

Impact of PMMA/ZnO Nanocomposite on the Polychromatic Performance of Contact Lens

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Abstract

Globally, many people suffer from refractive errors. Using the nanocomposite materials with a high Abbe number (vd) and a high refractive index (RI) has made an excellent promise for compound contact lenses (CLs) in correcting vision errors and as another solution to the discomfort of eyeglasses and (LASIK) surgery. In this work, the nanoparticles of Zinc oxide (ZnO-NPs) are used as a promising material to increase the reflective index and the high transparency of a poly-methyl methacrylate. The casting method was used to prepare ZnO-NPs and PMMA/ZnO CL at a concentration of 2 and 5% wt. The impact of contact lens on natural eye vision is evaluated using an optics design software ZEMAX. The eye performance was assessed using modulation transfer function (MTF), image spot size plot, the encircled energy, and image simulation. The results display that the PMMA/ZnO CL improved the vision quality at the white light. In addition, PMMA/ZnO is a promising filter for eye UV protection.

Keywords: PMMA/ZnO, contact lens, polychromatic vision, low dispersion material, high refractive index, modulation transfer function

1. Introduction

Nanotechnology is involved in many and varied fields, the most important of which is solar energy[1,2], contact lenses[3,4], and intraocular lens implants[5-6]. However, some peoples prefer to wear contact lenses instead of glasses to correct vision defects due to their lightweight, comfort, affordability, and providing excellent vision [7,8].

The selection of polymers or materials used in contact lens manufacturing comes in two categories: Organic glass (polymeric material or optical plastics) and inorganic glass (optical glass). Nanocomposition might increase polymer characteristics. Using titania-PMMA nanohybrids produce a high transparency thin films in the visible range, a high refractive index up to 1.780 was achieved, lowering the Abbe number to 31.80 for 40wt% TiO₂ composites [9-12]. A nanoparticle thin film that is made of TiO₂ and poly(epichlorohydrin and bisphenol-A) nanocomposite produced high transparency and (1.58-1.81) refractive index within the visible region as the TiO₂ concentration increased from 0 to 80 wt % [13]. Researches [14] adding a high refractive index additive to the di-ethylene glycol di(allyl carbonate) led to polycarbonate with a higher refractive index (1.49–1.66) and a lower

Abbe number (26–37). An organic polymer PMMA has been synthesized with zirconium oxide nanocrystal for getting polymerized material PMMA/ZrO₂ of over 95 % visible light transmittance and increment in refractive index to 1.534 in the case of using 38.8 wt % ZrO₂ content[15], PMMA/ZrO₂ utilized for improving the merits of the optical device. Optical properties can also be enhanced by obtaining metal-containing optical resins with an enhanced refractive index of up to 1.60 with an Abbe number greater than 30[16]. Furthermore, a chain of ZnS/PVP/PDMAA hydrogel nanocomposite contains ZnS nanoparticle within the range of (30-60) wt % to realize transparent nanocomposites, with (1.58-1.7) and (1.38-1.46) refractive index in the dry state and the hydrated state, respectively [17].

The optical polymers assisted researchers in improving contact lens performance, as Jung-San Chen and his colleagues did for PDMS-CLs. They discovered a method to avoid protein adsorption through sub-merging the lens in poly(ethylene glycol) methacrylate PEGMA [18]. Norbert Hampp and a group of researchers utilized TiO₂-NPs to increase the refractive index regarding poly-HEMA from 1.44 to 1.527 in the visible region [19].

The polymer has good optical transparency (90% transmittance) and a high Abbe number of 54, making it adequate for CLs and IOL fabrication. Researchers developed hydrogel nanocomposite ZnS NPs with polymerizable-group-capped ZnS NP, which copolymerizes with a mix of acrylic monomers of N, N-dimethyl acrylamide (DMA), 2-hydroxyethyl methacrylate (HEMA), methyl methacrylate (MMA) or glycidyl methacrylate (GMA). The resulting polymer has a visible transmittance of more than 92% in the visible range and a refractive index range of 1.652 and 1.751[20].

