

COMPARATIVE STUDY OF CLASSICAL AND NANOPHOTONIC MATERIALS FOR RGP CONTACT LENSES BY SCANNING PROBE MICROSCOPY

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Summary: In this paper comparative study of the classical (Soleko SP40TM) and new nanophotonic materials for contact lenses was conducted. Two photonic nanomaterials were made by adding fullerene (C₆₀) and fullerol (C₆₀OH₂₄) to the classic, commercially available, base material (PMMA- polymethylmethacrylate). Nanomaterials are added to the base material to change the transmission characteristics of light, because of different electromagnetic properties of the materials. Two new nanophotonic nanomaterials, along with the base material were investigated with Scanning Probe Microscopy methods of Atomic Force Microscopy and Magnetic Force Microscopy (AFM/MFM) to determine roughness, electro-magnetic properties of materials, and static Force-distance curve for investigating materials mechanical characteristics. Results and analysis of investigations for all three materials are compared and presented in the paper.

Keywords: PMMA, contact lenses, fullerene, nanophotonic, AFM, MFM.

1. INTRODUCTION

Contact lenses, along with glasses are the main devices for correcting human vision. Since humans receive up to 90% of information through sight it is obvious why good vision is important. Up until few decades ago contact lenses were used just to refract the light and make it converge right on the human fovea, however more recent trends have been focused on making other uses of these biomedical devices. The best known use is to have an on-head display inside the lens and to have glucose measurements by the lens itself [1]. It is also proposed that optical aids can have another medium which will interact with light and alter its electromagnetic properties. Since the light that comes to human eye will influence the entire brain functioning it is proven that the change in that light will also cause the changes in brain activity which can be monitored through their EEG activity [2]. Proposed medium for the light filter was originally fullerene C₆₀ as a thin film on glasses which was added for its electromagnetic properties [3]. Materials for contact lenses are suitable for incorporating nanoparticles inside them thanks to polymerisation type production, i.e. by introducing nano materials into compound during

the polymerisation. A new contact lens material was created with fullerene C₆₀ added to the base material, which is a commercially available contact lens material called SP40, produced by Soleko, Italy. With this material, another material was created in the same manner, which contained fullerol C₆₀OH₂₄ because of its better biocompatibility properties.

Characterizations of these materials are done by Atomic Force Microscopy (AFM) [4] and Magnetic Force Microscopy (MFM)[5]. These methods can provide an insight into micro and nano structure of the materials based on sharp probe interactions with the surface of the sample. Since interactions between the probe and the surface of the sample arise from atomic, molecular and magnetic forces (among others) it is possible to distinguish the magnetic influences of the material. This can be used to characterize magnetic properties of the sample, which will provide the information on changes in electromagnetism of nanophotonic materials.

2. MATERIALS

In this paper three different materials were compared, one material that is already in use for

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production of contact lenses (SP40, Soleko, Italy), and two materials with added nanomaterials introduced to change its photonic characteristics (SP40+C₆₀ and SP40+C₆₀(OH)₂₄). All materials were processed in a cylindrical shape with the surface properties as a final contact lens. The only difference between preparing contact lens materials and final contact lens is in the absence of the contact lens curvature. Materials storage and experiments were done at room conditions.

The first material is polymethylmethacrylate and siloxane-acrylate copolymer made by Soleko (Italy) branded as SP40. This material has a refractive index of 1.472 and its transmittance is 90% in visible and 60% in ultra-violet spectrum. Hardness of this material was previously measured to be 82 by the method of Shore D [6]. This material was used as a base material for new nanophotonic materials. New materials were made by adding nanomaterials (C₆₀ and C₆₀(OH)₂₄) to SP40 during polymerisation.

The first nanophotonic material investigated, named Material A was created by adding fullerene C₆₀ to the base material. Fullerene is known to be very electromagnetically active molecule so that the light transmitted through it would change its electromagnetic properties. One gram of fullerene was added to 300 grams of the SP40 compounds during polymerisation. Polymerisation was homogeneous, because measuring of the material concentration on top, middle and bottom of the rod was done. Measured hardness of this material by the Shore D was between 82 and 83 and a slight change in hardness was detected [6].

