A Review of the Development and Evolution of Contact Lenses Materials

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Abstract: Contact lenses is a type of modern treatment for abundance of ophthalmic disfunction. With over 150 million global utilizers these days, the demand for contact lenses is massively. Four major contact lenses' materials in the market currently are silicone-based hydrogel, hydrogel, PMMA (polymethyl methacrylate) and RGP (rigid gas permeable). To meet the abundance demand of consumers, each material have their different characteristics. The materials' developments, evolution and applications are discussed in this review, along with their pros and cons on both chemical and physical properties.

1. Introduction

The ascending tendency of people suffering from eye disfunction or oculopathy has been a common phenomenon in the modern society, and therefore the massive needs of eyesight correction, treatment, and other practical solutions have emerged.

Among all the solutions, wearing glasses, especially contact lenses, has become one of the major choices over 150 millions of worldwide consumers[1]. Possessing an estimated value of around $9 billion with a two-to-three points of growth rate in 2019 all over the world, the market of contact lenses has experienced a rapid development and customers' requirements on the quality and cost-effectiveness of contact lenses have increased simultaneously.

In order to meet the needs of market, manufacturers have improved their manufacturing techniques, to attract different groups of consumers, chemically and physically. Various kinds of properties, such as the oxygen permeability and water containing, have been continuously improved, and different functions, covered from cosmetic contact lenses to the medical ones, have been developed.

The history of contact lenses can be traced back to the year of 1508, when Leonardo da Vinci first introduced his paper titled *codex of the eye* [2].

Over hundreds of years of attempting and improving, the first hybrid contact lenses composed of glass and plastic came out in 1936 [3], followed by the invention of non-gas permeable polymethyl methacrylate (PMMA) lenses during 1940s [4-7] and massive production in 1960s [8]. However, the major disadvantage about poor air permeability of PMMA has become a non-negligible problem to users of that time, so from 1970s to 1990s, a variety of gas-permeable lenses were developed to overcome this drawback, all these sets of material can be called as rigid gas permeable, also known as RGP materials.

Subsequently, the first soft lenses made by hydrogel were invented in 1960s, and then rapidly replaced the role of rigid lenses in the market in terms of its much greater comfortableness.

During the next 25 years, the manufactures of contact lenses have been enhanced from different aspects, such as gas permeable and water content.

In the year of 1998, the lenses with brand new materials, silicone hydrogel, came out. Considering the extremely high oxygen permeability and comfortableness than previous hydrogel materials, it plays a dominated role in the contact lenses market till today. It is worth mentioning that, apart from silicone hydrogen itself, the second generation (galifilcon A and sentfilcon A) [9] and the third generation (comfilcon A and enfilcon A) were created with modified molecules and no variation of silicone structure, to enhance their physical and chemical properties to satisfy consumers' demands and willingness.

In this article, we focus in detail on the four main kinds of contact lenses materials mentioned above, including silicone hydrogel, hydrogel, rigid gas permeable (RGP) and polymethyl methacrylate (PMMA), and evaluates the differences in their properties and application ranges. It provides a reference for consumers to choose the type of contact lenses.

2. Contact Lens Materials

2.1 Overview

Selecting suitable material is an inevitable and crucial preparation step before the manufacturing of contact lenses. Contemporary, 4 kinds of main material including silicone hydrogel, hydrogel, RGP and PMMA has occupied the majority of the mainstream market. Those material are chosen according to their varieties of properties, and eventually to fit the different demand of customers. As shown in Table 1 and Figure 1-2, materials had shown different chemical properties and performance, as well as their pros and cons. (figure 1&2)(table 1)

Table 1 Advantages and Disadvantages of Different Contact Lenses Materials

Contact lenses materials	Advantages	Disadvantages
Silicone hydrogel	High oxygen-permeability durable	Expensive
Hydrogel (HEMA)	Low-cost High water content	Low oxygen-permeability
RGP	High oxygen-permeability	Expensive
PMMA	Low-cost	No oxygen-permeability