Also, diaphanous nanohybrid polyvinyl alcohol/Zirconium dioxide (P.V.A./ZrO₂) was prepared with different ZrO₂ concentrations (0 ~ 80 wt %); ZrO₂ the film has high transparency qualities and a (1.528 to 1.754) refractive index range [21]. Peili Zhao (2018) has suggested a new polymerizable-group capped ZnS NP Synthesis and ZnS-containing poly(HEMA-DMA) fabrication to get a high refractive index inorganic-organic hydrogels (1.38-1.45) as the ZnS content varied (30-60) wt % practical in CLs applications [22]. All non-hybrid polymers obtained and developed by adding other nanoparticle compounds have shown the same behavior. There is an increase in refractive index as nanocomposite content in the polymer increases[23]. At the same time, the Abbe number begins to decrease to show different behavior. In this work, ZnO-NPs doped PMMA with different concentrations were used to manufacture contact lens. The performances of this contact lens were evaluated based on the ray-tracing Zemax program. Compression between the healthy human eye (without contact lens) and the eye with PMMA/ZnO contact lens was done depending on the Liou and Brennan eye model (LBEM). Furthermore, the criteria used to qualify the eye image are the modulation transfer function (MTF), the image spot size (RMS.), the encircled energy (EE), and the image simulation.

1.1 The Analysis Parameters

1.1.1 The Modulation Transfer Function (MTF)

The lens's MTF is considered as a measurement of its capability for transferring contrast from an object to an image at a specific resolution. For an aberration-free system, the contrast of a sinusoidal pattern is [24]:

$$MTF(v) = \frac{2}{\pi} (\varphi - \cos\varphi \cdot \sin\varphi) \quad (1)$$

$$\varphi = \cos^{-1} \left(\frac{v}{v_c} \right) \quad (2)$$

$$v_c = \frac{1}{\lambda \cdot (f/\#)} \quad (3)$$

At a particular spatial frequency value, MTF will be zero; such spatial frequency (v_c) value is referred to as the cut-off frequency ($v_{cut \text{ off}}$). In equation (3), the cut-off frequency is measured in Cycles/mm at a specific wavelength (λ) on the retina. Thus, $f/\#$ or F-number is the lens's focal length (f) to its pupil diameter (PD).

1.1.2 The Root Mean Square (RMS)

The spot diagram depicts the distribution of rays on the image plane and is used to visualize the influence of aberration on image quality. The RMS is a measure for determining the size of an image's blur [25]:

$$RMS = \sqrt{\frac{\sum_{i=0}^N r_i^2}{N}} \quad (1)$$

Where N indicates the total number of rays traced, r_i refers to the distance between two points.

1.1.3 Encircled energy (EE)

Encircled energy (EE) refers to a measure of accumulated energy in an optical image. EE is indicated in the following formula [26]:

$$EE(z) = \int_0^{2\pi} \int_0^1 PSF(r) r dr d\varphi \quad (2)$$

$$PSF = \int_{-\infty}^{\infty} f(x) e^{-2\pi v x} dx \quad (3)$$

Where PSF represents the point spread function which is Fourier transform of pupil function $f(x)$; and it is a measure of the size and shape of the point source image.

2. Materials and Methods

2.1 PMMA-ZnO preparation

The samples of PMMA/ZnO were made using the identical procedures as in [27]. First, a 25 wt% solution of PMMA has been made by dissolving it in 40 mL of chloroform and stirring it at room temperature for 1.5 hours with magnetic stirring. After that, the PMMA solution was mixed with 2mL of TPM-ZnO solution for 15 minutes with magnetic stirring. The final solution has been poured into the model, and the solvents fully evaporated, yielding a transparent PMMA/ZnO nanocomposite film. Furthermore, polymerization was conducted for 12 hrs at 70°C with continuous shaking, yielding a transparent sample.

2.2 Optical modeling

An optical ray-tracing Zemax program was used to model, first, a healthy human eye without contact lens based on the LBM and, secondly, for an eye with a PMMA/ZnO contact lens. The simulations have been carried out at wavelengths of 510, 470, 610, 555, and 650 nm, with weights of 0.503, 0.091, 0.503, 1, and 0.107, respectively, in the white vision spectrum. Table 1 shows the optical parameters of the LBM model, whereas table 2 shows the contact parameters. The posterior and anterior surfaces of the cornea have been chosen as aspherical surfaces To eliminate the spherical aberration. The iris pupil is 4 mm in diameter and 0.50mm nasally decentered to the visual axis [28].

3. Results and discussion

The contrast transmission produced by the healthy eye (without CL) and the treated eye (with CL) was observed from the MTF metric: In addition to the spot diagram RMS, and geometric EE (as a function of radius from centroid).