The second nanophotonic material, named Material B was created in the same manner as Material A but the material that was added was fullerol (C₆₀OH₂₄). Like with Material A the amount of nanomaterials added was one gram to 300 gram of the SP40. The reason for replacing fullerene with fullerol was to have different electromagnetic influence on the transmitting light and to have higher biocompatibility because fullerol is a functionalized C₆₀ with OH groups [7]. Hardness of Material B was roughly the same as Material A [6].

3. METHODS

Atomic Force Microscopy (AFM- JEOL, Japan) was used to investigate the surface of the contact lenses material. AFM uses a probe called cantilever (MikroMasch, Estonia), with sharp tip the radiuses of which range from 1 nm up to 100 nm, depending on the properties of the material to be measured. The AFM has proven to be a great asset for characterization of surface properties of various

materials. It has been widely used even to measure different aspects of contact lenses, such as surface roughness [8–10], lateral forces [11,12] and also their magnetic properties [13,14].

In this paper mechanical properties of the contact lenses were investigated by the method of static AFM measurement. These measurements are based on monitoring the deflection of the cantilever when it is forced into the contact with the material. Deflection can easily be converted into force by the Hooke's law:

$$F = k \cdot x \quad (1)$$

where k is a spring constant of the cantilever and x is deflection of the cantilever. After measuring the forces arising during the material-cantilever interaction a force-distance curve can be drawn. Differences between these materials can be presented graphically.

For this measurement the cantilevers used were MikroMasch CSC37/AlBS. For all measurements the tip B was used (length 350 μm, tip radius <10 nm, force constant was around 0.3 N/m). The distance that the sample travelled was 1 μm in both directions.

In addition to force-distance curves, surface morphology was measured by AFM. This investigation was done in parallel with measurements of the gradient of the magnetic field by Magnetic Force Microscopy (MFM). From measuring surface topography it is possible to calculate surface roughness as it is an important parameter for contact lenses. Roughness was calculated automatically on WinSPM software, by two approaches. The first approach included an average roughness (R_a), given by:

$$R_a = \frac{1}{S_0} \int_0^{x_{\max}} \int_0^{y_{\max}} |f(x, y) - Z_0| dx dy \quad (2)$$

where Z_0 is the middle height of the entire surface calculated by:

$$Z_0 = \frac{1}{S_0} \int_0^{x_{\max}} \int_0^{y_{\max}} f(x, y) dx dy \quad (3)$$

The second approach involved roughness calculation as a root mean square roughness R_q . This parameter was calculated by

$$R_q = \sqrt{\frac{1}{S_0} \int_0^{x_{\max}} \int_0^{y_{\max}} (f(x, y) - Z_0)^2 dx dy} \quad (4)$$

Magnetic force microscopy (MFM) is done by observing changes in distribution of magnetic properties of the material. Materials in their nature can be ferromagnetic, paramagnetic and diamagnetic. Even slight changes in any of these properties will

induce different forces on the cantilever and by measuring changes in oscillation parameters of the cantilever we can monitor these changes - this will represent a gradient of magnetic field. Magnetic field gradient measurement by MFM and surface topography measurement by AFM are done simultaneously. After measuring each line of the profile, one line of phase imaging which collects magnetic signals was obtained. This method is called a two-pass method, where magnetic image is an image of the phase shifts of the oscillating cantilever while it is separated from the sample by a given distance. Relation (5) is used to calculate the gradient of magnetic field with known parameters f_0 (resonant frequency of cantilever), k (force constant of the cantilever) and measured parameter is Δf , which is a change in phase of oscillation of the cantilever.

$$\frac{\Delta f}{f_0} = - \frac{\Delta F_{\text{magnetic}}}{2k} \quad (5)$$

To obtain magnetic information about the material the cantilever has to generate a magnetic field. For this reason specialized cantilevers with ferromagnetic coating have to be used. Cantilever

used in this investigation was MikroMasch NSC18/CoCr, which has tip radius of 10 nm coated with 50 nm of Cobalt and 30 nm of Chromium. Cantilevers were placed in the external magnetic field of 0.4T for 2 hours prior to experiments, because they would induce magnetic field themselves. The length of cantilever is 230 μm , resonant frequency is around 73 kHz and force constant is 3.5 N/m. The height of the second pass was set to 70 nm. All measurements are done under room conditions (temperature 20.8 $^{\circ}\text{C}$, humidity 43%).