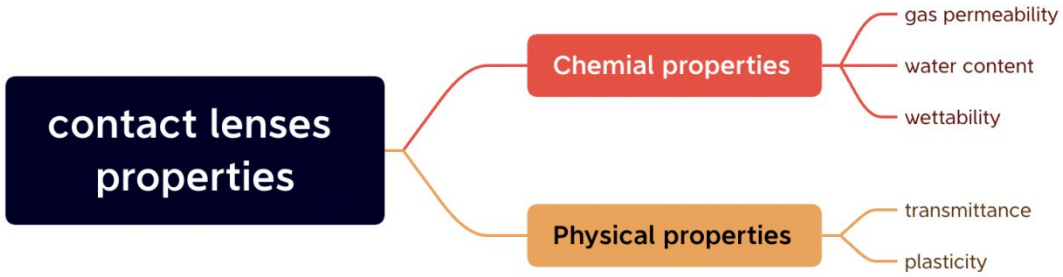

Fig. 1 Types of Physical and Chemical Properties of Contact Lenses

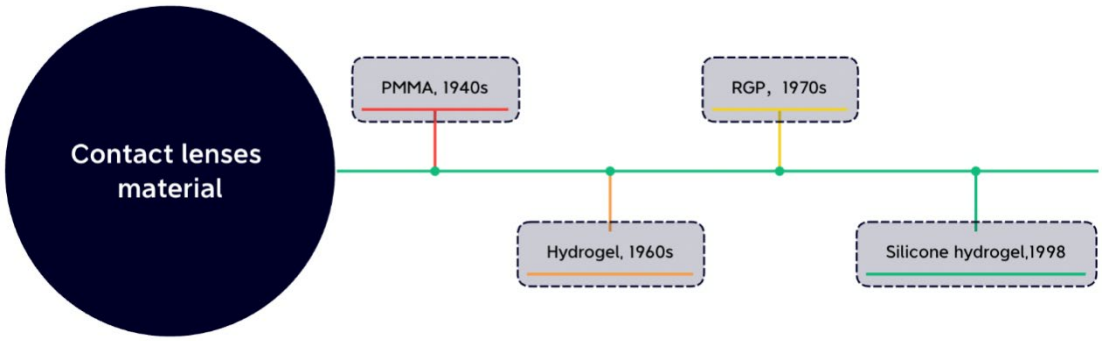

Fig. 2 Evolution of Contact Lens Materials

2.2 Silicone Hydrogel

Silicone hydrogel plays dominated role in the global contact lenses market with 69% of its market share, in the year of 2021[30], which had become the most popular contact lenses material in the world. Silicone hydrogel is a highly hydrophilic high polymer organic material, with honeycomb shape. It is created from the hybridization between silicone and hydrogel for the first time, in the year of 2002. The material's high popularity is mainly originating from is high oxygen

permeability (>100 Dk), because there are two tunnels, one of the silicone tunnels and the other hydrogel tunnel to transfer more oxygen to cornea. Comparing silicone hydrogel to the conventional hydrogel, the former material realizes the coexist of high oxygen permeability and low wettability, since silicone is a substance with well oxygen permeability. Due to its Si-O bonding, most of the material are durable, with higher modulus than other contact lenses material. At the very beginning of the invention of the material, the oxygen permeability and wettability are unsatisfactory, therefore, manufacturers introduce more polymers to enhance it. Until today, the revolution of silicone hydrogel has achieved the third generation. (table 2)(figure 3)

Table 2 Generations of Silicone Hydrogel

	1st Generation	2nd Generation	3rd e Generation
Material:	Lotrafilcon A Balafilcon A	Senofilcon A Galyfilcon A	Samfilcon A, Comfilcon A, Enfilcon A, Asmofilcon A
Features:	TRIS structures, plasma treated, high modulus	Modified Tanaka monomer, lack of coatings, higher Dk for water content	No TRIS structure, no surface treatments or wetting agents, breaks traditional water-Dk-modulus relationships

