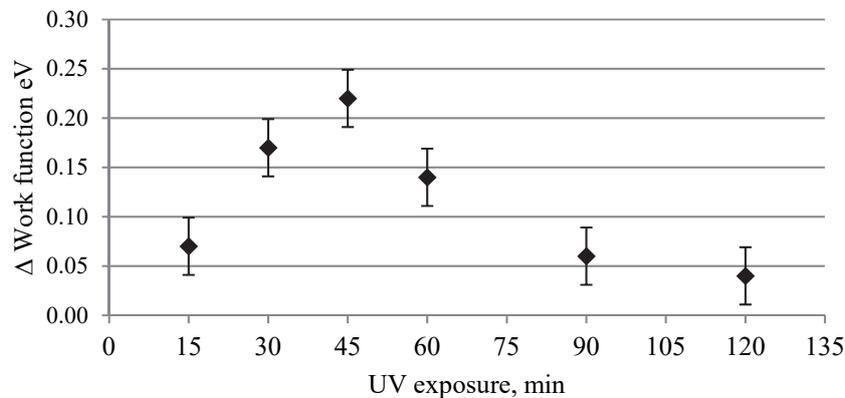


Fig. 3.1. Changes in work function of PMMA depending on UV exposure.

The electron work function varies nonlinearly with the increase in irradiation time (Fig. 3.1). The increase in the work function means that the surface becomes charged more negatively. If the surface becomes charged more negatively, the UV-excited electron requires the greater amount of energy to escape from the ground state to the surface of a material. The changes in the work function may indicate the formation of OH group on the surface [26] or another process. The work function maximum is observed after 45 minutes of irradiation.

PMMA wettability studies showed that the maxima of contact angle changes were observed after 5, 45 and 120 minutes of UV exposure (Fig. 3.2). This behaviour correlates with the changes in work function in Fig. 3.1 and the changes in surface energy in Fig. 3.3.

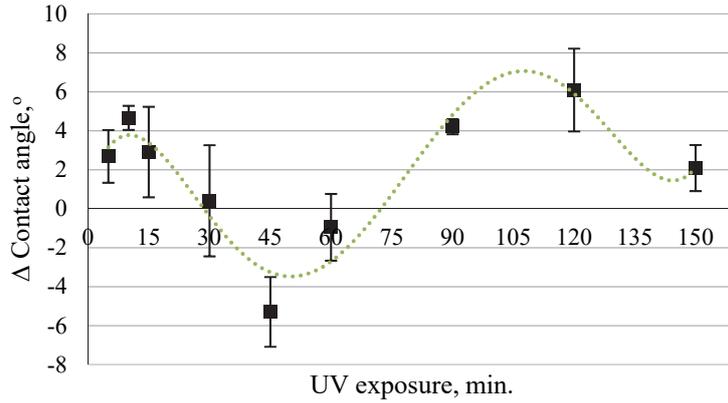


Fig. 3.2. Changes in PMMA contact angle depending on UV exposure.

Taking into account that the greatest changes in PMMA surface (wettability and work function) were observed after 15, 45 and 120 minutes of irradiation, the following results describe influence of these exposures on PMMA material.

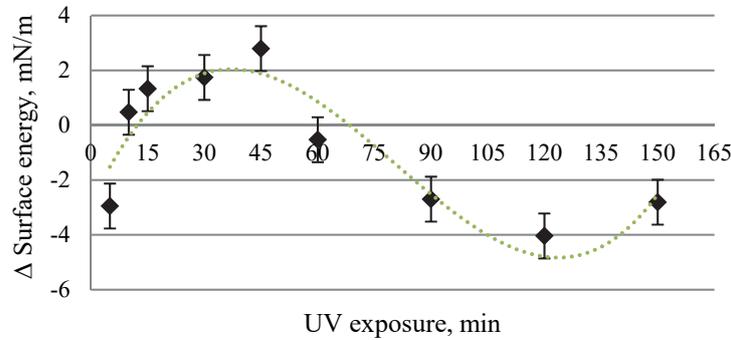


Fig. 3.3. Changes in PMMA surface energy depending on UV exposure.

The surface energy was calculated using contact angle measurements based on Young-Laplace method [71] and OWRK Equation (3.3) which describes that surface energy consists of polar and dispersive components. Increase in the polar component means that material becomes more hydrophilic [77].

$$\sigma_s = \sigma_s^D + \sigma_s^P, \quad \sigma_l = \sigma_l^D + \sigma_l^P, \quad (3.3)$$

where σ_s and σ_l – free surface energy of the solid and liquid respectively, mJ/m^2 ;
 σ_s^D and σ_l^D – the dispersive component of free surface energy of the solid and liquid respectively, mJ/m^2 ;
 σ_s^P and σ_l^P – the polar component of free surface energy of the solid and liquid respectively, mJ/m^2 .

