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Investigation of a High Refractive Index Polymer for Contact Lens Applications: Overview

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Abstract: An overview of high Refractive Index (RI), high abbe number (low dispersion) (ν_d) and high transmissivity optical plastics improved and used to get a perfect Contact Lens (CL) material and design, this review gathers optical plastics developments to choose the desired polymer in Cls applications. High performance CLs can be made of polymers with high transparency nanocomposites because of the need for optical plastic merits such as light weight, transparency, biocompatibility, the ability to modify its refractive index and Abbe number. Doping with nano-particles can be considered as a good candidate in CLs fabrication due to its rule in increasing the RI, ν_d and light transmittance higher. This study shows the evolution of polymer properties used in optical applications and focuses on RI, ν_d and transparency of the optical plastics that can be employed in the CLs fabrication or enhancement of them.

Key words: Contact lens, high refractive index, abbe number, hybrid materials, fabrication, enhancement

INTRODUCTION

Most people with visual impairments have resorted to the use of Contact Lenses (CLs) which were invented over 125 years ago due to their light weight or to avoid being subjected to LASIK surgery, to reduce distortion, refraction errors or astigmatism. August Muller, the medical student who was suffering from high myopia inserted his preformed CLs for only half an hour to feel uncomfortable when wearing them. Corneal CL was described by Feinbloom who proposed a scleral CL made of a glass part surrounded by a circular polymeric portion which was developed and amended then by Tuohy (1950). Lenses that made of glass are thick, impractical and impermeable to oxygen to the cornea for these reasons and after a lot of studies that confirmed the importance of oxygen passage to the cornea, the glass replaced by plastic. These lenses have the ability of bending the parallel light rays and focus them into the right focal point on the retina.

Hard (rigid) Cls: Rigid CLs are usually clear, have light blue, green or brown tint. Made of Polymethyl Methacrylate (PMMA) of RI:ν_d 1.49:59, light weight, high transparency, high resistant to scratching, a small size Cls and safe to the eye but it does not allow the permeability of water and oxygen (DK) (Koruga *et al.*, 2013) as Fig. 1. Rigid CLs tend to change the shape of cornea which makes it difficult to determine the patient's prescription to use after wearing CLs for one day.

Soft (hydrogel) CLs (1960s): Hydrogel CLs materials are fabricate of stable solid optical polymer component that

(a) (b)

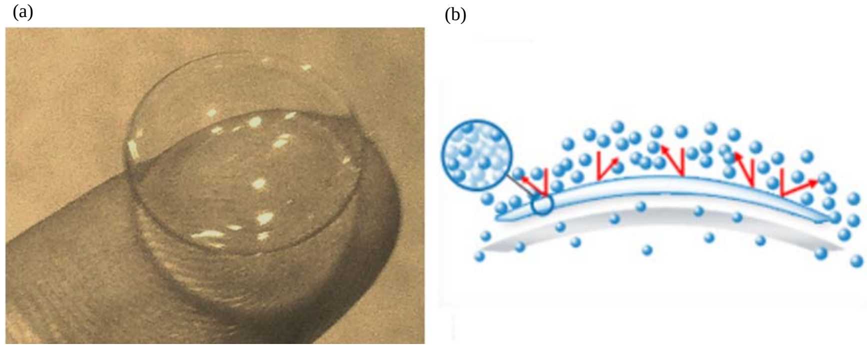

Fig. 1(a, b): Hard Cls made of PMMA, DK is oxygen permeability = 0

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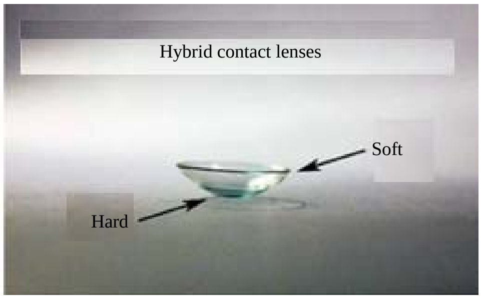


Fig. 2: Hybrid Cls consist of two regions the center area made of a hared polymer surrounded by a soft polymeric structure

can bind with water. Soft lenses are made up of polymers that its molecules are capable of absorbing water such as Hydroxy-Ethylmethacrylate (HEMA). Most of these lenses materials are copolymers. Soft CLs have been patented in 1960s by Wichterle (1960), they are more comfortable for longer periods of usage but its water absorbance making it brittle and may cause eye infection. CLs made of poly (2-Hydroxyethyl) Methacrylate (pHEMA) provides great hydrophilicity but the oxygen permeability is not great.

