

BIOCOMPATIBLE CARBON NANOLAYERS FOR COATING LENSES

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Abstract

As previous studies indicated, diamond-like carbon (DLC) layers exhibit outstanding biocompatible properties. Additionally, due to high hardness and high transmittance in infrared and visible parts of spectra it is possible to utilize for application ophthalmic optics. DLC layers are suitable for coating of spectacle lenses, contact lenses and even intraocular lenses. In this paper, we focused on transmittance and wear resistance of different commercially available spectacle lenses with surface modification and lenses with DLC layer. The lens transmittance depends on base material and its surface modification. Commercially manufactured lenses exhibit usual transmittance of 90±5%, while transmittance of DLC coated lenses was lower by 15%. Wear resistance is strongly dependent on surface modification. The results of DLC layers were similar or better than commercially manufactured lenses with surface modification.

Keywords

diamond like carbon, biocompatibility, intraocular lenses, contact lenses, spectacle lenses

Introduction

One of the most common optical instruments for the cataract treatment is Intraocular Lens (IOL); the same is valid for contact lenses as the replacement of glasses in case of refraction error treatment [1–7]. IOL consists of two parts—the haptic part serves as a fixing element and the optical part replaces the extracted lens. The lens materials are constantly being developed. There is an ongoing search for new materials, which are biocompatible, non-degrading, exhibit maximum transparency and have the right optical properties. The development in this field offers new possibilities for the cataract treatment and correction of refraction error [1–7].

Many lens classifications exist, depending on the fabrication material, lens placement, and focusing distance [5, 7]. IOL and contact lenses are inherently a “foreign body in the eye”, which implies requirements for biological compatibility. Biocompatibility is determined by biophysical and chemical properties of the material. It is one of the most important lens properties in prevention of pathological changes after operation [7].

The IOL material should comply with the following criteria: the material mass must not weight down intraocular structures; optical part should cover pupil both in the state of miosis (narrowed pupil) and mydriasis (dilated pupil); centring should not irritate the

eye structure; the material should be easily fabricated in high quality and exhibit high index of refraction; it should not necessitate antigen reaction (cell adhesion) and must be sterile. Similar properties are expected of contact lenses [6, 7].

From general (chemical) point of view, these materials can be divided into inorganic (glass) and organic (polymers such as polymethylmethacrylate (PMMA), acrylate, etc.) [6, 7]. Even though these materials are considered to be biocompatible they are not ideal. One of the improvement possibilities is the application of a thin film coating on the lens base material, which has improved biological properties. Diamond like carbon (DLC) could be used in this manner, serving as a protective and antiglare layer and/or DLC with silver dopation could function as an antibacterial coating that would protect against calcification [4, 8, 9].

Three factors are considered to assess the quality of surface treatments: transmittance, friction coefficient and wear resistance. These parameters are important for patient comfort and for extending the lens lifetime.

As some articles [4, 6–10] have shown, DLC could be this surface treatments and therefore we will focus on it in this article.

The aim of the study is to investigate the optical and mechanical properties of currently available spectacle lenses and to develop a surface treatments with similar or better properties.

Deposition protective coatings

Spectacle lenses (material CR39) were used as substrates, which were cleaned ultrasonically in ethanol and dried in air before being put into the vacuum chamber. DLC films were prepared by pulsed laser deposition using graphite target and KrF excimer lasers ($\lambda = 248$ nm, $\tau = 20$ ns) [10–12]. The laser beam was focused onto a high purity graphite target with energy density of 4, 6, 10 and 12 J·cm⁻², and repetition rate of 10 Hz. The lens was at a distance of 45 mm from the target. The DLC films were created at room temperature of the lenses. The base vacuum of the coating system was 5×10^{-4} Pa. The films were deposited in argon ambient (0.25 Pa). Deposition parameters are summarized in Table 1.

Table 1: Conditions for preparing DLC films on CR39 substrate.

Sample	DLC-1	DLC-2	DLC-3	DLC-4
NO	7 000	3 500	1 000	8 000
ED (J·cm ⁻²)	6	12	10	4
ALT (nm)	130	150	40	145

NO – Number of pulses;

ED – Energy density;

ALT – Approximate layer thickness

Characterization of properties

Optical transmittance

Transmittance was investigated by UV-VIS spectrophotometer UV-2600 (Shimadzu) from 200 nm to 1100 nm. Several parameters were compared, such as average transmittance in visible region; shorter wavelength cut-off (where the lens start to transmit light), and derivative from zero to maximum transmittance.