Free energy of the solid is determined by using the linear equation:

$$y = ax + b, \quad (3.4)$$

where:

$$y = \frac{1 + \cos \theta}{2} \cdot \frac{\sigma_l}{\sqrt{\sigma_l^D}}, \quad x = \sqrt{\frac{\sigma_l^P}{\sigma_l^D}}, \quad (3.5)$$

$$a = \sqrt{\sigma_s^P}, \quad b = \sqrt{\sigma_s^D}. \quad (3.6)$$

By substituting σ_l , σ_l^D and σ_l^P values, that characterize the liquid, and contact angle measurements into Equations (3.5), it is possible to obtain points lying on the straight line (3.4). After that, it is possible to calculate σ_s^D and σ_s^P values that characterize the solid using equations (3.6).

The behaviour of the polar and dispersive components shown in Fig. 3.4 suggests that the dispersive component has the greatest impact on the effects induced by radiation when the exposure time is less than 45 minutes. When the exposure exceeds 45 minutes, the effect of the polar component is greater (the maxima of surface energy shown in Fig. 3.3). It is possible to conclude that UV possibly induces two different mechanisms in PMMA. If the exposure is less than 45 minutes, the mechanism might be the attachment of OH groups, while after 60 minutes of exposure C=O group is attached. The resulting surface becomes either more hydrophilic or hydrophobic depending on the exposure (5 minutes of exposure – more hydrophobic, 45 minutes – more hydrophilic, 120 minutes – more hydrophobic).

In the case of PMMA for ocular prosthesis, 45 minutes of UV exposure is optimal because the surface becomes more hydrophilic which means better and longer wetting with liquids (tears, for example) and smaller friction between PMMA surface and eye lids.

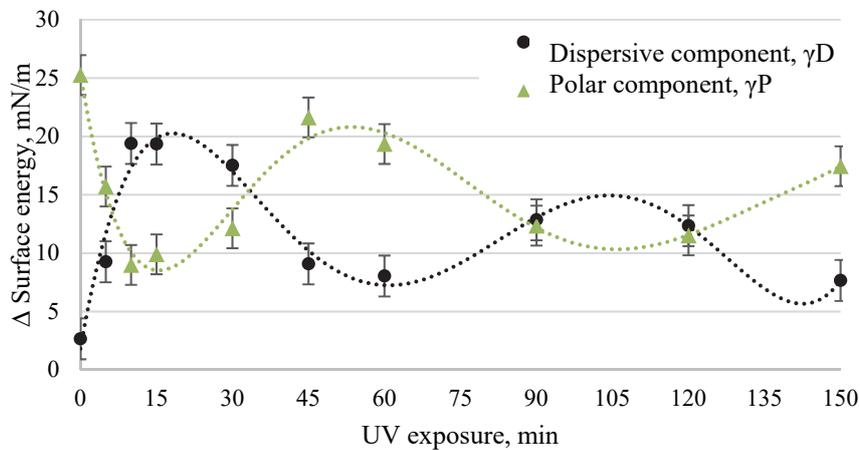


Fig. 3.4.att. Polar and dispersive components depending on UV exposure.

3.2. Morphological and Chemical Changes of PMMA

PMMA spectra before and after irradiation with UV were obtained using UV-Vis, FTIR-ATR, and XPS methods because each of these methods detect changes at different depths of the material. UV irradiation may result in low energy transitions in molecules. In turn relaxation of the excited states can result in electron transitions (UV-Vis range), breaking of bonds and bond vibrations (infrared region), and attachment of compounds to the surface (XPS). In addition, the processes can take place sequentially or simultaneously at different depths of the material [48].

By recording UV-Vis absorbance spectra after 15, 45 and 120 minutes of PMMA irradiation, characteristic maxima were detected (Fig. 3.5) that indicate electron transitions and concentration of the electric potential on the surface. The maxima for CH₃, OH and C=O coincide with the data mentioned in literature as well as with the previously identified changes [26]. In addition, two maxima at 222 nm and 243 nm were detected that are not described in the literature.

