Change of Physical Properties of Hydrogel Lens Polymer Containing Isocyanate Group with Ag Nanoparticle

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Abstract

A study that copolymerized Ag nanoparticle and furfuryl isocyanate with the crosslinking agent EGDMA (ethylene glycol dimethacrylate), HEMA (2-hydroxyethyl methacrylate), MMA (methyl methacrylate), MA (methacrylic acid) and the initiating agent AIBN (azobisisobutyronitrile) is presented. Measurement of the physical characteristics of the produced macromolecule showed that the water content is 32.08~32.67%, refractive index 1.446~1.448, visible light transparency 83.2~67.6%, contact angle 68.2~83.5° and tensile strength 0.541~0.755 kgf. It is also demonstrated that the addition of Ag nanoparticles is associated with the reduction of UV-B transmittance and increase in tensile strength. The results show that the produced copolymer can be used as a material for ophthalmic lenses with durability and UV-blocking properties.

Key words: Furfuryl Isocyanate, Ag Nanoparticle, UV-block, Spectral Transmittance, Tensile Strength

1. Introduction

There is a recent increase in demand for ophthalmic materials, but many materials carry the risk of causing medical problems as they are required to come in direct contact with the cornea.^[1-4] Wearing contact lenses can expose the eye to various diseases and Hart *et al.* reported that contact lenses of 35% of people wearing soft contact lenses are contaminated with bacteria. *Staphylococci*, *Pseudomonas aeruginosa*, *E.coli* and various fungi are among the most common pathogens that involve the eye that can cause diseases such as chronic bacterial conjunctivitis, acute catarrhal conjunctivitis, *pseudomonas* corneal ulcer, and fungal corneal ulcer. During 1920 and 1940, pharmacological studies were actively carried out on the antibacterial properties of Ag that reported that most pathogens can be eradicated by the Ag⁺ ion at 10~40 ppm concentrations in vitro settings.^[5] Currently, due to the advancement of nano technology, silver nanoparticles (Nano-Silver) under 20 nm in diameter can be produced. Silver nanoparticles offer

a high solubility for Ag⁺ ions and can control infections.^[6-7] Silver nanoparticles are broadly used as an antibacterial agent in home appliances, textile and construction materials as well as baby products and medical supplies, and silver nanoparticles are known to be effective against over 650 types of pathogens. Also, since pathogens are not capable of developing resistance against silver and owing to the advancements in nano technology since the 1990s silver nanoparticles are currently used in various types of products or are being considered for applications. In particular, the powerful antibacterial characteristic of silver (Ag) and Ag⁺ ion has been long known through studies on various fungi, bacteria and viruses that people commonly come into contact with. According to a research paper on the antibacterial mechanism of Ag or Ag⁺ ion, the thiol group, amino group, imidazole group and carboxylate group all have lone pair electrons that bind with Ag or Ag⁺. By binding with these groups, Ag⁺ inhibits the respiratory process or electron transport chain of microorganisms which results in their death. Water content, refractive index, spectral transmittance, contact angle and tensile strength are the basic physical properties of a contact lens among which basic properties such as water content, refractive index and tensile strength as well as functional properties such as antibacterial properties and

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UV-blocking properties are attracting the highest interest for which many studies are currently being carried out. The utility of silver nanoparticles in ophthalmic products that offer antibacterial and UV-blocking properties while satisfying the basic requirements for contact lenses was analyzed in this study.

2. Experimental Section

2.1. Reagents and Materials

The Ag (Silver nitrate volumetric standard, 0.1N solution in warwe) used to produce the silver nanoparticles and furfuryl isocyanate is a product supplied by Sigma-Aldrich. The HEMA (2-hydroxyethyl methacrylate) used in this experiment and AIBN which was used as the initiator for polymerization are manufactured by JUNSEI, the NVP (n-vinyl pyrrolidone) and EGDMA (ethylene glycol dimethacrylate) are manufactured by Acros and the MMA (methyl methacrylate) is manufactured by Crown Guaranteed Reagents. The structural formula of the furfuryl isocyanate used in this study is shown in Fig. 1.