Wear resistance and friction coefficient

Wearability test was performed by Tribometr Pin-on-Disk (TRB³ – Anton Paar) with linear movement (trajectory was 8 mm). Chromium steel (Ball type: Ac 100 Cr6) testing ball with 6 mm diameter was used. Speed of the testing ball was 5.03 cm·s⁻¹, total testing length 10 m, used loads during tests were 0.25 N and 1 N. The tests were performed in dry conditions. The friction was determined from the test records. More can be found in the literature [13].

Results

Optical transmittance

Figure 1 shows the optical transmittance of two basic lens materials (mineral and plastic lenses). The transmittance of both lenses in the visible region is virtually the same, the only difference being the point from which they begin to transmit light. The higher this value, the higher the protection of the eyes from the UV radiation.

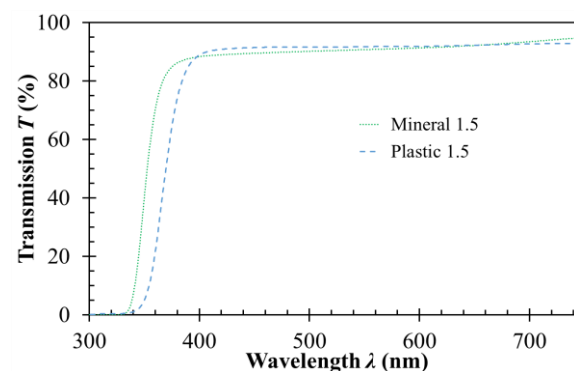


Fig. 1: The transmittance spectra of plastic and mineral spectacle lenses.

Other differences can be observed in case of plastic lenses with different refraction index (1.5; 1.56 and 1.6)—see Figure 2. The “starting” wavelength increases from 355 nm to 400 nm with increasing refraction index.

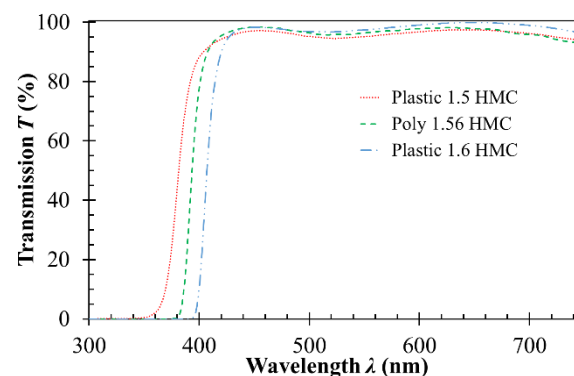


Fig. 2: The transmittance spectra of plastic spectacle lenses with various refractive indices.

Transmittance of DLC coated lenses is displayed in Figure 3. The layers DLC-1, DLC-2 and DLC-4 delaminated due to high thickness, while DLC-3 stayed undamaged. DLC-1, DLC-2 and DLC-4 data were rescaled to the same thickness as DLC-3 (40 nm) for this reason. The higher was the laser energy density at deposition the higher was the transmittance in the visible region of the spectrum.

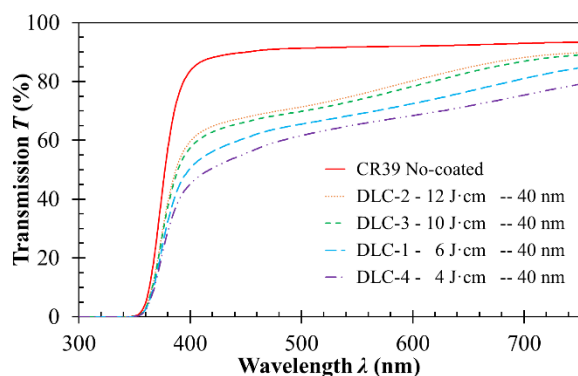


Fig. 3: The transmittance spectra of plastic spectacle lenses CR39 no-coated and CR39 with DLC films.

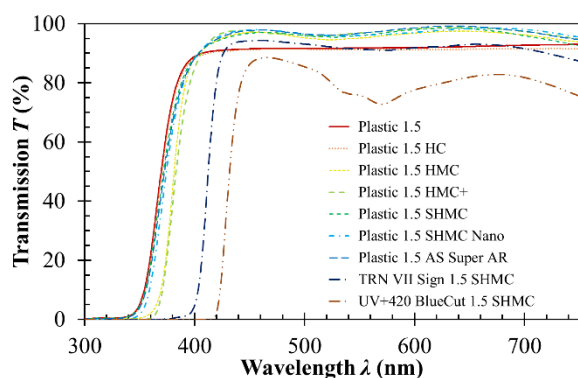


Fig. 4: The transmittance spectra of plastic spectacle lenses.