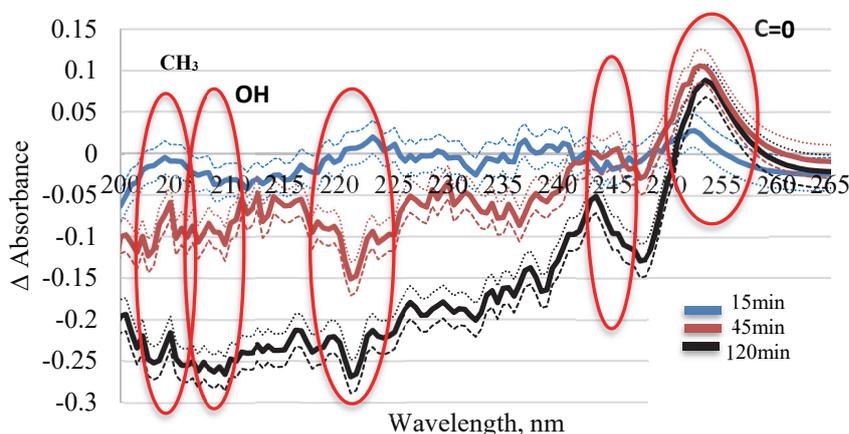


Fig. 3.5. Changes in UV-Vis spectra of PMMA depending on UV exposure.

FTIR-ATR results shown in Fig. 3.6. repeat the previously identified non-linear trend that depends on UV exposure. It is also seen that changes of surface electric potential correlate with transmittance changes.

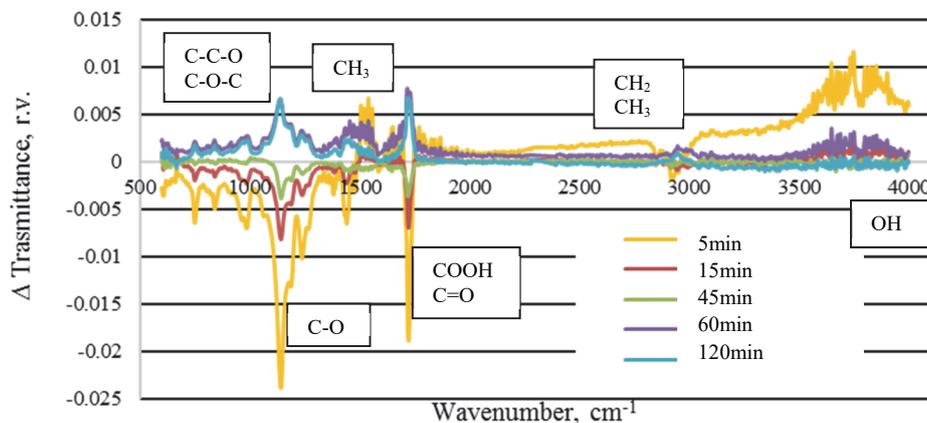


Fig. 3.6. Changes in PMMA FTIR-ATR transmittance spectra depending on UV exposure.

Changes in concentration of functional groups are observed at the same UV exposures as changes in work function and wettability. The results once again confirm that the changes might occur under influence of different mechanisms – one mechanism for 5, 15 and 45 minutes of exposure, and the second mechanism for 60 and 120 minutes of exposure.

The changes occur at certain wavenumbers, for example:

- 3437, 1641 cm⁻¹ – stretching and bending vibrations of OH group – the greatest changes after 45 minutes of exposure – the greatest changes of surface energy and contact angle;
- 2990–3050 cm⁻¹ – stretching vibrations of C-H bond in -CH₂, -CH₃- groups;
- 1732 cm⁻¹ – presence of COOH carboxyl group, stretching vibration of C=O group;
- 1395–1444 cm⁻¹ – deformation vibration of C-H bond in -CH₂, -CH₃ groups;

- 1150–1250 cm^{-1} – symmetric stretching vibrations of C-C-O bond;
- 1040–1260 cm^{-1} – antisymmetric stretching vibrations of C-O-C bond;
- 880–960 cm^{-1} – C-O-C deformations [20] [34] [48].

XPS results in Fig. 3.7. and 3.8. show characteristic peaks of PMMA and their changes after UV irradiation [5], [52]. Change in the intensity of the peaks and their shift along the X axis demonstrate an influence of UV on the following bonds:

- At 285 eV \rightarrow C-H bond, 285.6 eV \rightarrow C-C=O bond. The increase in the concentration of the bonds was observed that could mean the formation of the new compounds on the surface.
- At 286.7 eV \rightarrow decrease in the concentration of C-O-C bonds, 288.8 eV \rightarrow C=O bond did not change.
- At 532.3 eV additional peak of the oxygen adsorbed on the surface is seen. The area under the curve decreases from 20 % to 8 % after UV irradiation.
- An additional peak at 286 eV demonstrates disappearance of the ester group after UV irradiation.