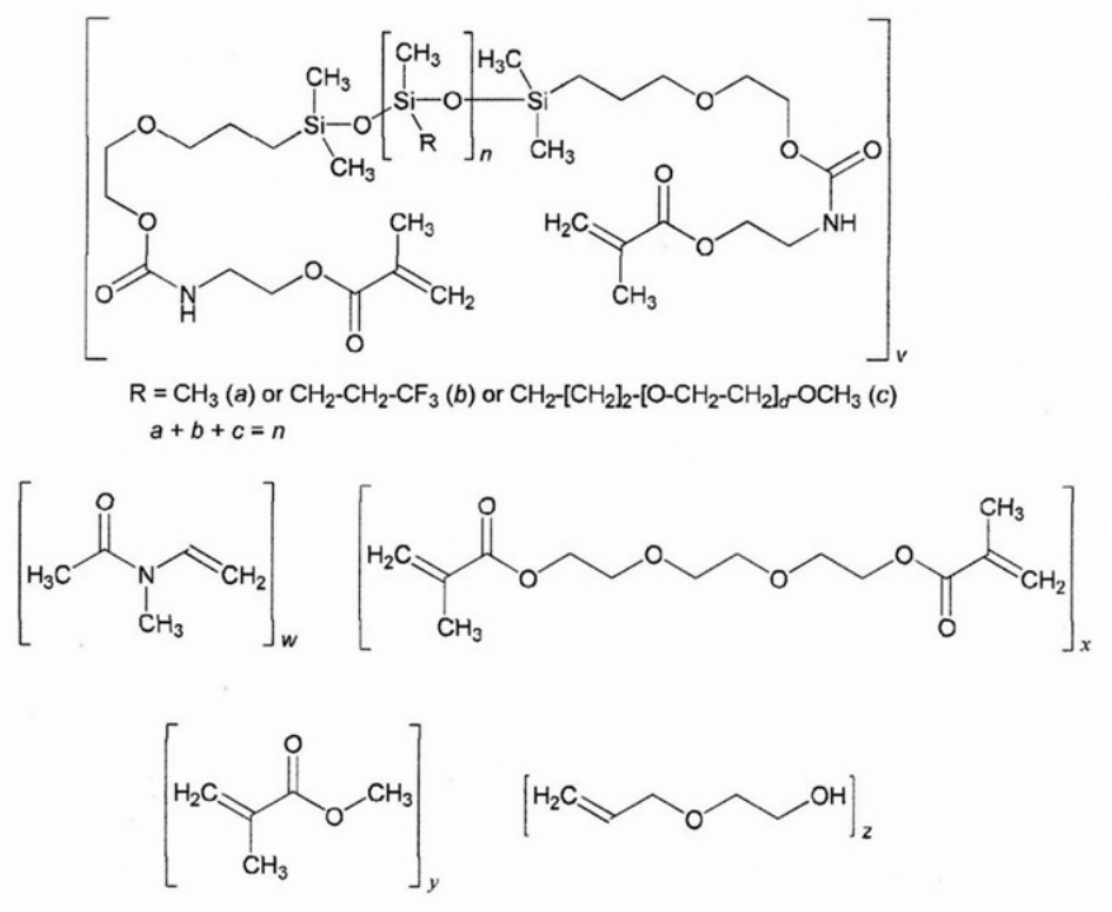

Fig. 3 Monomer Structure of Silicone Hydrogel

In the synthesis and characterization of silicone hydrogel contact lens from YanLong WANG has shown that after 2 hours reaction under 90 degrees celcius, the gas permeability (Dk/t) has reached 64.0*10-9 (cm^3 O_2 * cm)/(cm^2 * s* mmHg), moisture content of 38%, transmittance greater than 95.5% [11]. In another study Ionescu et al benchmarked the optical properties (transmittance, absorption and dispersion of a monthly displacement silicone hydrogel lenses. Compared to the contact lenses with different material, silicone hydrogel lenses tend to have higher transmittance and absorption, lower dispersion [18]. Jones *et al.* investigated the in vitro dehydration performance of silicone hydrogel and conventional hydrogel contact lens materials. The mass loss over time of five brands, *Focus Night&Day, PureVision, Optima, Acuvue and Proclear Compatibles* was

measured. In vitro dehydration is closely related to bulk water diffusion rates and, as a results of their low water content, silicone-containing hydrogel materials exhibit low levels of dehydration compared with high water content hydrogel contact lens materials [12]. Lira *et al.* evaluated the ability of four silicone hydrogel contact lenses (galyfilcon A, balafilcon A, lotrafilcon A and lotrafilcon B) to retain their equilibrium water content before and after wear, through measurements of refractive index and compare with another conventional hydrogel material (etafilcon A). The results presented show that after being worn the silicone hydrogel contact lens, show more capacity to retainor to reach their initial EWC than conventional hydrogel contact lenses. Since the refractive index is function of water content, the results of this study suggest that the presence of the hydrophobic organosilicone moieties in the silicone hydrogels, their lower EWC and the lower levels of proteins exhibited, compared to the conventional hydrogel lens, are the cause of apparent better water retention. This also suggests that the silicone hydrogel contact lenses are less susceptible to spoilation over time maintaining its biocompatibility and contributing to the clinical success of lens performance [13]. (Table 3)