Figure 4 shows transmittance of different lenses (different base material and coating), but with same (1.5) refractive index. Lens UV+420 BlueCut 1.5 SHMC and TRN VII Sign 1.5 SHMC are starting to let the light in at the latest.

Wear resistance and friction coefficient

The durability and quality of the lens surface was evaluated by measuring the tribological states and observing the damage to the test bead and the lens surface using a microscope—see Figure 5.

Three different cases were observed during friction coefficient measurement when force of 1 N was applied, see Figure 5.

- upper curve in the Figure 5—the friction coefficient was low and sharply increased after some time (such as Plastic 1.5 HMC).
- middle curve in the Figure 5—the friction coefficient rose very slowly with increasing path (such as Plastic 1.5 Nano UV).
- lower curve in the Figure 5—the friction coefficient started a bit higher and levelled at lower value after some time (DLC-3).

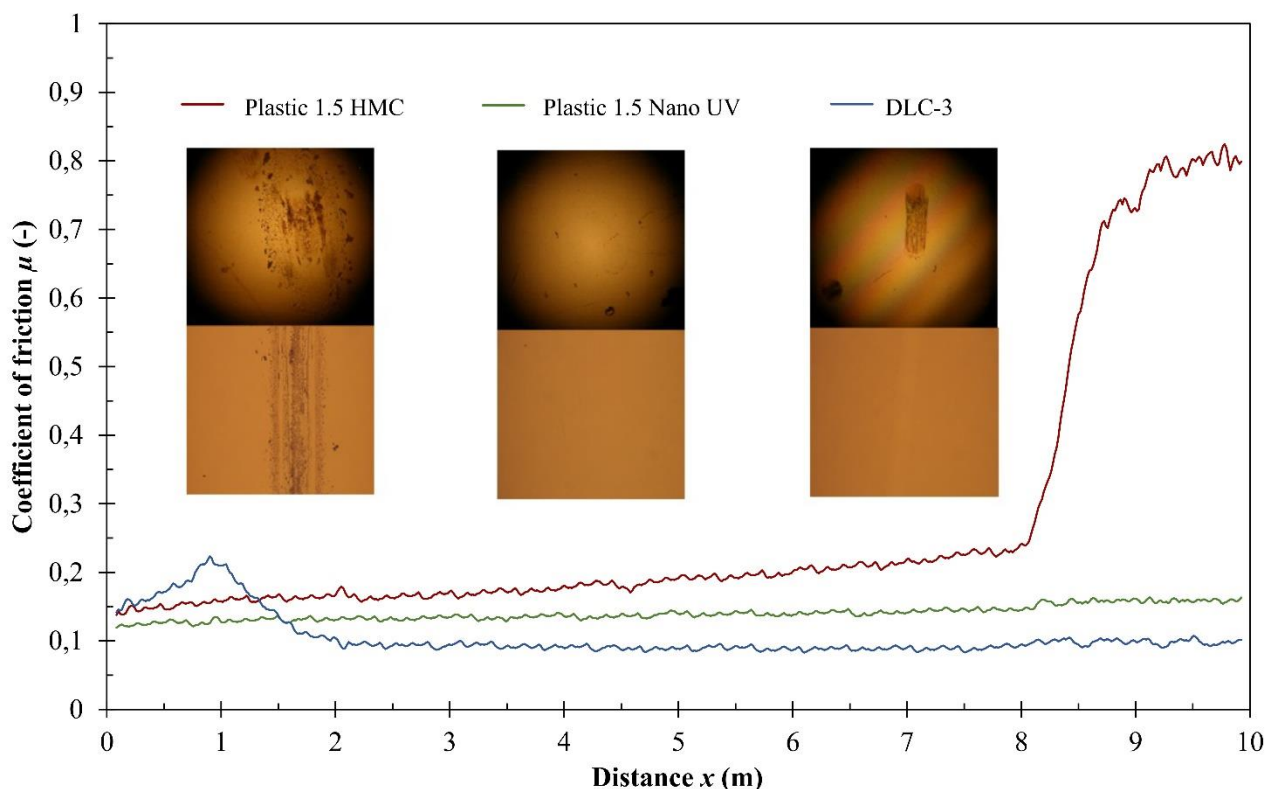


Fig. 5: The friction coefficient curves and the ball (upper) and lens (lower) wear (To better illustrate the trend, the data were averaged for each cycle).