By comparing the results with the other results from Sections 3.1 and 3.2 it was concluded that after 45 minutes of UV exposure the concentration of C-O-C bonds decreases, which means that PMMA side groups could be broken or detached (Fig. 1.5).

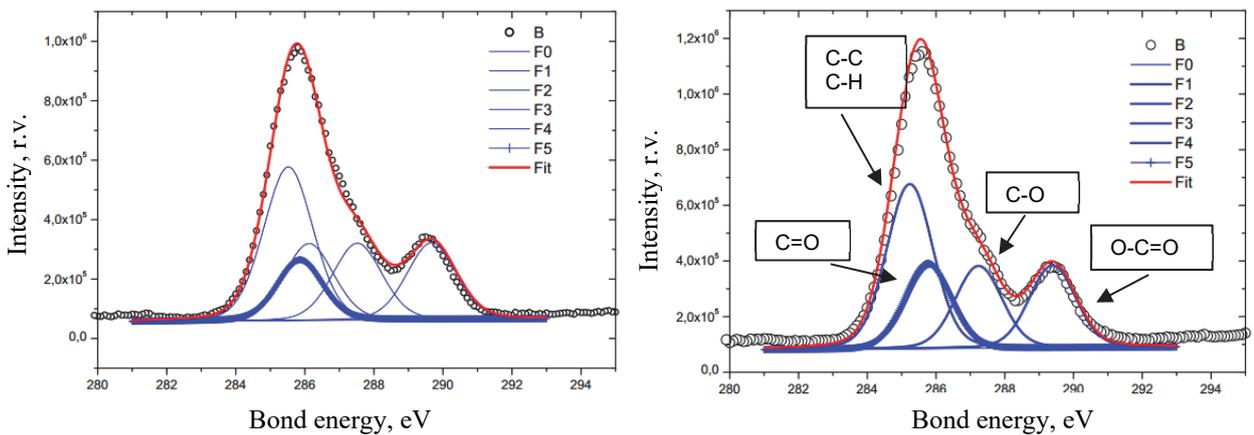


Fig. 3.7. XPS spectrum of PMMA before (on the left) and after (on the right) 45 minutes of UV exposure.

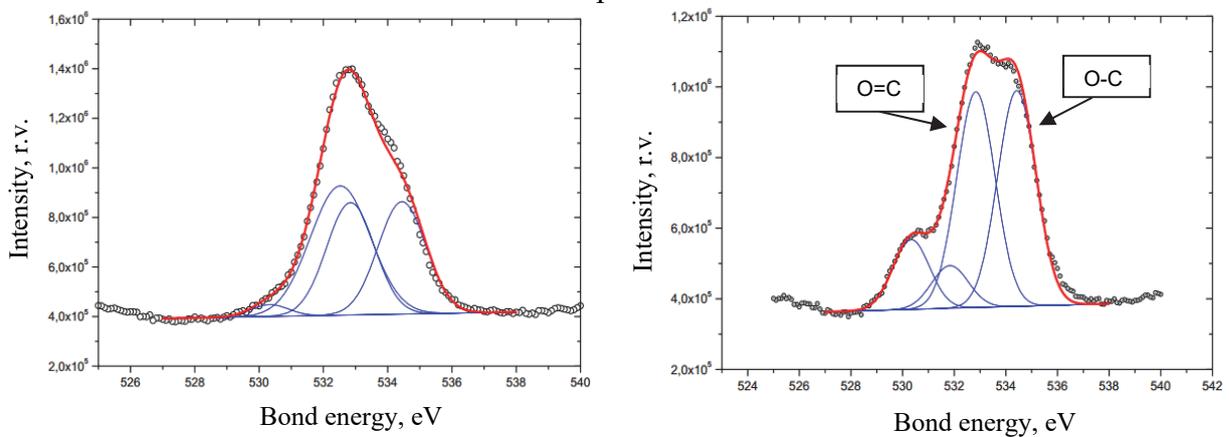


Fig. 3.8. XPS spectrum of PMMA before (on the left) and after (on the right) 45 minutes of UV exposure.

