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MECHANICAL PROPERTIES OF NANOPHOTONIC SOFT CONTACT LENSES BASED ON POLY (2-HYDROHZETHIL METHACRYLATE) AND FULLERENES

MEHANIČKE KARAKTERISTIKE NANOFOTONIČNIH MEKIH KONTAKTNIH SOČIVA NA BAZI POLI (2-HIDROKSIETIL METAKRILATA) I FULERENA

Originalni naučni rad / Original scientific paper
UDK /UDC: 615.46:678.6
617.741-76:678.6
Rad primljen / Paper received: 18.02.2016.

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Keywords
- hydrogels
- soft contact lenses
- fullerenes
- nanophotonic materials
- mechanical properties

Abstract

New types of materials for the soft lenses production based on hydrogel poly (hydroxyethyl methacrylate), HEMA, and incorporated fullerene, fullerene hydroxylate and fullerene-metformin-hydroxylate are developed. Fullerenes are used because of their good transmission characteristics in ultraviolet, visible and near infrared spectrum. The new nanophotonic materials are synthesized by incorporation of nanomaterials, fullerenes and their derivatives in base (commercial) materials for the soft contact lenses, Soleko SL38TM. In this study mechanical properties of the materials are investigated. Refractive index of the materials is determined. Tests have shown that the characteristics of nanophotonic materials such as refractive index and wettability met the criteria for soft contact lenses as well as the base material, and that the mechanical characteristics are improved compared to the base material. The results are applicable in practice and show that it is possible to develop a new generation of materials for soft contact lenses.

Ključne reči
- hidrogelovi
- meka kontaktna sočiva
- fulereni
- nanofotonični materijali
- mehanička svojstva

Izvod

Razvijene su nove vrste materijala za proizvodnju mekih kontaktnih sočiva na bazi hidrogela poli (hidroksietil metakrilata), HEMA, i inkorporiranog fulerena, fulerola i metmorfin-hidroksilata-fulerena. Fulereni su upotrebljeni zbog njihovih dobrih transmisionih karakteristika u ultraljubičastom, vidljivom i bliskom infracrvenom spektru. Inkorporiranjem nanomaterijala, fulerena i njegovih derivata u bazni (komercijalni) materijal za meka kontaktna sočiva, Soleko SL38^{TM}, sintetisani su novi nanofotonični materijali. U ovom radu ispitane su mehaničke karakteristike materijala. Određen je indeks prelamanja materijala. Ispitivanja su pokazala da karakteristike nanofotoničnih materijala kao što su indeks prelamanja i kvašljivost zadovoljavaju kriterijume za meka kontaktna sočiva kao i bazni materijal, a da su mehaničke karakteristike poboljšane u odnosu na bazni materijal. Dobijeni rezultati su praktično primenljivi i ukazuju da je moguć razvoj nove generacije materijala za meka kontaktna sočiva.

INTRODUCTION

Hydrogels are weakly cross-linked hydrophilic polymers capable for the absorption of water in a large amount or biological fluids, whereby characterised by swelling and non-dissolving /1, 2/. As such, the hydrogels are used in biomedicine including active substances controlled release as well as contact lens applications. One of the most used hydrogels is poly (2-hydroxyethil methacrylate), pHEMA, which is used as core component in soft contact lenses. It is expected that the biocompatibility of this material is a reflection of its water content, oxygen, permeability and surface wettability, /3-5/.

The main advantage of HEMA is its ability to absorb water. The water content in it might reach a value up to 38%. This provides the necessary and sufficient elasticity and softness of contact lenses as well as oxygen transmission. However, the main drawback of this material is restricted to transmission of oxygen compared to modern materials with higher water content. For increasing the water content in the material, HEMA is combined with a variety of monomers. Polymers obtained based on HEMA, differ precisely in the amount and composition of added monomers. All of these agents are affecting differently, not only the content of water in the lens, but also electric charge and other physical properties of the polymer.

One of the ways that can be used to improve the characteristics of the material for soft contact lenses is the application of nanotechnology.

Fullerene is a molecule which contains 60 carbon atoms arranged on the surface of the sphere in pentagons (12) and hexagons (20). As an individual molecule, C_{60} is stronger than diamond, however, when crystallized, the crystal lattice is soft almost like graphite. Although very stable, C_{60} molecule has significant applications that are expected in the coming decades, /6, 7/.