Numeric values of curves shown above are displayed in Table 2, namely: the friction coefficient at the beginning of the measurement and before protective layer abrasion (in parentheses); position x , where a change in friction or abrasion occurred during 10 meters path length; the last column shows the friction coefficient

after the change in friction or abrasion and in parentheses at the end of the measurement.

The lens and ball damages were observed by microscope (100× magnification) after the measurement. Some of the protective layers were abraded and the base material damaged (The scratch width relates with damage intensity). For comparison see Figure 5 and Table 3.

Table 2: Detailed results of friction coefficient measurement using force of 1 N.

Type of lens	Friction coefficient μ (-) at measurement start (before abrasion or change in friction)	Position, where change in friction occurred x (m)	Friction coefficient μ (-) after change in friction – centre (at the end)
Mineral 1.5	0.143	1–2 (abrasion)	0.660 (0.751)
Plastic 1.5	0.194		(0.285)
Plastic 1.5 HC	0.150	0–1 (abrasion)	0.699 (0.744)
Plastic 1.5 HMC	0.191	8–9 (abrasion)	0.805 (0.805)
Plastic 1.5 HMC+	0.101		(0.133)
Plastic 1.5 SHMC	0.076		(0.093)
Plastic 1.5 SHMC Blue	0.134	4–6 (abrasion)	0.578 (0.640)
Plastic 1.5 Nano	0.072		(0.114)
Plastic 1.5 Nano UV	0.128		(0.159)
Plastic 1.5 SHMC Nano	0.053		(0.087)
UV+420 BlueCut 1.5 SHMC	0.143		(0.213)
DuralVision Platinum 1.5	0.229		(0.255)
EyeDrive 1.5	0.126		(0.140)
SV LotuTec 1.5	0.099		(0.195)
CR39 No-coated	0.119		(0.199)
DLC-3	0.111 (0.155)	0–2 (change)	0.099 (0.100)

Table 3: Evaluation of lens and ball damages after tribological tests using force of 1 N.

	Lens damage evaluation – scratch width	Ball damage evaluation
Mineral 1.5	Visible damage – 236 μm	Visible damage
Plastic 1.5	Visible damage – 59 μm	No visible damage
Plastic 1.5 HC	Visible damage – 318 μm	Visible damage
Plastic 1.5 HMC	Visible damage – 299 μm	Visible damage
Plastic 1.5 HMC+	Visible damage – 195 μm	No visible damage
Plastic 1.5 SHMC	No visible damage	Layer material deposited on ball
Plastic 1.5 SHMC Blue	Visible damage – 204 μm	Visible damage
Plastic 1.5 Nano	No visible damage	Layer material deposited on ball
Plastic 1.5 Nano UV	No visible damage	Layer material deposited on ball
Plastic 1.5 SHMC Nano	No visible damage	Layer material deposited on ball
UV+420 BlueCut 1.5 SHMC	No visible damage	No visible damage
DuralVision Platinum 1.5	No visible damage	Layer material deposited on ball
EyeDrive 1.5	No visible damage	Layer material deposited on ball
SV LotuTec 1.5	Visible damage – 211 μm	Layer material deposited on ball
CR39 No-coated	No visible damage	No damage
DLC-3	No visible damage	Visible damage

Discussions

The main finding of the study is that the properties of commercially available spectacle lenses are dependent on the material from which they are made and the surface treatment and that DLC as a lens coating is a suitable material because it can match or even surpass the properties of the materials used today. These results can help improve spectacles.

As previous studies shown [11, 12, 14], DLC layers are biocompatible and due to high hardness and high transmittance in visible and infrared regions they can be used for eye optics applications—spectacle lenses, contact and intraocular lenses. Smooth surface of DLC layers has a positive impact on cleanness of spectacle lenses, because the “nano” smoothness (roughness parameters around 1 nm) causes fewer dirt particles to stick to surface. In this paper, we studied transmittance and wear resistance of spectacle lenses with surface modification and DLC coated lenses fabricated by PLD method.