The results obtained in Sections 3.1 and 3.2 are summarized in Table 3.1. The table shows the changes in PMMA surface detected using UV-Vis, FTIR and XPS methods.

The opposite intensities in UV-Vis and FTIR spectra could mean that the destruction takes place at first followed by the cross-linking with other groups, therefore the process is detected at different wavelengths than the initial process. In addition, various processes are possible during photooxidation, for example, when C-C bond is broken, both C-O and C=C oxidizing is possible.

Possible explanations for the occurring photochemical processes are given below. However, additional research in the field of chemical science is required.

When irradiating PMMA with 5 minutes UV exposure, oxygen from surrounding environment is attracted and forms OH group at the surface of PMMA which was detected by FTIR method. When higher irradiation times are used (15 minutes and higher), OH group has not been detected at the surface (FTIR, UV-Vis). Intensity decrease in UV-Vis spectra indicate that several secondary reactions might happen, for example, oxygen or hydrogen spall and following the formation of free polymer atom orbitals, thus further reactions. It can be concluded that by increasing UV exposure time, several different photo chemical processes might take place as described in section 1.3. (fig.1.5.) in the Thesis.

In the beginning, splitting of the acrylic group -COO-CH₃ takes place. The second stage comprises of oxidation of the main chain and -CO- or COO can be formed. At the same time, the concentration of the methyl groups CH₃ has to decrease.

In turn bonds of C=O and COOH groups are broken after 5 and 15 minutes of the irradiation (FTIR – stretching), after 45 and 120 minutes adsorption and increase in a concentration of new groups takes place.

From Table 3.1 it can be concluded that after 45 and 120 minutes of UV exposure the main contribution to more hydrophilic surface is made by the increase in the concentration of C=O and COOH groups on the surface and detachment of CH₃ groups.

Table 3.1

Summary of UV-Vis, FTIR and XPS results.

UV exposure, min →	UV-Vis			FTIR					XPS
	15	45	120	5	15	45	60	120	45
OH	v	vv	vvv	^^^	^	^	^	-	
C=O, COOH	-	^	^	vvv	vv	v	^^	^^	-
CH ₃	-	v	vv	v	-	-	^	^	
C-O-C				vvv	vv	v	^^	^^	v
C-C-O				vvv	vv	v	^^	^^	^
CH ₂				vv	-	-	^	^	^
C-O				vvv	vv	v	^^	^^	
Change in contact angle, Δ	^^	vv	^^		^^	vv		^^	vv
Change in surface energy, Δ	-	^^	vv	vv	-	^^		vv	
Change in polar component, Δ	vv	^^	vv	^^^	vv	^^		vv	
Change in dispersive component, Δ	^^	vv	^^	vvv	^^	vv		^^	

v – the smallest changes, vvv – the greatest changes detected by the increase in the intensity of the spectral peaks. The green colour means that the surface becomes more hydrophilic, the orange – more hydrophobic.

PMMA surface roughness depending on UV exposure was measured using tapping mode of AFM (Fig. 3.10, Equation (3.7)). It was found that the roughness did not change after exposures up to 60 minutes and the irradiation method can be used to modify prostheses surface.

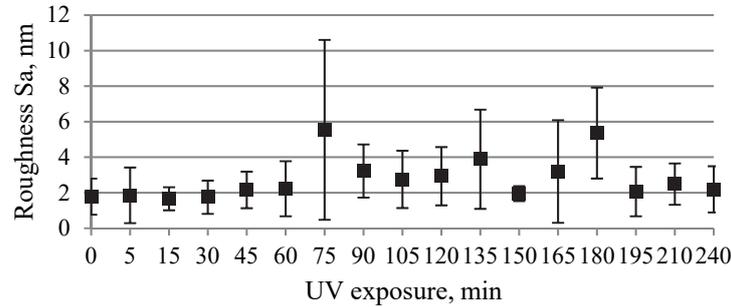


Fig. 3.9. PMMA surface roughness depending on UV exposure.

Roughness parameter S_a (Fig.3.11.) describes the difference in height (Z) of each surface point compared to the arithmetical mean of the surface [4] and is automatically calculated by AFM software:

$$S_a = \frac{1}{A} \iint_A |Z(x, y)| dx dy, \quad (3.7.)$$

where $Z(x,y)$ – the function that describes the surface profile analysed in terms of height (Z) and positions (x) and (y) of the sample over the evaluation area (A).