3.1 UV-Vis absorption Spectrum

The optical transmittance spectra have been recorded using a Perkin-Elmer Lambda 19 spectrophotometer. The UV-vis transmittance spectra related to pure PMMA film and PMMA/ZnO nanocomposite film, respectively, are

shown in Fig. 1. Compared with pure PMMA, the visible light-transmitting efficiency of PMMA/ZnO film drops by just around 10% at a wavelength of 600 nm. The homogeneous hybrid structure is responsible for the PMMA/ZnO film's exceptional transparency in a visible band. PMMA/ZnO film has a transmitting efficiency of about zero% in the UV band up to 340 and 360 nm for wt=2, and 5 % respectively, suggesting that this hybrid film has better UV-prevention capability than commercially available UV-blocking contact lenses. The reported increased transmittance for the produced ZnO - PMMA nanocomposites is significantly higher than that observed in earlier studies [23,29].

3.2 The Polychromatic MTF

The MTF criteria describe the contrast of the retinal image. The lens must have a contrast of more than 50% (0.5) at 15 cycles/mm for optimal image quality. The polychromatic modulation transfe (MTFp) simulations and the Chromatic (MTFc) have been acquired and compared with the natural eye (without CL) results (Liou model). Figure 2, shows that the MTFc is higher than the MTFp for all cases. In addition, the MTF for eye with the hybrid PMMA/ZnO CLs exhibited high image contrast at mono- and polychromatic vision for all spatial frequencies (0-30 cycle/mm). This result proves that the refractive index change affected the eye image performance due to adding small amounts of dopant ZnO NPs.

Table 1: The Liou-Brennan eye model construction parameters

Surface No.	Medium	Radius of Curvatures (mm)	Conic constant	Thickness (mm)	Refractive index @555nm
1	Cornea	7.71	-0.18	0.50	1.376
2	Aqueous humer	6.40	-0.60	3.16	1.336
3	1 st surface Crystalline lens	12.40	-.94	1.59	$n_a(z, r)$
4	2 nd surface Crystalline lens	∞	-	2.43	$n_p(z, r)$
5	Vitreous	-8.10	0.96	16.27	1.336

Table 2: Construction data of polymeric PMMA/ZnO

Material	CL Front Radius [mm]	CL Back Radius [mm]	CL Front Thickness [mm]	CL Back Thickness [mm]	RI	γ_d
BHESP/PA/Al	7.748	7.8	0.1	7.8	1.63	53
Conic = 0.035, PD = 4 mm and F.O.V. = 5 degrees						

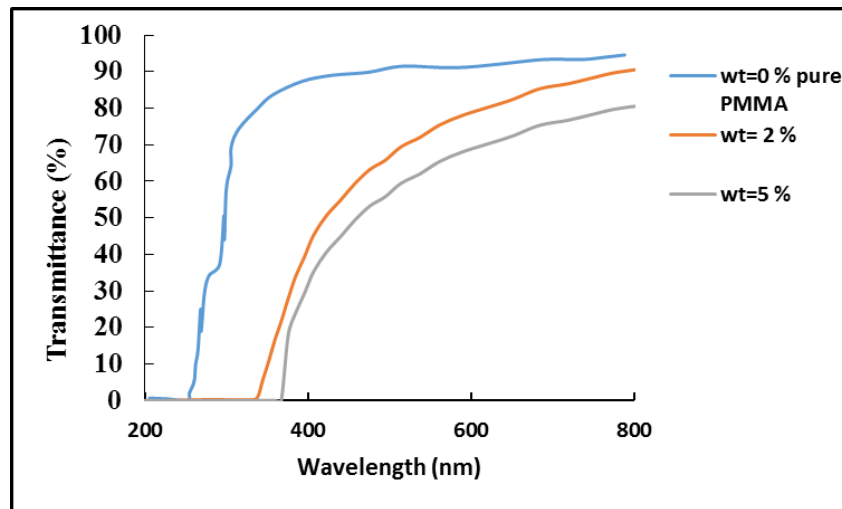


Fig. 1: UV-vis absorption spectrum for pure PMMA, and PMMA-ZnO NPs (40 nm) and 2 and 5% wt of ZnO-NP

Figure 2 indicates that at low spatial frequency (15 cycles/mm); for natural eye the MTFp value was decreased by 10% compared with MTFc. While there was no decrease by in the eye with PMMA/ZnO CL. Also, it is clear that at high frequencies (25 cycles/mm), the MTFp degrade by 32% and 2% compared with MTFc for the natural eye and with PMMA/ZnO contact lens. Therefore, the use of PMMA/ZnO contact lens improved the polychromatic vision above 17% and 41% at 15 and 25 spatial frequencies, respectively— this enhancement is owing to its excellent refraction characteristics and high visible light transmissivity. The existence of spherochromatic aberrations in the eye can be blamed for the MTFp reduction[24]. The chromatic aberration is caused by dividing white light into its wavelength components and focussing

on various focal points, dependent on the refractive index. In the case when PMMA/ZnO CL is wearing on the eye, such aberrations are decreased.