4. RESULTS

4.1. Surface topography

All scans were done on the surface area of 2x2 μm with 256x256 resolution. Topography images were obtained along with magnetic force microscopy images with the same experimental setup. Collected images of topography were processed in WinSPM and WinSxM software [15] and presented as a 3D view of the selected surface area.

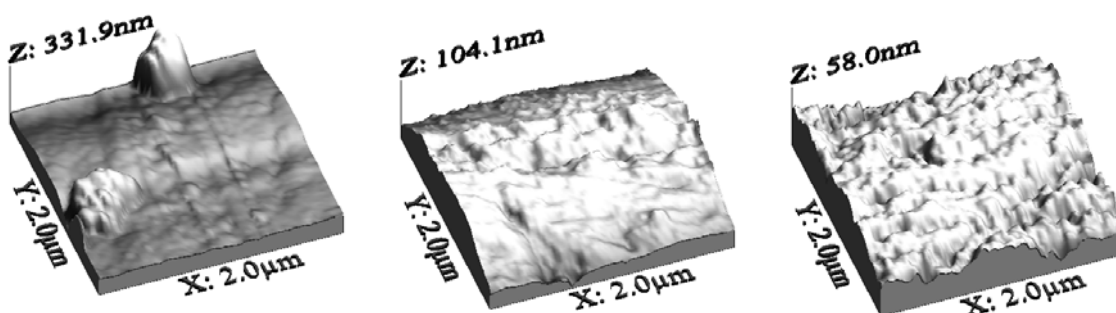


Figure 1. Topographies of all materials presented in 3D view. Base material SP40 (left), Material A - SP40 with added fullerene C_{60} (middle) and Material B - SP40 with added fullerol $\text{C}_{60}(\text{OH})_{24}$ (right)

Magnetic properties

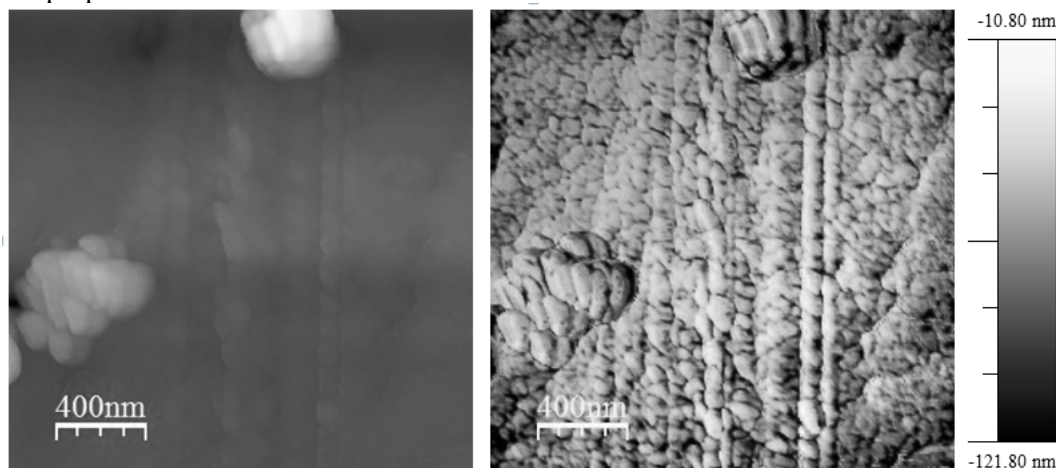


Figure 2. Topography and corresponding image of the gradient of the magnetic forces of the base material SP40. Colorbar describes values of the phase shift angles on the magnetic image
 Surface topography (left), Gradient of magnetic forces(right)