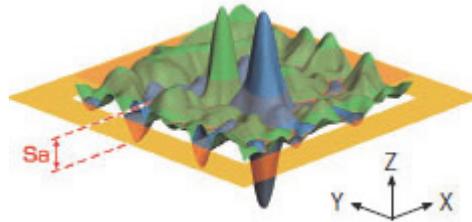


Fig. 3.10. Schematic image of arithmetical mean height parameter S_a .

4. METHOD FOR PMMA WETTABILITY REGULATION USING UV RADIATION

In accordance with the fourth task, the methods for regulation of PMMA wettability was developed.

Task No.4: To develop the method for regulation of PMMA wettability by using UV.

Task No.5: To evaluate the economic efficiency of the developed method of PMMA wettability regulation for application in ocular prosthetics.

As the result of the studies, the following parameters of the wettability regulation method have been determined:

1. PMMA has to be cleaned before UV exposure in the ultrasonic bath in distilled water.
2. exposure conditions:
 - Mercury-xenon UV source, 200 W.
 - Irradiation under room conditions at 20–55 % humidity and 23 ± 3 °C temperature.
 - Time of UV irradiation is up to 60 minutes.
 - Distance to the sample is 40 cm or less if the light intensity incident on the surface is 17.5 W/m^2 .
 - Exposure:

- to obtain hydrophilic surface – 45 minutes;
- to obtain hydrophobic surface – 5–15 minutes.
- 3. filters – to obtain hydrophilic surface, the filter with light transmittance 320 ± 25 nm has to be used.
- 4. exploitation time before the repeated irradiation – 20 days.
- 5. the most stable PMMA storage conditions – in a glass container.

Economic efficiency of the developed method and its comparison with the cost of prosthesis replacement is evaluated based on the prices in 2017. It is assumed that the method is applied in a prosthetist's office. Methods that employ specific conditions such as plasma treatment or vacuum, chemical or biological methods are not considered as they require the use of complicated equipment, customized laboratories, and specifically trained personnel, which would cause many difficulties when applying the methods in practice.

- 1) **Option A: prosthesis replacement once in 1.5 years, 1050 EUR in total:**
 - a) a visit to a specialist (making measurements) – 25 EUR;
 - b) fabrication of ocular prosthesis – 1000 EUR;
 - c) a visit to a specialist (prosthesis fitting) – 25 EUR.
- 2) **Option B: UV irradiation of the prosthesis once per month, sending and receipt of the prosthesis by post, 216 EUR in total for all irradiations during 1.5 year period.**

Cost per one irradiation:

$$\frac{2800(a) + 120(c) + 3780(d)}{3200(b)} = 2.09 \text{ EUR} \quad (4.1.)$$

With a markup of 50 %, shipping and packaging costs, approximate price for one irradiation is 6 EUR. During 18 months 18 re-irradiations are required, so the total costs are $18 \cdot 6 = 108$ EUR. The sum is multiplied by 2 to include administrative expenses (rent, amortization, etc.) with a large reserve. The final price is 216 EUR.

- (a) Equipment and materials, 2500 EUR in total: UV source 1500 EUR, UV lamp 600 EUR, the light guide 300 EUR, the support stand 100 EUR, ultrasonic bath 200 EUR, antistatic wipes 50 EUR, prosthesis holder 50 EUR. The prices defined by current (January 2017) price level from internet resources and may differ [28] [29].
- (b) Evaluation of UV lamp capacity. In total it is possible to irradiate 3200 eye prostheses prior to lamp replacement, irradiating one prosthesis per one irradiation with 45 minutes of exposure.
 UV lamp lifetime 3000 hours: $((3000 \text{ h} \cdot 60 \text{ min})/45 \text{ min}) = 4000$ prostheses, however, this quantity was reduced to 3200 prostheses taking into account decrease in lamp intensity with operating time (Section 2.2).
 9 prostheses per day: $((8 \text{ h} \cdot 60 \text{ min})/45 \text{ min}) = \sim 10.6$ (reduced to 9 prostheses taking into account 5 min treatment in ultrasonic bath and other manipulations)
 180 prostheses per month – one UV lamp can be used for 20 months approximately (or 1 year and 8 months). Taking repairs into account, duration of use of one UV lamp is estimated to be equal 18 months or 1.5 years.
- (c) The power consumption of 200W UV lamp, 120 EUR during 3000 hours lifetime:
 price for 1 kWh – 0.2 EUR
 Energy cost during lamp lifetime: $0.2 \text{ kW} \cdot 3000 \text{ h} \cdot 0.2 \text{ EUR} = 120 \text{ EUR}$

- (d) Personnel costs: 14 h/month (~40 min/day) – 210 EUR/month – 3780 EUR per 18 months, including maintenance of the UV lamp, prosthesis cleaning, packaging and shipping.