2.2. Polymerization of Polymers

HEMA, NVP, MMA and EGDMA were used as the basic combination for polymerization and AIBN was used as the initiator. Also, in order to add functionality after mixing the Ag nanoparticles for each ratio, 3% furfuryl isocyanate was added to the monomer after which

the product was disintegrated for approximately one hour in an ultrasonic benchtop cleaner (branson 2510) and the compounded monomer was injected into a mold for thermal polymerization. Cast molding was used to manufacture the soft ophthalmic lens. Each lens sample was hydrated in 0.9% NaCl normal saline for 24 hours after which the physical properties such as refractive index, optical transmittance, contact angle and tensile strength were evaluated. Each sample used in the experiment was added with 3% furfuryl isocyanate and sorted based on the ratio of the Ag nanoparticle of which each were named Ref., FI3Ag1, FI3Ag2, FI3Ag3 and FI3Ag5. A total of five samples were produced for all combinations and the average value was calculated of the five samples. The mixture ratios of the contact lens samples used in this study are shown in Table 1.

2.3. Instruments and Analysis

The refractive index was measured based on the ISO 18369-4:2006 and the average of three measurements of the hydrated contact lens was obtained using an ABBE refractometer (ATAGO NAR IT, Japan). The gravimetric method was used based on the ISO 18369-4:2006 to measure and calculate the water content. Optical transmittance was obtained for UV-B, UV-A and visual light using a spectral transmittance meter (TOPCON TM-2, Japan) and was described as percentage values. The wettability of the produced lenses was measured and evaluated with the contact angle while FE-SEM (JSM-7500F+EDS, Oxford) was used to analyze the surface of the lenses. To measure the tensile strength, AIKOH Engineering's Model-RX series was used to measure the maximum value when the lens is destructed when 0.00~2.00 kgf force is applied for 0-20 seconds. An atomic force microscope (XE-100, Parks System) was used to analyze the nanoparticles included in the macromolecular polymer.

Fig. 1. Chemical structures of additive.

Table 1. Percent compositions of samples

						Unit: %
Sample	HEMA	MMA	MA	EGDMA	FI	Ag*
Ref.	96.62	0.97	0.48	0.24	-	-
FI3Ag1	93.02	0.93	0.47	0.23	2.84	0.93
FI3Ag2	92.17	0.92	0.46	0.23	2.82	1.84
FI3Ag3	91.32	0.91	0.46	0.23	2.79	2.74
FI3Ag5	89.69	0.90	0.45	0.22	2.76	4.48

Ag* : Ag nanoparticle

Results and Discussion

3.1. Macromolecular Polymerization and Production of Ophthalmic Lens

The ophthalmic lenses produced through macromolecular thermal polymerization were hydrated for 24 hours in a normal saline solution, and the lenses produced by mixing Ag nanoparticles after which 3% fur-

furyl isocyanate was added resulting in transparent, colorless and hydrophilic contact lenses as well as light-brown polymers. Generally, a higher ratio of Ag nanoparticles resulted in a darker lens. The exteriors and colors of the produced ophthalmic lenses are shown in Fig. 2. Also, the results of the SEM analysis to investigate the surface of the lenses are shown in Fig. 3 and 4.

Fig. 2. Photograph of tinted ophthalmic hydrogel lens.

Fig. 3. Surface analysis of polymer by SEM.

Fig. 4. Analysis of Ag nanoparticles by SEM

3.2. Physical Characteristics

3.2.1. Water Content

The measurement of the water content of the produced lenses showed that the average water content of Ref. where furfuryl isocyanate and Ag nanoparticles were not added is 36.53%. The average water content of FI3Ag1 where 3% furfuryl isocyanate and Ag nanoparticles were added at each ratio showed to be 32.08% which is lower than that of Ref. Also, the average water content of FI3Ag2 was 32.29%, FI3Ag3 32.48% and FI3Ag5 was 32.67% showing that the water content increases slightly. However, the increase in ratio of 3% furfuryl isocyanate and Ag nanoparticles did not have a significant effect on the water content. The water content and refractive index of each combination are shown in Fig. 5.

3.2.2. Refractive Index

The refractive index of each lens was 1.436 for Ref., 1.448 for FI3Ag1, 1.449 for FI3Ag2, 1.448 for FI3Ag3 and 1.447 for FI3Ag5. As with the water content, the increase in the ratio of 3% furfuryl isocyanate and Ag nanoparticles did not have a significant effect on the refractive index. Also, the refractive index showed to be in reverse proportion to the water content. The water contents of each combination are shown in Table 2.