Table 3 Results from Refractive Index Measured in Unworn and Worn Contact Lenses

		No.	minimum	maximum	Mean±S.D.	Significance(p)
Etafilcon A	u	30	1.361	1.405	1.398±0.008	0.000
	w	30	1.405	1.413	1.410±0.002	
Galyfilcon A	u	22	1.405	1.414	1.408±0.002	0.127
	w	22	1.405	1.413	1.409±0.002	
Balafilcon A	u	20	1.417	1.424	1.421±0.002	0.467
	w	20	1.418	1.425	1.422±0.002	
Lotrafilcon A	u	24	1.425	1.428	1.426±0.001	0.319
	w	24	1.425	1.487	1.429±0.124	
Lotrafilcon B	u	19	1.421	1.423	1.422±0.008	0.500
	w	19	1.419	1.423	1.421±0.001	

Liu *et al.* set up an experiment with 40 people involved in and separated them in to two groups, letting them wear the monthly-disposal silicone hydrogel (20 people) and hydrogel (20 people) contact lenses for 2 years. After the experimental duration, they checked their ocular surface and change of their tear-film. The results were that the testers who wear silicone hydrogel had a significant improve on the lack of oxygen of their cornea, their newborn blood vessel were less too [14]. Luo *et al*. evaluated the effect of wear silicone hydrogel contact lenses after SMILE surgery, the effect including: any subjective discomfort symptoms, changes on ocular surface and tear-film and objective visual quality. 62 testers worn the contact lenses after their surgery on one of their eyes, the lens was taken out after one day wearing. In this research, the subjective discomfort score (feedback from patients), of unworn eye was higher than the eye which worn the lens. The corneal fluorescein staining score of worn eyes after one day was lower than unworn eye. The breakup time of tear film of worn eye after one day was longer than the unworn eye. Moreover, after 16 hours of wearing, the objective visual quality of the eye with contact lens was lower than the eye without [19]. Fu *et al.* investigated the influence of short periods wearing of silicone contact lenses to the thickness of cornea and the posterior corneal surface height. They selected 20 volunteers to wear a random silicone hydrogel contact lenses on one eye. The value before the wearing and 8 hours and one day of was measured. The results given show that the short-term wearing of hydrogel silicone would not result in the significant edema of cornea, but might lead to a slightly forward protrusion of the posterior surface [34].

Overall, silicone hydrogel is one of the most advanced materials of contact lenses. The oxygen permeability the most significant feature of it, followed by noteworthy moisture content, transmittance and absorption. Although wearing silicone hydrogel contact lenses may lead to some negligible problem such as protrusion of posterior, it is actually being a common phenomenon lead by all species contact lenses. In addition, silicone hydrogel can also be useing in recovery of eyes after a variety of corneal surgeries which offer comfortable feelings to patients. In conclusion, silicone hydrogel is an outstanding material that worth continues promotion.

2.3 Hydrogel

Hydrogel is one of the most typical soft contact lenses material. Thanks to its advanced plasticity, hydrogel has very high convenience and low adaption time. The oxygen permeability of these gels is also suitable for longer wear, but not to the same extent of silicone-based lenses. HEMA and those hydrogels which related to it have high water content, usually between 20-80%. The PHEMA lenses have water content of 38%, with great polar effect on its surface, and the Dk value of approximately 8.0-8.5. The other HEMA-derived hydrogels gain different properties due to the copolymerization of other monomers, such as: EDGMA, MAA, PVA, GMA and NVP. The adding of NVP and PVA can increase the oxygen permeability, hydrophilic and wettability. The adding of GMA can improve the material's hydrophilic and precipitation resistance. MMA can enhance the stability and optical properties. HEMA-derived hydrogel also owns a decent global market share of 22% [30].

Lu *et al.* used AM and HEMA to prepared non-ionic hydrogel contact lenses material with more than 74% of high water content. The performance and property test prove that the transmittance, mechanical strength and saturated water content can fully satisfied the requirement of manufacturing hydrogel contact lenses [20]. Wang *et al.* conducted a polymerization between HEMA and NVP to make hydrogel material. NVP has good water solubility and biocompatibility. According to the gas permeability of the material they made, the requirement of manufacturing contact lenses was reached. They also used the lenses which they synthesized as the carrier of medicine, the sustained release time can reach 2 hours, significant improved from the action time of eye drops [21]. The experiment conducted by *Li et al.* The co-polymerization of NVP HEMA and MMA or EMA produced a colourless, transparent hydrogel material. The hydrogel's transmittance exceeds an average of 96% within the area of ultraviolet and visible light. The acidity and alkalinity were also close to the level of human's body fluid. Therefore, this hydrogel is a suitable material for the manufacture of contact lenses. Moreover, the increase in NVP content in the hydrogel can result in the improvement of balance swelling degree, however, to avoid the cloudy appearance in the hydrogel and the strength decrease, the content of NVP should be under 20% of the volume. MMA and EMA can decrease the water content of the hydrogel, but they enhance the anti-dehydration performance of the material. Taking all aspect into consideration, the volume of EMA should be 6% of the whole volume [16].