Application of fullerenes has not missed the industry of contact lenses, as seen in the example /18/ where a review of the new interdisciplinary field states that polymers based on C_{60} should enable the improvement of the material. Integration of fullerenes and photo-active and electro-active building blocks in the polymer structure should result in the development of new properties in real applications. In this regard, 20 years after the discovery of fullerenes, the scientific community is looking for the right application of the new allotropic forms of carbon. They concluded that the polymer workability can be the key to the implementation of fullerenes in practical purposes.

A large number of papers presents the results of research and experiments in the field of incorporation of fullerenes into the polymer structure, /9, 10/. The research in the field of characterization of rigid gas permeable contact lens with fullerene structured materials for their production is conducted, /11/. However, it is not known about conducted research and published results in the area of characterization of soft contact lenses with incorporated fullerene nanomaterials and their derivatives. Mechanical properties of hydrogels are very important for their application. They can be controlled by changing the degree of crosslinking or hydrogel composition or by synthesis of copolymer hydrogels, whereby with changes in the types of comonomers and comonomers ratio in the copolymer, the desired mechanical properties might be achieved. These variations not only affect mechanical properties but also overall behaviour of hydrogels /12, 13/. Contact lens variations not only affect the mechanical properties but also overall behaviour of hydrogels, /12, 13/. The contact lens materials can be synthesized to contain optimal amounts of water or biological fluids in aqueous environment, to have appropriate mechanical properties, oxygen permeability, biocompatibility, shape stability and softness similar to soft tissues /14-16/. Numerous studies /4, 5, 7, 18, 19/ are aimed at developing and improving the characteristics of materials for soft contact lenses, all with the aim of achieving the best possible vision correction, greater wearing comfort, ensuring sufficient amounts of oxygen to the cornea and less medical complications while wearing soft contact lenses.

Also in the field of optics and materials for soft contact lenses, it is necessary to develop a new material that would, after processing, improve optical properties of transmission of visible and near visible light.

The aim of this study is to comparatively examine the properties of base- and nanophotonic materials, which are synthesized at the company Soleko (Italy). Basic (SL38) and nanophotonic materials SL38-A, SL38-B and SL38-C for soft contact lenses are obtained by radical polymerization of 2-hydroxyethyl methacrylate and fullerene, fullerene hydroxylate and fullerene metforminhydroxylate. Fullerenes are added due to absorption transmission characteristics in the ultraviolet, visible and near infrared spectrum.

EXPERIMENTAL PART

Mechanical properties

The Vicker's method is used for testing microhardness of the material. As an indenter, the diamond pyramid with a square base at an angle of 136º at the top has been used. The microhardness of the samples is tested under 200 g load (HV0.2) using a Buehler Micromet Microindentation Vickers Hardness Tester, Model Micromet 5101.

Compression strength testing and elongation is carried out on the Instron device 1185, at the rate of 2 mm/min.

Refractive index

In this study, values of the refractive index of 2 wavelengths in the visible spectrum are measured on the basis of which is determined by Abe's number for all 4 materials. The measurements of the refractive index are carried out at 20°C (room temperature) and 36°C (the temperature of the eye) for the materials SL38, SL38-A, SL38-B and SL38-C.

The refractive index of the material is measured by a refractometer ATR W, Schmidt + Haensch GmbH & Co., Germany.

Wettability-wetting angle

Wettability is defined as the ability of the material to maintain a thin tear film on the surface of the contact lens while it is in the eye, despite external influences and gravity /20/. A measure of wettability of the material is its wetting angle, θ_e, that represents the angle between the tangent on the drop fluid (saline) and the material surface (Fig. 1). If the wetting angle decreases, the wettability of the material increases.

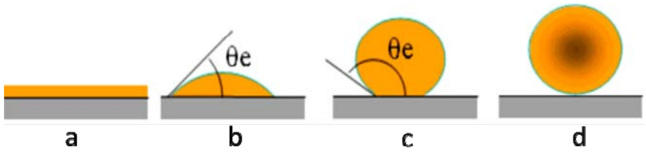

Figure 1. Wetting: (a) complete, (b) good, (c) bad, (d) zero, /21/.