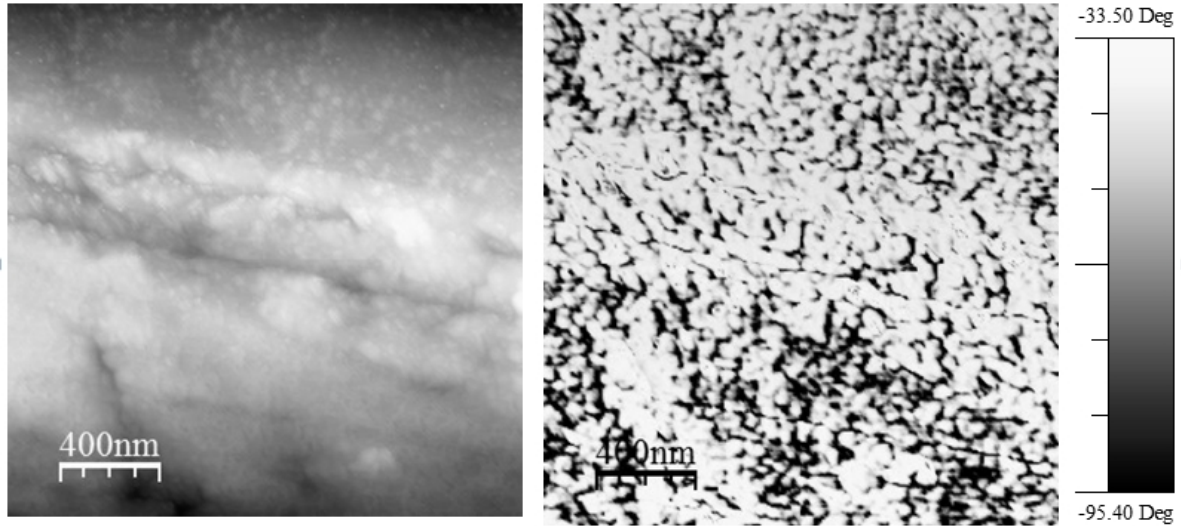


Figure 3. Material A – Topography and gradient of magnetic forces (phase image)
Topography (left), Gradient of magnetic forces (right)