To conclude, hydrogel material is mainly produced from the co-polymerization of different monomers which can enhance its convenience and other property. The ability of create new things from hydrogel is still exciting.

2.4 Pmma (Polymethyl Methacrylate)

PMMA (polymethyl methacrylate) was once considered the most suitable material for the contact lens. Moreover, trace back to 1940s, when the first mass-market contacts lenses were developing, they were all produced by this well-known, rigid, nonporous and inexpensive material. However, with the introduction of a variety of other contact lenses materials into the market, PMMA only occupied 1% of the market sharing in the year of 2021 [30]. One of the most noteworthy properties of PMMA is that it has nearly no oxygen permeability. This is mainly because of the polymer chains of PMMA are lack of mobility, therefore they prevent the flow of oxygen or internal water to mediate the flow of O_2. (figure). They are optically clear-they are able to transmitting up to 92% of visible light, which would be useful to manufacture eye lenses. PMMA is also a strong, tough, and lightweight material. It has a density of 1.17–1.20 g/cm^3, which is less than half that of conventional glass. The material also does not shatter, It has good impact strength, higher than both glass and polystyrene. PMMA is an inert material, professionals refer to it as biocompatible in medical science. Therefore, people rarely have to consider the security problem of it although the materials have to be put on utilizers' cornea as a foreign, as they does not trigger an immune response.

Patient who has experience post-corneal refractive surgery had wear a variety of lenses under the help of Alio *et al.*, and the RGP PMMA lenses had shown the best performance in the experiment.

The impact of PMMA contact lenses on cornea was first reported by Boberg-Ans, he used his own-made measuring perception instrument to measure the cornea after 2 hours worn of contact lenses, the results were slightly decrease in cornea's perception. After the contact lenses had been use for 1 day, the cornea perception declined for about 3 times [17]. Michel *et al.* had done an experience that their test subject worn on the PMMA lens in the morning, and then they measured the corneal sensitivity after 4,8,12 hours respectively. After 3 hours, there was a slightly decline of sensitivity. After 8 hours of testing, the centre corneal sensitivity experienced a decrease of 94%, the around sensitivity has descended for 116%. The overall drop of sensitivity after 10 hours is 110%. Wang *et al.* investigated the contact lenses' bacteria adhesion ability made by different material. The results presented that PMMA has a greater ability of bacteria adhesion than other two material [24]. Alio *et al.* comprised 140 eyes of 140 patients who had phacoemulsification and implantation of IOLs of various materials: acrylic, silicone and PMMA or HSM PMMA (heparin-surface-modified PMMA). The results has shown that the HSM PMMA group had the lowest incidence of inflammation relapses [22].

In conclude, PMMA is the material that gradually disappearing from the contact lenses market, due to its non-gas permeability, poor plasticity and uncomfortableness etc. however, PMMA has advantages of great transmittance, low cost and stable polymerization form. So I believe that PMMA may exist as the fundamental contact lenses material for both science understanding and commercial utilization.

2.5 Rgp (Rigid Gas Permeable)

Rigid gas permeable (RGP) contact lenses are rigid lenses made of durable plastic. Apart from other rigid lenses such as PMMA contact lenses, the most significant property of RGP lenses are high oxygen permeability just as its name. Most of RGP lenses contain silicone, which makes the lenses more flexible than the conventional plastic material, and silicone provide a tunnel for the transportation of gases especially oxygen. Because of the gas permeability, GP lenses can be made larger than conventional hard contact lenses, and the edges of GP lenses can be fitted closer to the surface of the eye. These design changes make modern rigid GP lenses more comfortable and easier to get used to than old-fashioned hard contacts. They also help GP contacts stay more securely on the eye when worn during sports and other activities. RGP contact lenses contain no water, so organic materials such as protein and lipids from users' tears will not adhere to the lenses as readily as they do to soft lenses. Moreover, RGP lenses can also provide better vision, durability and deposit resistance than some soft contact lenses. And because they last longer than soft lenses, they can be less expensive in the long term.