The wetting angle depends, above all, on the surface energy, i.e. intermolecular adhesion forces between the lens material and air (σ_{SV}), liquid and air (σ_{TV}), and liquids and materials (σ_{TM}) (Fig. 2).

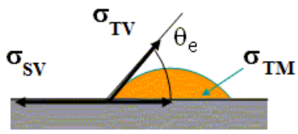

Figure 2. The balance of adhesion forces and wetting angle.

Young's law is defined as the angle of wetting balance of these three forces, which is given by the relation:

$$\sigma_{SV} = \sigma_{TM} + \sigma_{TV} \cos\theta \quad (1)$$

Contact lenses made from four types of material are photographed, where the frontal surface is inflicted with one drop of saline. For the experimental purpose, a camera Nikon D90 and lens Nikon AF-S 60 mm f2.8 were used.

RESULTS AND DISCUSSION

Mechanical properties

For the hydrogels application it is of great importance to achieve appropriate mechanical properties which are characterized by their behaviour under force. The hydrogels mechanical properties are affected by many factors that may be structural (chemical structure of monomers, supramolecular structure, molecular weight, connectivity and branching, crystallinity, copolymerization, plasticizers, fillers ...) or external (temperature, temperature changes, time, pressure, deformation type ...), so it is necessary to determine them experimentally.

To test the mechanical properties of hydrogels, various methods have been proposed. The most applicable and therefore the most commonly used methods are those involving the analysis of tension or compression /23/. In this study, Vicker's method for determining the material microhardness is used. For testing of compressive strength and Young's modulus of elasticity, a microtesting machine is used. The obtained results are shown in Table 1. All values represent average values of three measurements.

Table 1. Values of microhardness, compression strength, Young's modulus, and elongation.

Sample	Micro hardness HV0.2	Force F (N)	Dry lenses		Swollen lenses	
			Young's modulus (GPa)	Contract. ε_p (%)	Young's modulus (GPa)	Contract. ε_p (%)
SL38	311.7	96.7	21.58	0.23	0.7	0.96
SL38-A	312.0	165	26.63	0.22	1.21	0.87
SL38-B	323.7	153	29.77	0.18	1.13	1.01
SL38-C	234.7	162	45.9	0.09	0.44	1.06

Microhardness results are obtained by a spread of results which may indicate a high elasticity of materials. Nanophotonic material SL38-A has approximately the same hardness value as the base material. Sample SL38-C has the lowest value of hardness and has showed outstanding compression characteristics. Even after the application of the force of over 600 N it did not break like the other test samples but deformed into a flat plate. Upon termination of the force within a few minutes (5–10 min) it has returned to its original shape. Nanophotonic materials, SL38 and SL38-B, also have better compression characteristics compared to the base material. Higher strength values provide easier handling for the patient. However, the limit value for the lens material strength should be taken into consideration because higher values of material strength lead to less comfort during usage. For more detailed interpretation of the results, additional tests on more samples are required.

Contraction values are small (less than 2%) so the investigated material belongs to the class of brittle materials. What one would expect are different values of the Young modulus of elasticity for soft contact lenses in dry and hydrated state. SL 38-C in the dry state has a maximum value of Young's modulus, and other materials in a dry state are approximately the same. In the hydrated state SL38-A has a maximum value of the Young's modulus, and SL38-C has a minimum. Materials with higher values of the elasticity modulus retain their shape better and thus provide more visual acuity /23/ so that it can be concluded that the material SL38-C has better performance in dry condition as compared to other materials, while the SL38-A has better performance in the hydrated state. A soft contact lens is placed on the eye in hydrated state so the hydrated state of the lens is the most important characteristic for the patient.

Hydrogels have a faster recovery of shape after the deformation as compared to other materials. These materials are brittle. Polished hydrogel (in dry condition) undergoes great changes due to hydration, thus the impaired mechanical properties. In general, hydrogels have poor mechanical properties, allowing their use to be limited for some cases. By improving these properties, hydrogels would become more acceptable for many future applications, so the tendency to overcome these disadvantages has resulted in a large number of different approaches.

Refractive index

The values of the refractive index and Abe's number of tested samples are shown in Table 2.