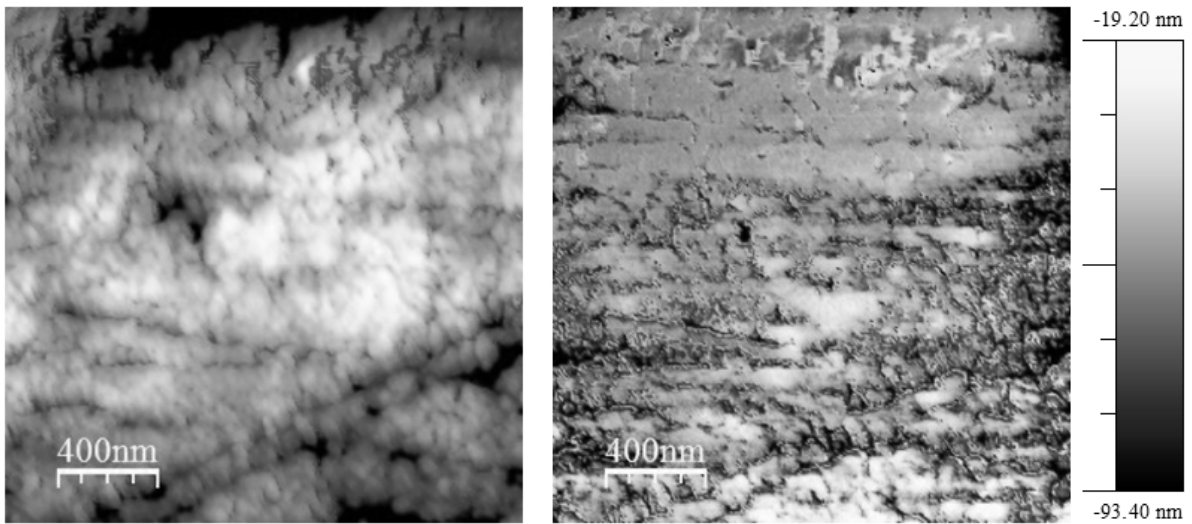


Figure 4. Surface topography and gradient of magnetic forces of the Material B
Surface topography (left), Gradient of magnetic forces (right)

Force-distance diagrams

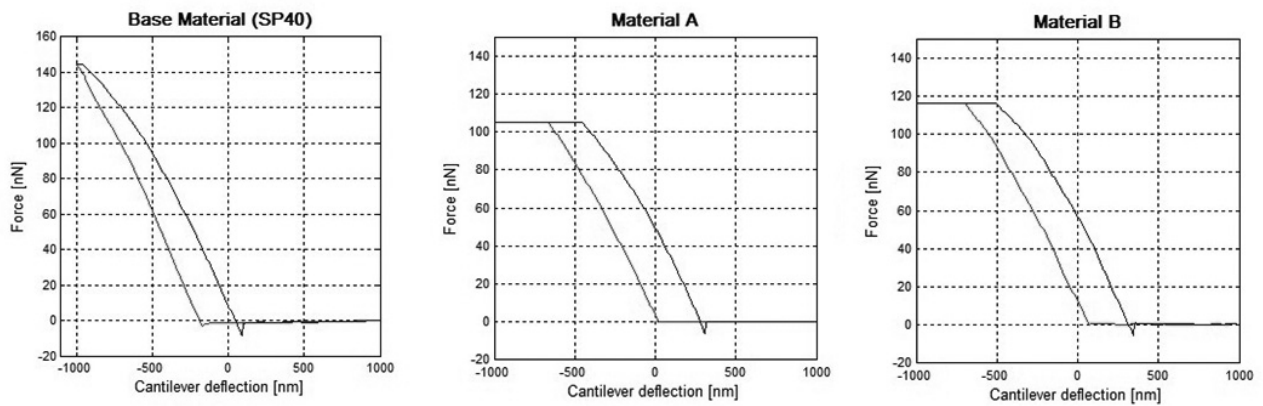


Figure 5. Force-distance diagrams of contact lens materials
Base material, SP40 (left), Material A (middle) and Material B (right)

5. DISCUSSION

From surface topography (Figure 1.) it can be seen that the highest peak values are of the base material (SP40), which have the highest height difference of 331.9 nm. Nano materials have significantly smaller height differences of 104.1 (Material A) and 58.0 (Material B). Also, the roughness of the base material is larger than of the nanophotonic materials. Roughness values along with height difference are given in table 2.

It can be seen (Table 1) that new nanophotonic materials (A and B) have much better surface topography compared to the original material (SP40), due to their smoother surface.

Magnetic force microscopy investigation shows that there are changes in magnetic properties of the materials based on the value of the phase shifts angles in the MFM image (Figures 2,3 and 4). Relevant parameters like minimal and maximal phase shift angle and their difference are different for all three materials. These results are presented in Table 2.

Table 1. Comparison of materials according to their roughness and height difference

Material	Height diff. (Rz) [nm]	Avg. Roughness (Ra) [nm]	RMS roughness (Rq) [nm]
Base material (SP40)	331.9	23.3253	36.131
Material A (SP40+C ₆₀)	104.1	13.869	16.91755
Material B (SP40+ C ₆₀ (OH) ₂₄)	58.0	7.1957	8.9595

Table 2. Phase shifts angle analysis on the magnetic force microscopy images of all three materials

Material	min phase angle [°]	max phase angle [°]	Difference [°]
Base material (SP40)	-10.8	-121.8	111.8
Material A (SP40+C ₆₀)	-33.4	-95.4	61.9
Material B (SP40+ C ₆₀ (OH) ₂₄)	-19.2	-93.9	74.2

It is obvious (Table 2) that all materials have negative phase shift angles which indicates that materials are paramagnetics. Base materials have the largest difference of the phase shift angles which may point to the highest variance in magnetic properties. Fullerene in the material tends to reduce phase shift angles spectrum but also contributes to more paramagnetic properties as entire spectrum is shifted towards more negative values. Fullerol contribution is also to reduce the phase shift angles difference and give the material more paramagnetic properties.

