Contact Lens Materials and Their Modification Methods

Keying Xu*

University College London, London, United Kingdom

*Corresponding author: zccakxu@ucl.ac.uk

Abstract. Contact lenses are one of the most successful materials. They are used by over 125 million people around the world. This review gives an description on history, properties and modifications of contact lens materials. Starting from a piece of glass to current silicone hydrogel lenses, contact lens material development has witnessed a huge step. Properties of typical contact lens materials are introduced, including mechanical properties, equilibrium water content, oxygen permeability, and surface properties. Tensile stress is mentioned as a significant mechanical property, whereas wettability and friction are discussed in surface properties. Corresponding modifications to increase wearing comfort are also discussed in this review, such as copolymerization, cross-linking and surface modification. These methods are applied to materials typically silicone hydrogels to increase water content and oxygen permeability or to optimize the mechanical and surface properties. Nowadays, contact lenses in the market provide users with longer wearing time and more comfortable wearing experiences.

Keywords: Contact lens materials; silicone hydrogels; surface modification; cross-linking.

1. Introduction

Since Leonardo da Vinci raised the idea of contact lenses in 1508, materials of it have been evolving to improve biocompatibility throughout decades. The first pair of contact lenses was tested to be made of glass, which is silicon dioxide. The maximum wearing time of this lens was limited to 2 hours due to its hardness and big diameter. In the late 1960s, a developed corneal lens made of Polymethyl methacrylate (PMMA) became popular. However, methyl methacrylate (MMA) is hydrophobic and hard. Extremely low oxygen permeability caused friction between the lens and corneal. Rigid Gas permeable (RGP) materials were used to improve wearing comfort. Meanwhile, hydrogel contact lenses consisting of polyhydroxyethyl methacrylate (PHEMA) were created. The hydroxyl groups (OH) are located at the end of each composing monomer, which can attract water molecules to form hydrogels. The water content of PHEMA can be up to 40% if fully hydrated. Interestingly, this material was supposed to be synthesized for implantation into human tissue. However, scientists soon realized its application on contact lenses. In 1998, the first silicone hydrogel contact lens was manufactured. Unique properties of silicone components equip this new lens with high oxygen permeability. It shortly became the most popular type of contact lens in the market. After decades of development, most modern contact lens materials are made of HEMA and silicone hydrogels, combined with other biomaterials, such as polyethylene glycol (PEG) and cellulose [1]. In 2018, 35% of the global population were contact lens wearers [2]. Nowadays, there are approximately 150 million contact lens wearers worldwide. However, half of them suffer from adverse ocular sensations, generally dry eyes [3]. This review aims to introduce the properties of different silicone hydrogel lens materials and their modifications used to improve wearing comfort.

2. Properties of the Contact Lens Materials

2.1. Mechanical Properties

Mechanical properties always have significant effects on wearing comfort of contact lenses. As lenses cover and deform the corneal shape [4].

Tensile stress, an important mechanical property, usually describes linear elastic materials. However, scientists found that a simple linear relationship cannot scale the eyelid pressure for contact lenses. To avoid misunderstanding, compression is used here. If the material has a low modulus, the contact lenses tend to be more deformable and offer less resistance. Instead, when the compression modulus is high, there is more friction. For example, although silicone hydrogels have higher oxygen permeability, they always have higher moduli values compared with other hydrogels [5]. When there is too much friction between the lens and cornea, issues of comfort occur. To solve this problem, two methods are feasible, copolymerization and surface modification, which will be introduced in the modification section.

2.2. Equilibrium Water Content

Most hydrogels are soft under a fully hydrated condition. On the contrary, materials with low water content tend to be hard and brittle. The equilibrium water content (EWC) of a material can be calculated through the following formula:

$$\mathrm{EWC} = \frac{\text{Weight of water in polymer}}{\text{Total weight of hydrated polymer}} \times 100 \quad (1)$$

EWC is mutable since it can be changed by environmental conditions, such as temperature, pH and tonicity. Since there is a mathematical relationship between the refractive index and EWC, the value of EWC can also be measured by using an instrument called contact lens refractometer [6]. Oxygen and ion permeability, being another significant comfort factor, are always influenced by EWC [7].

2.3. Oxygen Permeability

Oxygen permeability can be presented by Dk. D presents the diffusivity of a material, which shows the speed of oxygen travelling through a surface. Whereas k is the solubility of a material. Oxygen permeability is always related to the equilibrium water content. Their relationship can be expressed in a simple formula, where e presents the natural logarithm.

$$\mathrm{Dk} = 1.67e^{0.0397\mathrm{EWC}} \quad (2)$$

It is necessary to mention that ion permeability also plays an important role in the on-eye movement of the lenses. Ion transport through the lens helps form a fluid hydrodynamic boundary layer. To obtain a material with high ion and oxygen permeability, hydrophilic monomers are copolymerized with hydrophobic siloxane monomers. It is difficult to make hydrophilic and hydrophobic monomers stable in the same phase. Thus, a macromer is introduced and the polymerized silicone hydrogel matrix is designed [8]. From that time, silicone hydrogels became the most studied materials.