The results obtained by measuring the refractive index and Abe's number indicate that all three newly developed nanophotonic materials belong to the group of materials with standard values for the refractive index (slightly below 1.5), but with high levels of Abe's number (between 59 and 62). This means that these materials can be used for producing lenses with standard geometry (thickness in the centre and periphery), but with a small chromatic dispersion (good quality image).

Table 2. Values of Abe's number and the refractive index.

Sample	Abe's number		Refractive index n			
			T = 20°C		T = 36°C	
			λ (nm)			
	T = 20°C	T = 36°C	546.1	589.3	546.1	589.3
SL38	62.00	61.00	15.100	14.972	14.968	14.951
SL38-A	61.22	58.52	14.396	14.379	14.371	14.353
SL38-B	59.73	57.66	14.391	14.374	14.376	14.357
SL38-C	61.47	56.07	14.395	14.376	14.360	14.339

Values of the refractive index for materials SL38-A, SL38-B and SL38-C do not differ significantly from the refractive index of the base material SL-38. A slight deviation, but without affecting the optical parameters of the lens, appeared only in sample SL38-C, at 36°C (eye temperature).

Wetting angle (wettability)

Figure 3 shows photographs of all four materials. On the spherical frontal surface of polished workpieces of soft contact lenses, one drop of saline is applied by a micropipette. The volume of the drop is 5 μl.

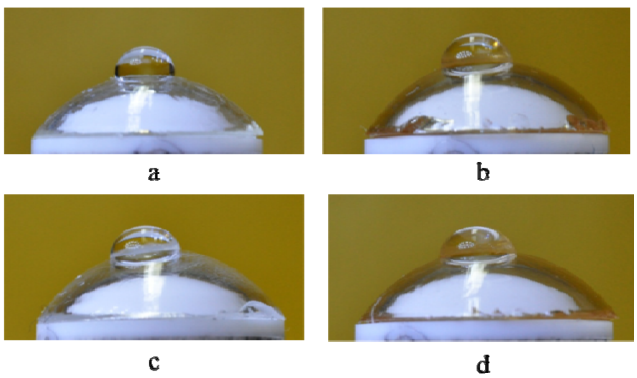

Figure 3. Wetting angle: a) SL38, b) SL38-A, c) SL38-B, d) SL38-C.

Results presented in photographs (Fig. 3) show that the wetting angle of material SL38 is larger than for materials SL38-A, SL38-B and SL38-C, which means that wettability of the nanophotonic material is better than for the base material. Further research should show the exact values of angle measurements, as well as how this is a result of the roughness of the surface of the material.

CONCLUSION

In this paper the properties of the base material and new nanophotonic materials have been examined and compared. Mechanical properties of materials and the wetting angle have been investigated and the refractive index of the tested materials was determined.

It is shown that nanophotonic material SL 38-A has approximately the same hardness value as the base material SL38. Sample SL38-C has the lowest value of hardness and has showed outstanding compression characteristics. Nanophotonic materials, SL38-A and SL38-B, also have better compression characteristics compared to the base material. The values of elongation are very small (less than 2%) so the tested materials belong to the class of brittle materials. Based on values of the modulus of elasticity it can be concluded that the highest flexibility in the dry state shows SL38-C and in a hydrated state SL38-A. Regarding the fact that materials with higher values of modulus of elasticity better retain their shape and thereby provide greater visual acuity, it can be concluded that the material SL38-C has better performance in a dry condition compared to other materials, while SL38-A shows better in the hydrated state.

The results obtained by measuring the refractive index and Abe's number indicate that all three newly developed nanophotonic materials belong to the group of materials with standard values for the refractive index, but with a high level of Abe's number. Values of the refractive index of nanophotonic materials do not differ significantly from the refractive index of the base material SL38. The results show that the wetting angle of SL38 is larger than for SL38-A, SL38-B and SL38-C, which means that the wettability of the nanophotonic material is better than for the base material.

From this study it is concluded that nanophotonic materials for soft contact lenses have significant advantages compared to the base material.