3.3 Spot Diagram

Figure 3 shows the spot diagrams RMS of an LBEM eye at chromatic light ($\lambda=550$ nm) and at polychromatic visual light (8.854 and 9.044 μm), respectively. While for the treated eyes with PMMA/ZnO CL are (5.991 and 6.001 μm) for monochromatic and white vision, respectively. The CLs reduced the spot sizes and their RMS by over 30% for white vision than the eye without CL because chromatic aberrations are reduced due to the high CL refractive index.

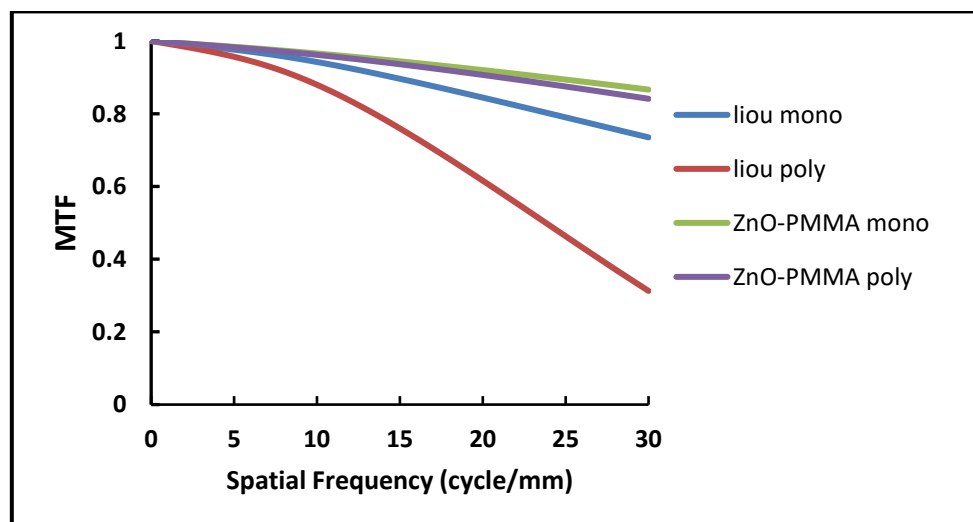


Fig. 2: MTF of human eye without CL (blue-mono; red-poly), and with PMMA-ZnO CL (green-mono; violet-poly):. Pupil diameter is 4 mm

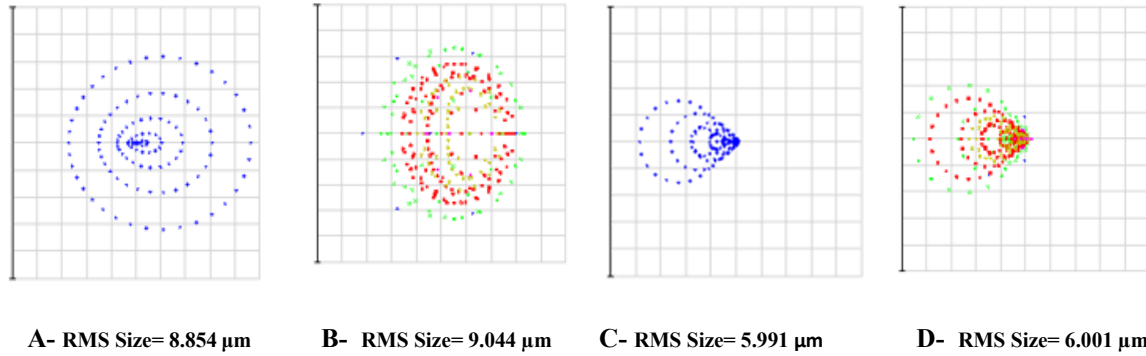


Fig. 3: The Retina image spot size for eye ; without CL- mono (a), (b) without CL- poly (b), with PMMA-ZnO CL- mono (c), and (d) with PMMA-ZnO CL- poly(d)

3.4 Encircled Energy (EE (z))

It is shown from figure 4 that the encircled energy curves have different slopes. Since the maximum slope means a small blur spot size (small aberrations), Hybrid ZnO with PMMA contact lens reduces the aberrations and spot size. The R 80% (the radius (in mm) of 80% encircled energy) is

shown in figure (5) for commercial (LBM) and ZnO doped PMMA contact lens in chromatic and white light. The R80% is (10.6 and 11.2 mm) for the eye without CL which means that the energy on the retina is reduced by using white light. Figure 5 shows that the R80% is (5.4 mm) for both mono- and polychromatic light, which refer to the benefit of using PMMA/ZnO CL.