2.4. Surface Properties

The surface properties of the material always affect the contact between the hydrogel lens and the cornea. Good surface properties keep the tear layer stable, which reduces discomfort including dry eye, and increases wearing time.

Wettability is one of the most important surface properties. It is used to describe the ability to spread liquid on the surface of the contact lenses [8]. Contact angle is used to characterize the wettability. It can be measured by an instrument called Contact Angle Goniometer. Small contact angles always indicate the high wettability of the material. Interestingly, wettability is material-dependent, there is no obvious wettability difference between silicone and traditional hydrogel contact lenses.

Another surface property is frictional characteristics. The contact lens slides during blinking, which brings friction and forces between the lens and the cornea (as shown in Figure 1). The coefficient of friction (CoF) is used to describe the friction between two surfaces. There is no accepted technique to measure an exact value of CoF since it is difficult to mimic the dynamic movement of lenses under the pressure of the eyelid. For example, a microtribometer set-up was used to measure CoF of different commercial contact lens materials. This friction set-up measured an inadequate sliding distance. It is uncertain to determine if the friction is static or dynamic [8]. From existing experiments and statistics, silicone-based hydrogel always has higher CoF [9].

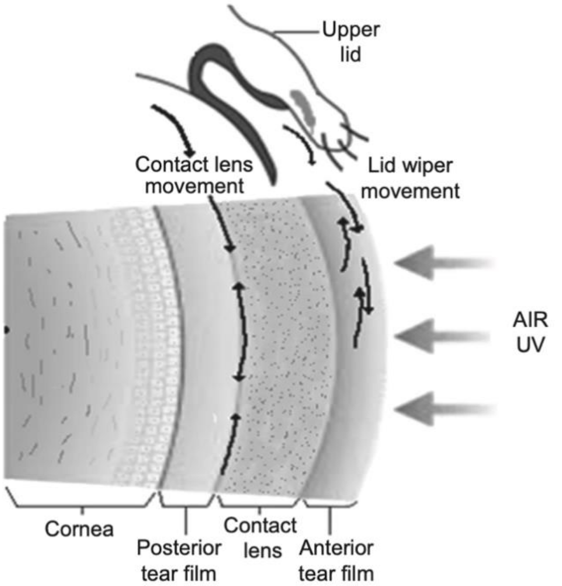

Fig. 1 Interfacial movement of contact lens surface [8]

3. Modification Methods

3.1. Copolymerization

Since the demand for material with higher oxygen permeability increased, wide-ranging research has been carried out. A copolymer was designed, consisting of HEMA and a famous siloxymethacrylate monomer called tris(trimethylsiloxy)-γ-methacryloxy-propylsilane (TRIS). As mentioned in the previous section, HEMA is a common hydrophilic monomer. TRIS is made of segments of silicone rubber structure, connected by a modified Methyl methacrylate molecule. However, this material has a low optical transparency after copolymerization, caused by phase separation. Thus, several improvements were made. The first one is to replace HEMA with other hydrogels containing the -N-CO- linkage, by which two monomers can stay in the same phase. The second method is to use more hydrophilic TRIS invariants (as shown in Figure 2). This also helps two substances mix better [10].

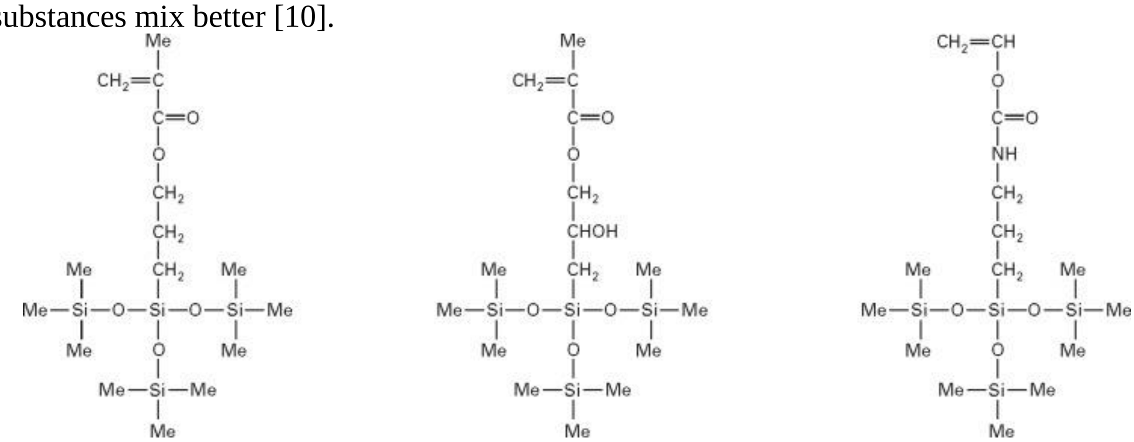

Fig. 2 Variants of TRIS monomer [9]

Under decades of development, the water content of silicone hydrogels increased from 24% to 74%, with moduli decreasing from 1.4 to 0.3 MPa [7].