4.1. Practical Application of the Method

In accordance with the fifth task, the achieved results were approbated.

Task No.5: To approbate the achieved results by determining the influence of PMMA surface properties modified by UV on microorganism adhesion and induction of surface electric potential. To evaluate the possibility of implementing the developed method to regulate wettability of eye prosthesis material.

4.1.1. Bacterial Contamination of the Surface

The wettability deteriorates over time and dry eye syndrome develops. In the case of the syndrome, yeast from environment penetrate into eye cavity more easily, this causes inflammations [40]. Therefore, the aim of the research was to evaluate a degree of adhesion of the yeast cells to the irradiated PMMA. The method of yeast cell immobilization described in [69] was used in which adhesion between the cells and the surface is governed by electrostatic attraction forces. The electric potential of the cell surface interacts with the surface electric potential of the substrate [40]. Yeast cells prefer neutral pH 7 or weakly acidic environment for optimal growth. Carboxyl group (COOH) forms an acidic environment, therefore, a concentration of the cells on PMMA surface depends on irradiation conditions and side groups that are formed in PMMA [45].

The number of the yeast cells immobilized per unit area was determined using optical microscope Leica DM-1000 and image processing software *ImageJ*.

It was found that exposures up to 60 minutes (Fig. 4.1) did not influence cell adhesion – the number of immobilized yeast cells did not increase. Therefore, the wettability remains constant and PMMA can be used in the biological environment. After 120 minutes of PMMA exposure the yeast cells are repelled from PMMA, however, measurements of the contact angle show that the surface becomes more hydrophobic which is opposite to the desired effect.

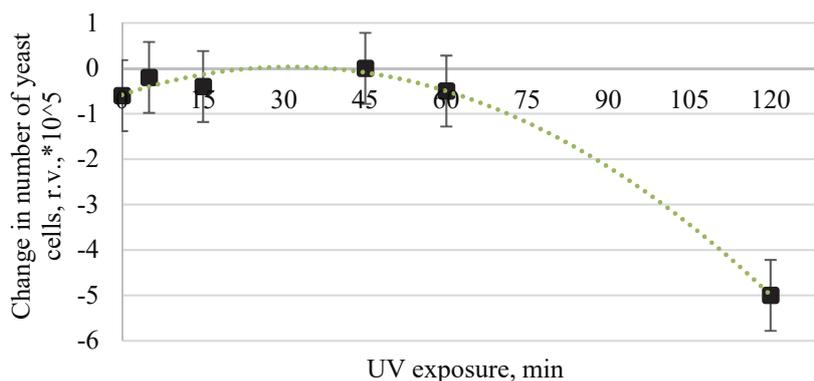


Fig. 4.1. Change in number of yeast cells immobilized on PMMA surface depending on UV exposure.

4.1.2. Regulation of Wettability to Obtain Coatings

TiO₂ coating is known for its good biocompatibility and enhanced mechanical strength [26]. The coating can be potentially applied to further improve surface wettability – wettability of TiO₂ can be regulated with UV and changes in contact angle can achieve 40 degrees [50]. In collaboration with Institute of Physics of the University of Tartu TiO₂ coating was deposited on PMMA surface using atomic layer deposition (ALD) method. TiCl₄

reagent at temperature 60 °C was used. Adsorption reagent deposition sequence: 10-10-10-25 seconds. The thickness of the deposited TiO₂ coating was 17.5 nm and 22.4 nm. The more detailed description of the deposition process is given in Section 2.4.5 of the Doctoral thesis. Irradiation of PMMA using the developed method influences surfaces electric potential of TiO₂ coating if the irradiation is performed before the deposition of the coating (Fig. 4.2 and 4.3).

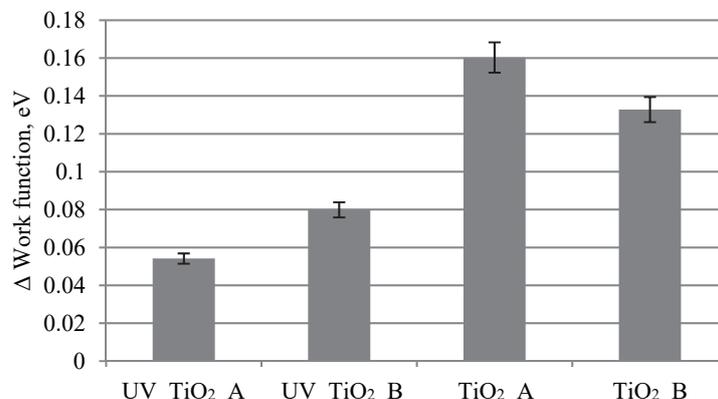


Fig. 4.2. Change in work function of TiO₂ coating that was deposited on non-irradiated and 5 minutes with UV-irradiated PMMA substrate.