Rigid Gas Permeable CLs (RGP) (1978): The first RGP lenses were introduced in 1978. Made of material with molecular that permits the Oxygen (O_2) and Carbon dioxide (CO_2) permeability but no water content. It was made up of a silicone-incorporated monomer to increase Dk (Walker, 1992). This process worked well by increasing the proportion of silicon content or by producing cellulose acetate butyrate, pure silicone, Silicone Acrylate S/A (Siloxymethacrylate copolymer) and Fluoro-Silicone Acrylate F-S/A to increase the surface wettability and lens Dk. In attempts of reducing protin deposition, studies have proved that F-S/A CLs deposit less protein than that made of S/A while maintaining surface wettability and high Dk rates (Bark *et al*., 1994).

Hybrid CLs (1990s): Hybrid Cls (gas permeable and HEMA copolymer composition) became productive in the 1990s; they are designed in such a way that the central zone made of material of high oxygen permeability surrounded by hydrogel area as shown in Fig. 2, this kind of CLs is hard because of their rigidity and comfort to the eye as the soft lenses (hydrogel CLs) (Schifrin and Rich, 1984).

POLYMERS WITH HIGH REFRACTIVE INDEX AND HIGH ABBE NUMBER

The selection of polymers or materials used in contact lens manufacturing comes in two categories: organic glass (polymeric material or optical plastics) and

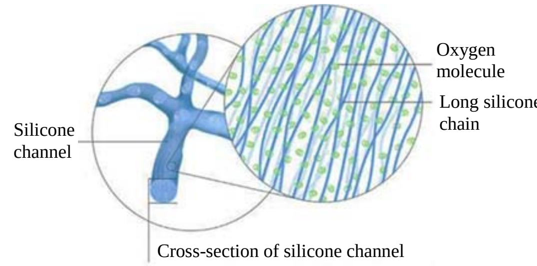


Fig. 3: Silicone based contact lens structure with long silicone chains

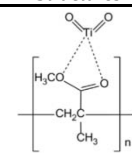
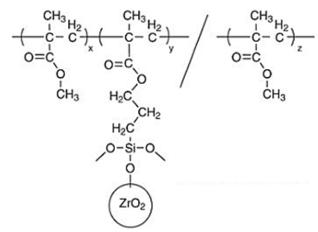
inorganic glass (optical glass). Investigation of optical polymers have been the subject of different excellent review papers (Musgrave and Fang, 2019). In the following text we discuss the development and improvement of polymers used in optical applications in terms of permeability, refraction and dispersion properties.

Silicone based polymers: The development of silicone hydrogels (long chains of Si derivatives as in Fig 3 has been consumed extensively by CLs manufacturers because it has a role in increasing gas permeability through silicone channels up to four times the gas permeability in conventional hydrogel CLs and maintaining the water content of the Cls (Gonzales-Meijome *et al*., 2014). Silicone hydrogel CLs have patented by Yuwen and coworkers made of a polymerizable silicone and hydrophilic monomers compound (Liu *et al*., 2017). Then Scott and colleagues invented a silicone based high RI rigid gas permeable CL built up from a liquid crystal layer sandwiched between two rigid polymer layers (Kennedy *et al*., 2018). The two previous CLs patents have an improved gas permeability and are appropriate to the eye tissues.

Recently, two CLs made of silicone hydrogel were integrated with Polyvinylpyrrolidone (PVP) to obtain a smooth water preserved CLs useful for people who are suffering from vision problems and working long time periods on computers (Schafer *et al*., 2018).

Polymethacrylates: Include, Polymethyl acrylate (PMA), PMMA, HEMA and pHEMA. Hybrid PMMA-dioxide systems have been reported widely (Table 1 and 2), focusing mostly on PMMA-SiO_2 (Soni *et al*., 2018), PMMA-TiO_2 (Fujita *et al*., 2015), PMMA-ZrO_2 (Gad *et al*., 2018). An organic polymer PMMA has synthesized with zirconium oxide nanocrystal by Otsuka and Chujo (2010) to get polymerized material PMMA/ ZrO_2 of above 95% visible light transmittance and increment in RI to 1.534 when applying 38.8 wt.% ZrO_2 content. Hybrid PMMA-ZrO_2 obtained by sol-gel deposition method resulted highly transparency ~90% and 1.57 RI at 532 nm (Alvarado-beltran *et al*., 2015).