Force-distance curves also point to certain differences in new materials. After indenting and increasing the force between the materials (thinner line), and material starts to separate from sample, the base material shows the largest peak of negative forces. It created the force around 8.44 nN while this force with Material A was 6.56 nN and with Material B it was 5.39 nN. This indicates that adhesion forces between cantilever and this material are bigger than the rest. It should be noted that these materials are investigated as flat surfaces, so the curvature of the contact lens would greatly increase the adhesion forces of the materials.

6. CONCLUSION

This paper presents characterizations of newly made nanophotonic materials and their comparison to the standard ones. Comparisons made by the Atomic Force Microscopy and Magnetic Force Microscopy show that these materials have certain differences compared to base material.

From surface morphology it can be seen that new photonic nanomaterials are by their surface roughness even smoother than the base material SP40. This leads to an assumption that their topography is more compatible with human cornea. The base material has the highest peaks at 331.9 nm while nanomaterials are much more uniform and do not have such big changes in surface topography.

Form static measurement it can be seen that adhesion forces are slightly bigger in base material. Since force difference between materials is in order of few nN, it can be expected that new nanomaterials have similar adhesion forces as human tear film, because contact lens shape is a more significant factor.

Adding fullerene and fullerol to base material changed electro-magnetic properties of the material, reducing the differences between magnetism of par-

ticles in the structures of the material which can be seen on gradient change of magnetic field images. According to the average phase shift angle of SP40 materials and SP40 with fullerene and fullerol, both nanomaterials contribute to the described paramagnetic properties of the material. Therefore it can be said that the presence of nanomaterials in the base material changed its electromagnetic properties. Further investigation should be made in the direction of investigating the exact influence of these changes on human brain functioning. According to previous investigation [2] it may be expected that transforming diffuse light into ordering one by nanophotonic material can help people who are suffering from depression, if the ordering light reaches the eyes of the patients in longer period.

7. ACKNOWLEDGMENTS

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КОМПАРАТИВНО ИСТРАЖИВАЊЕ КЛАСИЧНИХ И НАНОФОТОНСКИХ
МАТЕРИЈАЛА ЗА РГП КОНТАКТНА СОЧИВА
СКЕНИРАЈУЋОМ СОНДНОМ МИКРОСКОПИЈОМ

Сажетак: У овом раду извршена су компаративна истраживања класичног материјала за тврда (гас пропусна сочива) сочива и два нова нанофотонска материјала за контактна сочива. Фотонични наноматеријали су добијени додавањем фулерена C_{60} и фулерола $C_{60}(OH)_{24}$ основном материјалу SP40 (Soleko SP40TM) на бази полимета-метакрилата (PMMA). Наноматеријали се додају основном материјалу да би се промијенила трансмисиона карактеристика свјетлости због другачијих електромagnetних карактеристика самих материјала. Основни и два нанофотонична наноматеријала су испитивани методама скенирајуће сондне микроскопије: метода микроскопије атомских сила (Atomic Force Microscopy, AFM) и метода микроскопије магнетних сила (Magnetic Force Microscopy, MFM). Испитиване су и одређене разлике у електромагнетним својствима материјала, а статичким одређивањем силе, у функцији растојања сонде од узорка, приказане су механичке карактеристике материјала. У овом раду су међусобно упоређени и приказани резултати истраживања и анализе ових трију материјала.

Кључне ријечи: ПММА, контактна сочива, нанофотоника, фулерен, АФМ, МФМ.