These days, most of RGP contact lenses are utilized as treatments for different eye situation and disease.

Liu *et al.* have observed the RGP contact lenses' usage after the LASEK and LASIK surgery. Since some patient suffered from degree residual, degree fallback and irregular astigmatism, which negatively influenced their normal live and work, some of the patients even could not go back to their optimum vision after the surgery.(figure) Therefore, 48 patients started to wear RGP lenses 6 month after the surgery. All the patient reached their optimum vision after they worn the lenses. In the follow-up check after 1 week, 1 month and 3 months, all the patient had stable vision and maintain the initial state during the wearing of lenses [23].(table 4)

Table 4 Comparison of Comprehensive Optometry and Rgp Glasses to Correct Visual Acuity

Refractive state		Eye number	Comprehensive optometry correction			RGP correction		
Spherical mirror	Cylinder mirror		Lowest	Highest	Average	Lowest	Highest	Average
-3.0- -6.0	-1.0- -2.0D	30	0.4-0.6		0.54	0.8-1.0		0.86
	-2.0- -3.0D	16	0.3-0.6		0.48	0.8-1.0		0.83
	-3.0- -4.0D	6	0.3- -0.5		0.42	0.7-1.0		0.80
overall		52	0.3-0.6		0.50	0.7-1.0		0.85

Wang *et al.* compared the adherence ability of bacteria between RGP (hexafacon and enflufocon) and PMMA material. Methyl thiazolyl tetrazolium colorimetric method and vortex method were used in the research. The results suggested that hexafacon and enflufocon had less likely to attached bacteria compare to the PMMA material. Li *et al.* investigated the correction performance on aphakic eyes after cataract surgery by RGP lenses. 26 aphakic eyes after the surgery were examined through RGP trial wear and compare among natural visual acuity, corrected visual acuity on all eyes. The tests output found out the corrected visual acuity by spectacle or RGP lenses was significantly better than natural visual acuity on all eyes, significant statistical differences were found among the three kind of visual acuity. YaJie WANG invested people with different curvatures of myopia wearing RGP lenses effect on the growth of diopter. 63 patient (126 eye) involved in the research. 31 patients worn RGP lenses and 32 patients worn normal eyeglasses. Recorded their initial corneal curvature and diopter and compared with the data after 2 years. The results showed that patient with different corneal curvature who worn RGP had similar myopia growth rate. The patient who worn RGP lenses had lower myopia growth rate than those who worn normal glasses [26]. Schachet *et al.* aimed to prove that high Dk RGP lenses provided superior on eye performance. They conducted a double masked study comparing three different RGP material: Paragon HDS (Dk=58), Boston ES (Dk=31) and Boston IV (Dk=26.3), 33 patients involved in this study. All the patients needed to wear each pair of lenses for 30 days. Their feedbacks would be record during the wearing. In conclusion, paragon HDS gained the highest overall satisfaction on the aspect of fewest symptoms and least cleaning requirement, but as the lenses with highest Dk value, it had the equivalent clinical performance to the lenses with lower Dk values [35].

To conclude, RGP contact lenses have excellent oxygen permeability as rigid lenses. It also has good retain in shape when people are wearing it, which make it suitable as treatment after surgery or used for ortho-k. Although users must wear it regularly to maintain the maximum comfort and best effect. And RGP lenses is still the kind of lenses that worth wider publicity and utilization.

3. Conclusion

The aim of this review is to give a brief introduction about four major contact lenses materials. From the perspective of physical and chemical, both modern contact lens such as HEMA- or silicone- hydrogel and old-fashioned material like PMMA and RGP material is analyzed in this work. The silicone hydrogel material has outstanding properties and is now reached the third generation, is it able to enhance its properties continuously as it is the most advanced material. For the HEMA based hydrogel, the most significant and worth-attention fact is the ability of co-polymerization with other material, which offers improvements on its characteristics. I assume that more combination of co-polymerization will be discovered in the future to make better hydrogel material. PMMA can be seen as an outdated material which is rarely used these days. However, this well-studied polymer may still be used for fundamental understanding of contact lenses. RGP materials are rigid material with most of the soft lenses materials' advantages, this is one of the reason why it is used in recovery of eye surgery and the treatment of myopia, although RGP lenses is not widely used for daily aspect. Overall, the future contact lenses material will definitely continuous to pushing the limitation and develop to form better material due to the improving demand of utilizers.

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