3.2. Cross-linking

Compared with rigid gas-permeable lenses, hydrogels usually have higher water content. They are softer and more comfortable to wear. A cross-linking agent is always used to connect these hydrophilic polymer chains to make the desired contact lens material. However, different cross-linking methods lead to different mechanical properties of the materials. Take acrylic soft lenses as an example. This lens is made by ethylene glycol dimethacrylate (EGDMA). During polymerization, cross-linking cores form at the same time, which makes the network structure suppressed in stability but lose flexibility. As a result, contact lenses made from this material always have low tensile strength and easily tear. Therefore, a better cross-linking method was developed. A research team managed to form a site-to-site linking network through a photodimerization reaction. Under test, their product had higher mechanical strength [10].

3.3. Surface Modification

As mentioned in the previous section, copolymerization can improve wearing comfort by changing the mechanical properties of the material. However, when other functional groups or monomers are introduced, the oxygen permeability of the original bulk is affected spontaneously. As a result, surface modification was developed. The polymer layer formed needs to satisfy two important characteristics, which are high ionic strength and stability in ocular environments [10].

The first method is simply to form a hydrophilic polymer layer on the surface. Silicone hydrogels are commonly covered with PEG, poly(NVPy), and other polyelectrolytes [10]. A 6-hour clinical study on a PEG-covered lens was carried out and indicated that both oxygen permeability and water content for this lens are biocompatible [11]. The second approach is to reduce protein absorption besides increasing water content [10]. For instance, using poly(HEMA-co-TRIS) to immobilize hyaluronic acid on the silicone hydrogel substrate (Figure 3). Covering the surface with lubricin to reduce friction is also feasible, where esterification from proteoglycan 4 is carried out in a mild condition to form proteoglycans and lubricin. Moreover, plasma irradiation can also be performed. However, it is difficult to control the direction of the polar groups. As a result, well-defined structures of polymers are used to replace normal ones. Phospholipid liposomes, being cell surface-mimicking substrates, are also used to improve surface properties. They help prevent tear evaporation.

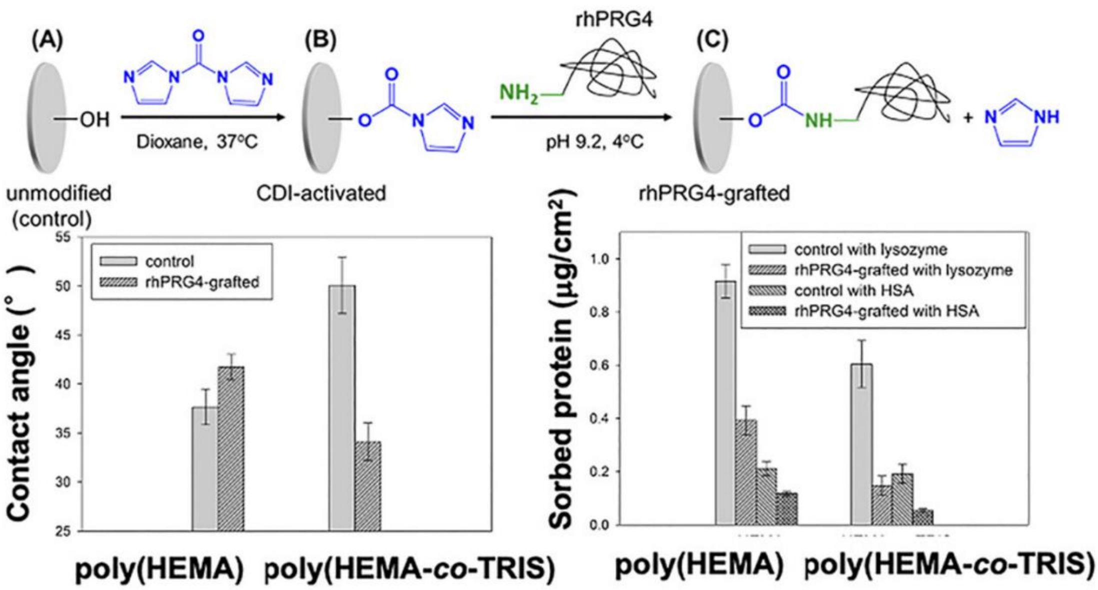

Fig. 3 Immobilization of hyaluronic acid by using poly(HEMA-co-TRIS) [10]