Table 1: Chemical properties of high-RI and high-vd polymers used in contact lens applications

Common names	Polymer abbreviations	Chemical formulas	Structures	References
Titania-PMMA	TiO_2-PMMA	TiO_2-$(C_5O_2H_8)_n$		Fujita *et al*. (2015)
Poly (Methyl methacrylate)/ Zirconium Oxide	PMMA-ZrO_2	ZrO_2-$(C_5O_2H_8)_n$		Otsuka and Chujo (2010)

TiO_2-PHEMA hydrogel TiO_2-PHEMA hydrogel

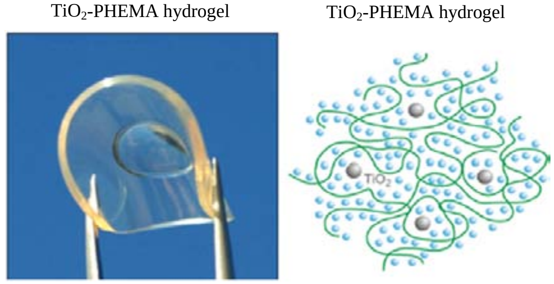


Fig. 4: TiO_2-pHEMA hydrogel possess good flexibility (Reinhardt *et al*., 2016)

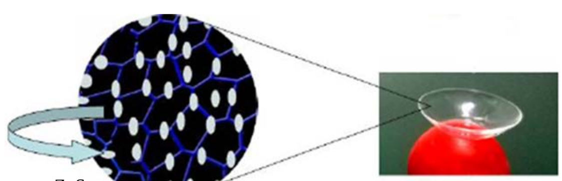


Fig. 5: ZnS-inorganic hydrogel CL (Zhao *et al*., 2018)

In 2014, PVA-TiO_2 and PMMA-TiO_2 nanocomposites exhibited light transmittance between 80 and 90%, they were prepared by Sugumaran and Bellan (2014) and realized good optical merits of (1.6 and 2.3) RI. (TiO_2/PMMA) inorganic-organic polymer has prepared by Masato Fujita and coworkers; this thin film presented a high transmittance 89% and RI of (1.86) when the TiO_2 nanoparticle contents about 20 vol.% (Fujita *et al*., 2015). Reinhardt *et al*. (2016) have investigated a flexible TiO_2-pHEMA hydrogel (Fig. 4) that high transparency in the visible range when it is applied in optical applications, high ν_d of 54 and RI = 1.527 with an excellent transparency ~90% transmittance (Reinhardt *et al*., 2016), this nanostructure is therefore an attractive material in optical application that required high visual performance.

Table 2: The optical characteristics of high-RI and high-ν_d polymers used in contact lens applications

Polymer abbrevations	Transmittance (%)	RI	ν_d
TiO_2-PMMA	89	1.780	31.8
ZrO_2-PMMA	95	1.534	-
TiO_2-pHEMA	90	1.527	54.0

Vander work has discussed the PMMA relevancy as scleral lenses. Also, grading PEG onto PMMA is seen as a "prosthetic eye" replacement (Ko *et al*., 2017).

Zinc based polymers: According to Sung and Kim proposal, UV-block hydrogel CLs (78~90% transmittance in visible region) can be produced by inserting Zinc Oxide (ZnO) nanoparticle in addition to vinyl pyridine to MMA, HEMA and N-Vinylpyrrolidone (N-VP) blend to take out (1.429~1.450) RI polymer from this polymerization process (Sung and Kim, 2013). Incorporation of PVP and moisturizing agents into soft CLs has changed the surface wettibilty. These agents may results increased comfort and enhanced the stability of tear film (Fig. 5).

On the other hand, organic-inorganic Zinc bis (Allyl-Dithiocarbamate) (Zn $(ADTC_2)$) composed of allylamines, zinc nitrate and carbon disulfide were prepared by using Zn $(DADTC)_2$ and Zn $(APDTC)_2$ content of 18 and 30 wt.%, respectively; the resultant polymer characterized by high flexibility and high transparency to achieve (1.71 and 1.67) RI (Nagayama and Ochiai, 2016). Zinc also used extensively to prepare nanoparticle antibacterial coatings applied on CLs surfaces (Tuby *et al*., 2016), also the hybrid ZnO/PMMA polymer provides a colorless film of (1.6) RI which can be considered useful in such applications (Wang *et al*., 2017). ZnS nanoparticles have employed to obtain polymerized nanocomposite grafted with ZnS where a copolymerization process with a mixture of N, N-dimethylacrylamide (DMA) and (HEMA) or Glycidyl Methacrylate (GMA) or Methyl Methacrylate (MMA), the produced polymer exhibits a transmittance above 92% in visible region and RI range of 1.652 and 1.751 after changing ZnS content from 33.4-50.3 wt.%