REFERENCES

1. Peppas, N.A., Bures, P., Leobandung, W., Ichikawa, H. (2000), *Hydrogels in pharmaceutical formulations*, Eur. J Pharm. Biopharm. 50: 27-46.
2. Brannon-Peppas, L., *Preparation and characterization of cross-linked hydrophilic networks.* In L. Brannon-Peppas and R.S. Harland (Eds.), Absorbent Polymer Technology, Elsevier, Amsterdam, 1990, pp.45-66.
3. Ketelson, H.A., Meadows, D.L., Stone, R.P. (2005), *Dynamic wettability properties of a soft contact lens hydrogel*, Colloids Surf. B Biointerfaces 40: 1-9.
4. Kumar, A.P., Depan, D., Tomer, N.S., Singh, R.P. (2009), *Nanoscale particles for polymer degradation and stabilization - trends and future perspectives*, Prog. Polym. Sci. 34: 479-515.
5. Efron, N., Contact Lens Practice, Butterworth-Heinemann, 2001.
6. 2-Hydroxyethyl methacrylate, CAS N°: 868-77-9, SIDS Initial Assessment Report for SIAM 13, Bern, Switzerland, 6-9 Nov. 2001.
7. Koruga, Dj., Hameroff, S., Loutfy, R., Withers, J., Sunderes-han, M., Fullerene C60: History, Physics, Nanobiology, Nanotechnology, Elsevier (North Holland), Amsterdam, 1993.
8. Giacalone, F., Martın, N. (2006), *Fullerene polymers: synthesis and properties*, Chem. Rev. 106(12): 5136-5190.
9. Aalbers, W., Basic optics: everything everyone in the optical industry should know about optics: a complete guide to basic optics, Gopher Publishers, 2002.
10. Bowden, T., Contact Lenses: The Story, Bower House Publications, 2009.
11. Stamenković, D., Kojić, D., Matija, L., Miljković, Z., Babić, B. (2010). *Physical properties of contact lenses characterized by scanning probe microscopy and optomagnetic fingerprint*, Int. J of Modern Phys. B 24(6-7): 825-834.
12. Anseth, K.S., Bowman, C.N., Brannon-Peppas, L. (1996), *Mechanical properties of hydrogels and their experimental determination*, Biomat. 17: 1647-1657.
13. Liu, Y., Huglin, M.B. (1995), *Effective cross-linking densities and elastic-moduli of some physically cross-linked hydrogels,* Polymer 36: 1715-1718.
14. Safrany, A. (1997), *Radiation processing: synthesis and modification of biomaterials for medical use*, Nuclear Instrum. & Methods in Phys. Research Section B-Beam Interactions with Materials and Atoms. 131: 376-381.
15. Rosiak, J.M., Yoshii, F. (1999). *Hydrogels and their medical applications, Nucl. Instrum. & Methods in Phys. Research Sec. B-Beam Interac. with Mater. and Atoms* 151, 56–64.
16. Opdahl, A., Kim, S.H., Koffas, T.S., Marmo, C., Somorjai, G.A. (2003). *Surface mechanical properties of PHEMA contact lenses: viscoelastic and adhesive property changes on exposure to controlled humidity*, J of Biomed. Mater. Research Part A 67: 350-356.
17. Kim, S.H., Opdahl, A., Marmo, C., Somorjai, G.A. (2002). *AFM and SFG studies of PHEMA-based hydrogel contact lens surfaces in saline solution: adhesion, friction, and the presence of non-crosslinked polymer chains at the surface*, Biomat. 23: 1657-1666.
18. Kopeček, J. (1993). *Hydrogels: from soft contact lenses and implants to self-assembled films*, J of Applied Phys. 743: 669-672.
19. Ahmed, R.M., El-Bashir, S.M. (2011): *Structure and physical properties of polymer composite films doped with fullerene nanoparticles*, Int. J of Photoenergy 2011, Art. ID 801409, p.6
20. Tranoudis, I., Efron, N. (2004), *Water properties of soft contact lens materials*, Eye & Contact Lens 27: 193-208.
21. Barthelemy, B., Contactologie, Lavoisier, 2004.
22. http://uqac.ca/chimie_ens/Chimie_physique/Chapitres/chap_10.htm
23. Meyvis, T., Stubbe, B., Van Steenbergen, M.J., Hennink, W.E., De Smedt, S., Demeester, J. (2002). *A comparison between the use of dynamic mechanical analysis and oscillatory shear rheometry for the characterisation of hydrogels*, Int J Pharm. 244(1-2): 163-168.