Optical transmittance

The transmittance of surface modified lenses is strongly dependent on the lens base material. We observed significant difference between mineral and plastic lens (refraction index of 1.5 for both)—see Figure 1. Mineral lens starts to transmit at approximately 335 nm and plastic at approximately 360 nm. It follows that plastic lenses generally have better UV protection than mineral lenses, which are hardly used anymore. A similar shift from 355 nm to 400 nm can be observed for lenses with different refractive indices (1.5; 1.56 and 1.6)—see Figure 2. As the index increases, UV protection increases, which is due to the lens material.

Figure 3 shows the effect of the energy density used in deposition on the transmittance of the lens. The higher the energy density the higher the transmittance. The DLC layer transmittance is dependent on sp^3 bonds content, which has been shown by our previous study [14]. The higher the sp^3 content the higher the transmittance. The CR39 lens with a DLC coating exhibits a similar trend in transmittance as CR39. The transmittance of the DLC coated lens is by 25% lower at 400 nm compared to the uncoated CR 39 lens and gradually increases to values close to 90% at 750 nm.

Figure 4 shows that the highest UV protection is provided by UV+420 BlueCut 1.5 SHMC and TRN VII Sign 1.5 SHMC. On the other hand, the highest transmittance is provided by lenses with additional antireflective coating (plastic HMC and SHMC). The transmittance of TRN VII Sign 1.5 SHMC lens corresponds to lens manufactured from 1.67 refraction index material. The best results were observed in case of UV+420 BlueCut 1.5 SHMC, which limits transmittance of blue part of spectra, that is starts to transmit light at 420 nm, see Figure 4. The result of many surface

layers is non-linear transmittance in visible part of spectra, compared to other lenses. Specifically, the transmittance is lower by 15% at 570 nm.

The results show that all materials have at least some UV protection. The mineral lens had the least, it started transmitting light at 335 nm. The highest was the special UV+420 BlueCut 1.5 SHMC lens (422.0 nm). Measurements have shown that the UV protection increases with a higher refractive index of the lens.

The derivative (rate of change) from 0% to the typical transmittance for a given lens is one of the other lens quality parameters. The larger the value, the better the separation of unwanted UV radiation. In this respect, the UV+420 BlueCut 1.5 SHMC, TRN VII Sign 1.5 SHMC and SHMC coated lenses performed best.

The last parameter investigated was the average transmittance from 400 nm to 750 nm, which was $90 \pm 5\%$ for all commercially available lenses and by 15% lower for the DLC coated lenses.

Wear resistance and friction coefficient

Figure 5 shows that three different cases were observed during friction coefficient measurement.

- upper curve in the Figure 5—the friction coefficient was low and sharply increased after some time, which indicated protective layer abrasion and start of measuring lens base material (such as Plastic 1.5 HMC). In this type of coating, the surface was not very durable and damage occurs very easily.
- middle curve in the Figure 5—here there was a very slow distortion of the lens surface and the ball, which resulted in a slightly increasing coefficient of friction (such as Plastic 1.5 Nano UV).
- lower curve in the Figure 5—the coefficient of friction first increased and then began to decrease. The increase is attributed to droplets forming as a side effect of PLD. The decrease was due to the removal of the droplets during the test and the formation of a graphitic slip layer.

The lenses with the highest wear resistance also exhibited the lowest friction coefficient (Plastic 1.5 Nano, Plastic 1.5 SHMC Nano a DLC-3). The hardness of the DLC layer is so high that there was damage to the ball but the layer remained intact. From this point of view, DLC layers are very suitable as protective layers for spectacle lenses. Their only disadvantage is the drop in transmittance mentioned above.

Conclusion

In this study, the optical and mechanical properties of currently available spectacle lenses were investigated and a surface treatment (DLC) with better tribological properties and slightly worse transmittance was applied.

The lens transmittance is strongly influenced by the base material and type of surface treatment (this includes UV light protection):

- Mineral materials transmit light at lower wavelength than plastic ones.
- Materials with higher refraction index transmit light at higher wavelength.
- Specially modified lenses, such as UV+420 BlueCut 1.5 SHMC, transmit light at higher wavelengths, but transmittance is lower in visible region.
- Surface treatments such as anti-reflective coatings increase the transmittance in the visible spectrum.

Wear resistance is strongly dependent on the surface modification. The best results were observed on materials with low friction coefficient, in which no damage was observed and thus no transmittance impairment occurred. The DLC layers performed best in this respect, where the coefficient of friction at the end of the measurement was the lowest and there was no observable damage to the lens. The tribological behaviour of the DLC layers can be attributed to the graphitic interface layer that is formed during friction.

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