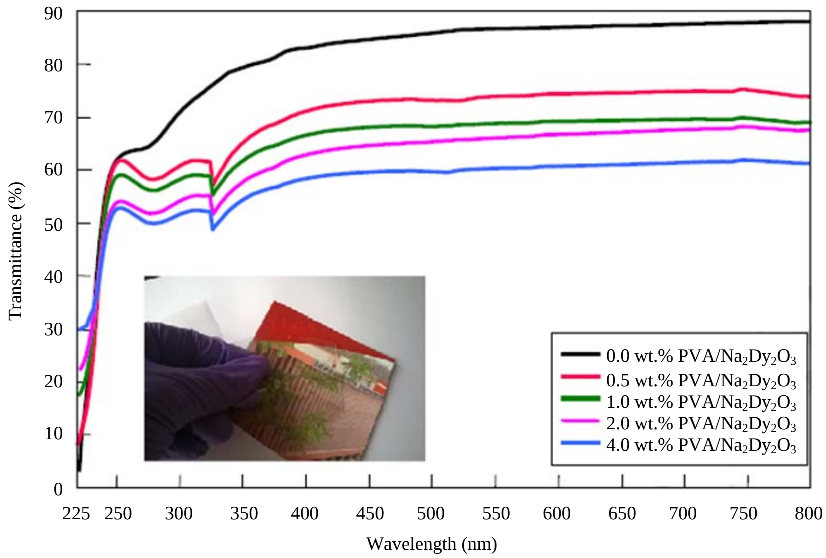


Fig. 6: Effect of $Na_2Dy_2O_4$ content (wt.%) on ($PVA/Na_2Dy_2O_4$) transmissivity

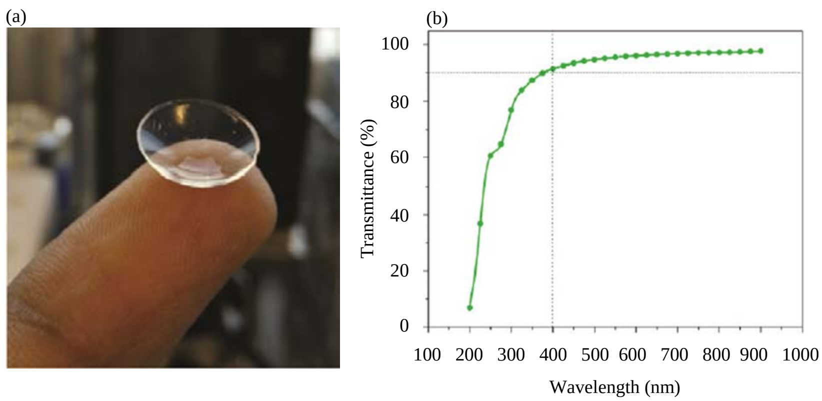


Fig. 7(a, b): PVA hydrogel CL and its light transmission (%) data (Tummala *et al*., 2016)

(Xu *et al*., 2018). Zhao *et al*., (2018) has suggested a ZnS-inorganic hydrogel CLs (Fig. 5) by copolymerizing ZnS-polymerizable group with HEMA monomer to get RI with a range of (1.38-1.45) as the ZnS content varied from (30-60) wt.% (Zhao *et al*., 2018).

Poly (Vinyl Alcohol) (PVA): Highly transmittance about 97% can be achieved by PVA utilization. Nanocomposite thin film, poly(vinyl alcohol)/Sodium Doped Dysprosia ($PVA/Na_2Dy_2O_4$) has developed by Shilpa and coworkers to obtain high transparency ($PVA/Na_2Dy_2O_4$) at (4 wt.%) of $Na_2Dy_2O_4$ nanofiller. Figure 6 explains the influence of $Na_2Dy_2O_4$ content variation from (0-4) wt.% on optical transmittance, the RI rises up to (1.9) and ratable ν_d (Shilpa *et al*., 2017). Recently, diaphanous nanohybrid Polyvinyl Alcohol/Zirconium dioxide (PVA/ZrO_2) was prepared with different ZrO_2 concentration values (0~80) wt.%, ZrO_2 film has highly transmittance and1.528 to 1.754 RI range (Xia *et al*., 2018). PVA hydrogel material was the topic of investigation in the 1990s. In addition, Polyethylene Glycol (PEG) surface coating has invented by Imafuku (2014) to improve the Si-based CLs hydrophilicity. Low cost, high wettability and bioavailability PVA hydrogel make it relatively important to hydrogel CLs industry compared with silicone and HEMA hydrogels (Fig. 7).

CONCLUSION

The first material used in CLs fabrication was heavy, non-wettable, rough and uncomfortable when wearing them and don't allow the oxygen to through to the cornea, so, researchers resorted to employ plastic materials where they started with PMMA that had replaced by another polymer nanocomposites because of unsuitability to wear because it prevent water and oxygen to transmit. Choosing of the suitable polymer for contact lens fabrication based on specific characteristics such as high-RI, high-ν_d, gas permeability, high transparency within the visible spectrum, nanocomposite content, suitability with eye tissue and scratching resistance to get the desired image quality when wearing them.

After a brief review of polymers characteristics (copolymers, homopolymers and organic-inorganic). As long as it is possible to change polymeric optical properties by changing the nanoparticles content in every kind of polymers, then it is possible to change polymers properties according to the required purpose ophthalmology applications. Choosing the suitable Cls for wearing is limited by the ocular, system consideration and patient eye noncompliance. Most patients can wear CLs from 10-12 h a day.

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