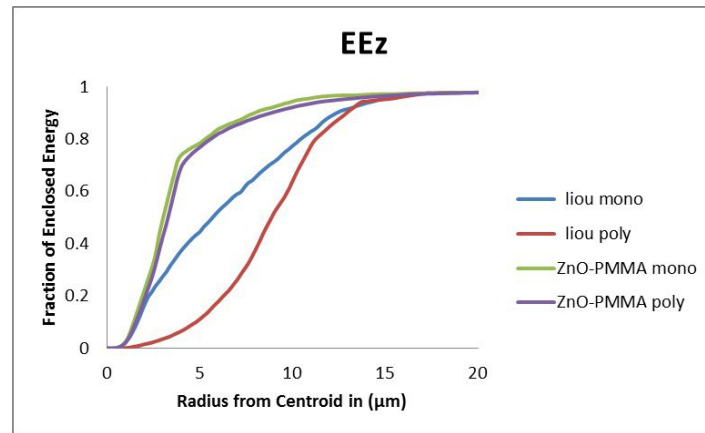


Fig. 4: Encircled energy EE of the human eye image; without CL mono (a), without CL poly (b), with PMMA-ZnO CL mono (c), with PMMA-ZnO CL(d): Pupil diameter is 4 mm

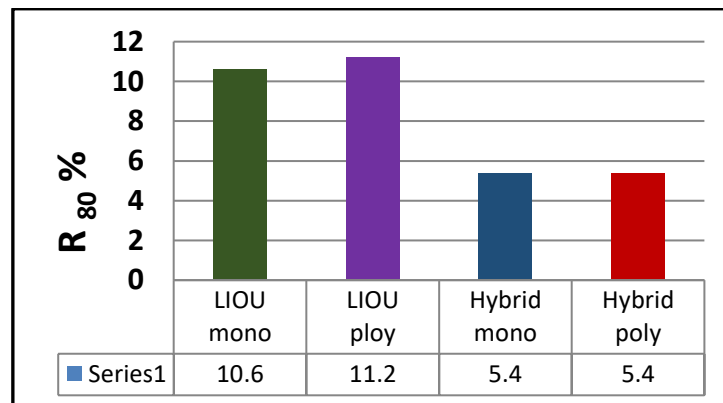


Fig. 5: The R₈₀% for the encircled energy human eyes image; without CL mono(a), without CL poly(b), with PMMA-ZnO CL mono(c), with PMMA-ZnO CL poly(d): Pupil diameter is 4 mm

3.5 Image Simulation

The retina images are shown in Figure 6. The image with ZnO-PMMA CL revealed the best image clarity for both chromatic (C) and polychromatic (D) light sources. The ZnO-PMMA CL reduces the spherochromatic aberration, and improves the image (C and D) compared with the image for the eye without CL ((A and B). There was a noticeable improvement in the image contrast, which proved what has been discussed in the MTF analysis. Only the highest refractive index CL carried out the best image correction.

4. Conclusions

Contact lenses made of polymers doped with nanomaterials are promising tools for vision correction. The results obtained from lenses

consisting of PMMA/ZnO are encouraging and essential for vision in mono-polychromatic light. The current study showed that contact lenses had improved the performance of the eye to be close to the healthy eye and better than lenses made of pure PMMA polymer. The use of the anterior aspherical surface of the CL has reduced the value of spherical aberration. While the presence of ZnO nanoparticles in the PMMA polymer, which has a high RI value of approximately 1.63, low dispersion ($vd = 53$), and high transparency in the visible range (T larger than 80% at 600 nm) was beneficial for reducing chromatic aberration at polychromatic light vision. Another significant result is that PMMA/ZnO CL can be used as a filter to protect the human eye from damage caused by ultraviolet radiation (less than 340 and 360 nm) for 2, and 5% wt ZnO-NPs concentration respectively.



Fig. 6: Image simulation (a) Liou-mono (b) Liou poly, (c) with PMMA-Zn-CL mono, and (d) with PMMA-ZnO-CL poly

5. References

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