UV_TiO₂_A – 17.5 nm thick TiO₂ coating that was deposited on PMMA substrate irradiated 5 minutes with UV.

UV_TiO₂_B – 22.4 nm thick TiO₂ coating that was deposited on PMMA substrate irradiated 5 minutes with UV.

TiO₂_A – 17.5 nm thick TiO₂ coating that was deposited on the non-irradiated PMMA substrate.

TiO₂_B – 22.4 nm thick TiO₂ coating that was deposited on the non-irradiated PMMA substrate.

Fig. 4.2 shows that UV irradiation of PMMA substrate prior to the deposition of TiO₂ coating results in the decrease of photoelectron work function of TiO₂ meaning that the surface of the coating becomes charged more positively (UV_TiO₂_A/B and TiO₂_A/B).

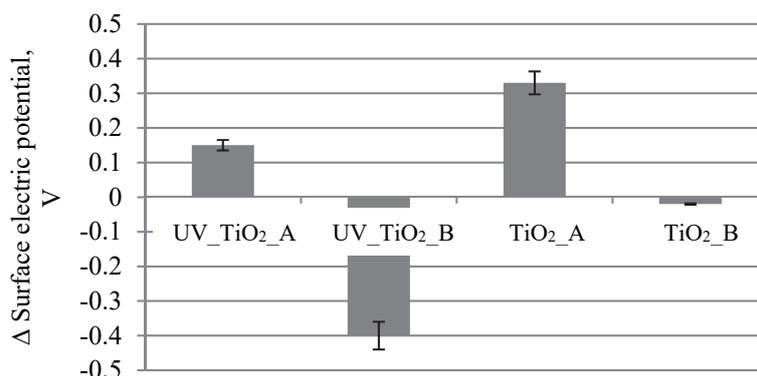


Fig. 4.3. Change in surface electric potential of TiO₂ coating that was deposited on non-irradiated and 5 minutes with UV-irradiated PMMA substrate.

UV radiation influences both PMMA substrate and TiO₂ coating.

UV treatment of PMMA substrate prior to TiO₂ deposition induces changes of surface electric potential (Fig. 4.3):

- The electric potential of the thinner TiO₂ increases compared to the coating deposited on the non-irradiated PMMA substrate.
- The electric potential of the thicker TiO₂ decreases compared to the coating deposited on the non-irradiated PMMA substrate.
- The surface electric potential and work function, or charge, change oppositely.
- Influence of UV radiation on TiO₂ coating after ALD is smaller than before ALD.

CONCLUSIONS

1. The method of PMMA wettability regulation has been developed that induces surface electric potential by using UV radiation in 200–400 nm wavelength range under atmospheric conditions (mercury-xenon UV source, 200 W).
2. The surface electric potential of PMMA depends non-linearly on UV exposure. By changing the potential using UV exposures from 5 to 120 minutes, it is possible to obtain either hydrophobic or hydrophilic PMMA surface without changing surface morphology.
3. UV exposure influences polar and dispersive components of PMMA surface energy. After 45 minutes of UV irradiation the polar component has the greatest impact on wettability. After 15 minutes of UV irradiation the dispersive component has the greatest impact on wettability.
4. The induced changes of PMMA wettability are stable for 20 days after UV exposure if PMMA is stored in a closed glass container at 23 ± 3 °C temperature and 20–55 % moisture.
5. Irradiation of PMMA influences adhesion of microorganisms to its surface. At exposures up to 60 minutes the adhesion does not change, but over 60 minutes the adhesion decreases. This means that exposures up to 60 minutes do not change interaction of PMMA with microorganisms.
6. Five-minute long irradiation of PMMA substrate before deposition of the biocompatible TiO₂ coating (atomic layer deposition) reduces the surface electric potential of the coating compared to the coating that was deposited onto the non-irradiated PMMA substrate.
7. Estimation of the economic efficiency shows that the application costs of the developed method are ~4 times smaller than the traditional approach – replacement of the prosthesis.

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