3.2.3. Spectral Transmittance

The average spectral transmittance of the FI3Ag combination was 34.2~40.4% for UV-B, 39.0~55.8% for

Table 2. Refractive index of samples

Sample	Refractive index
Ref.	1.436
FI3Ag1	1.448
FI3Ag2	1.449
FI3Ag3	1.448
FI3Ag5	1.447

Table 3. Spectral transmittance of samples (FI3Ag)

unit: %			
Sample	UV-B	UV-A	Vis.
Ref.	84.0	88.0	91.4
FI3Ag1	40.4	55.8	83.2
FI3Ag2	37.2	54.2	84.0
FI3Ag3	35.4	40.0	67.6
FI3Ag5	34.2	39.0	67.6

UV-A and 67.6~83.2% for visible light. Meanwhile, the ophthalmic lens showed to block approximately up to 65% of UV-B and up to 61% of UV-A. Also, the lens showed to block more UV-B, and the transmittance for UV-A was low showing that the lens is effective in blocking UV. The transmittance for visible light was low compared to other combinations, but this is considered to be a result of the color of the lens rather than the transmittance. The spectral transmittance of Ref. and FI3Ag are shown and compared in Table 3 and Fig. 6.

Fig. 5. Effect of FI3Ag on water content and refractive index.

Fig. 6. Spectral transmittance of sample (Ref., FI3Ag1 and FI3Ag5).

3.2.4. Contact Angle

The surface wettability of each sample was measured using the contact angle where a smaller contact angle was considered to indicate better wettability. The contact angle measured to evaluate the wettability of each sample was 52.76° for Ref., 68.72° for FI3Ag1, 74.60° for FI3Ag2, 78.80° for FI3Ag3 and 83.05° for FI3Ag5, indicating that a larger ratio of Ag nanoparticles results in a larger contact angle which can be interpreted as decreased surface wettability. The contact angles of two selected combinations are shown in Fig. 7.

3.2.5. Tensile Strength

The tensile strength measured to evaluate the durability of the produced ophthalmic lenses showed that the tensile strength of Ref. is 0.245 kgf. For each combination, the tensile strength was 0.541 kgf for FI3Ag, 0.635 kgf for FI3Ag1, 0.685 kgf for FI3Ag1 and 0.755 kgf for Ag1FI, and the FI1Ag combination added with

Ag nanoparticles at each ratio after adding furfuryl isocyanate also showed a higher tensile strength than general hydrogel contact lenses indicating that tensile strength increases with the increase of the ratio of silver nanoparticles which is considered to be a result of the basic properties of furfuryl isocyanate and Ag nanoparticles. The tensile strengths of each combination are shown in Table 4 and the tensile strength of a selected sample is shown in Fig. 8.

Table 7. Tensile strength of samples

Sample	Tensile strength (kgf)
Ref.	0.245
FI3Ag1	0.541
FI3Ag2	0.635
FI3Ag3	0.685
FI3Ag5	0.755

Fig. 7. Contact angle of sample (FI3Ag1 & FI3Ag5).

Fig. 8. Tensile strength of sample (Ref. & FI3Ag5).

Conclusion

Silver nanoparticles were added to a basic hydrophilic ophthalmic lens monomer at each ratio which then had 3% furfuryl isocyanate added to produce hydrophilic lens polymers. The physical and optical properties were evaluated to determine the performance of the lenses, and in particular, UV transmittance and tensile strength were measured to investigate the potentials of Ag nanoparticles in improving the UV-blocking properties and durability of a contact lens. The results of this study show that a higher ratio of Ag nanoparticles is associated with an increase in water content, no significant change in refractive index and a decrease in spectral transmittance. Also, the contact angle increased indicating that the wettability is low which can hinder wearability, but the increase of the water was only minor which indicates that irritability can be compensated, and the tensile strength was significantly higher than that of general hydrogel contact lenses. The outcomes of this study indicates that compounding Ag nanoparticles at certain ratios when producing hydrogel ophthalmic contact lenses can be effective in improving durability and UV-blocking properties while not affecting physical properties such as the water content and refractive index.

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