4. Conclusion

In this review, the history of contact lens development is first briefly mentioned. Developed from glass, PMMA, and RGP, HEMA and silicone hydrogels were designed and became the most popular contact lens biomaterials. Meanwhile, the properties of contact lens materials are discussed. For mechanical properties, tensile strength is discussed. Lenses with lower modulus always improve wearing comfort. For surface properties, wettability and frictional characteristics are introduced. Wettability of a material can be determined by measuring the contact angle. For most materials, a smaller contact angle indicates higher surface wettability. Friction is another surface property that influences wearing comfort a lot. Hydrogels with smaller CoF were thus designed. The equilibrium water content of a material can be easily affected by its surroundings, such as pH and temperature. Normal hydrogels with higher water content tend to be softer. Silicone hydrogels always have higher oxygen permeability, allowing the formation of a fluid hydrodynamic boundary layer. Modifications including copolymerization, cross-linking and surface modification are introduced in this review. Products with higher oxygen permeability and water content can be made by combining a hydrophilic monomer and a siloxymethacrylate monomer. This can be achived by copolymerization. It is necessary to mention that various combinations of hydrogels and siloxymethacrylate monomers have been tested to give the best product. Another modification is to change the cross-linking method. Normal cross-linked structure gives a product with low mechanical strength. Specifically, a site-to-site linking network through a photodimerization reaction helps improve the modulus. Surface modification is also a feasible method to improve a material's properties. Two typical surface modifications are discussed in this review: forming a hydrophilic polymer layer on the surface of the lens, and reducing protein absorption. The main purpose of this type of modification is to prevent tear evaporation to reduce friction.

References

[1] Christopher Stephen Andrew Musgrave, Fengzhou Fang, Contact Lens Materials: A Materials Science Perspective. Materials, 2019, 12(2): 261

[2] Rosalia Moreddu, Daniele Vigolo, Ali K. Yetisen, Contact Lens Technology: From Fundamentals to Applications. Advanced Healthcare Materials, 2019, 8(15): 1900368.

[3] Maria Vidal-Rohr, James S. Wolffsohn, Leon N. Davies, Alejandro Cerviño, Effect of contact lens surface properties on comfort, tear stability and ocular physiology. Contact Lens and Anterior Eye, 2018, 41(1): 117–121.

[4] Ahmad H. Shihab, Ashkan Eliasy, Bernardo T. Lopes, Richard Wu, Lynn White, Steve Jones, Brendan Geraghty, Akram Joda, Ahmed Elsheikh, Ahmed Abass, Compressive behaviour of soft contact lenses and its effect on refractive power on the eye and handling off the eye. PLOS ONE, 2021, 16(2): e0247194.

[5] Eon Kim, Mou Saha, Klaus Ehrmann, Mechanical Properties of Contact Lens Materials. Eye & Contact Lens: Science & Clinical Practice, 2018, 44(2): S148–S156.

[6] José M. González-Méijome, Antonio López-Alemany, Madalena Lira, José B. Almeida, M. Elisabete C.D. Real Oliveira, Manuel A. Parafita, Equivalences between refractive index and equilibrium water content of conventional and silicone hydrogel soft contact lenses from automated and manual refractometry. Journal of Biomedical Materials Research Part B: Applied Biomaterials, 2007, 80B(1): 184–191.

[7] Cheng-Chun Peng, Anuj Chauhan, Ion transport in silicone hydrogel contact lenses. Journal of Membrane Science, 2012, 95–105.

[8] A. Mann, B.J. Tighe, Ocular biotribology and the contact lens, in: Biomater. Regen. Med. Ophthalmol., Elsevier, 2016: 45–74.

[9] Chirila, T., Harkin, D., Biomaterials and Regenerative Medicine in Ophthalmology, Elsevier, 2016.

[10] Kazuhiko Ishihara, Xinfeng Shi, Kyoko Fukazawa, Tetsuji Yamaoka, George Yao, James Yuliang Wu, Biomimetic-Engineered Silicone Hydrogel Contact Lens Materials. ACS Applied Bio Materials, 2023, 6(9): 3600–3616.

[11] Mingcong Sun, Jun Deng, Zengchao Tang, Jindan Wu, Dan Li, Hong Chen, Changyou Gao, A correlation study of protein adsorption and cell behaviors on substrates with different densities of PEG chains. Colloids and Surfaces B: Biointerfaces, 2014, 134–142.