J. Chosun Natural Sci.
Vol. 13, No. 1 (2020) pp. 13 – 18
https://doi.org/10.13160/ricns.2020.13.1.13

Preparation and Analysis of Functional Hydrogel Lenses Using Cerium Iron Hydroxide Nanoparticles

Su-Mi Shin and A-Young Sung†

Abstract

This study used cerium iron hydroxide nanoparticle with HEMA (2-hydroxyethyl methacrylate), the cross-linker EGDMA (ethylene glycol dimethacrylate), NVP (N-vinyl-2-pyrrolidone) and the initiator AIBN (azobisisobutyronitrile) for copolymerization. Also, the physical properties of the prepared lenses were compared, and their applicability as polymers for ophthalmic materials was experimented. The results of the measurement showed that the UV blocking rate and the wettability increased with the cerium iron hydroxide nanoparticles addition ratio, and the refractive index and water content were not affected. Thus, the produced copolymer is expected to be useful as a functional contact lens material while satisfying the basic physical properties of the hydrogel contact lens.

Keywords : Nanoparticles, Cerium, UV Blocking, Wettability

1. Instruction

Nanotechnology, which is used based on nanoscale materials, is widely used in real life.[1] In particular, many researchers are conducting extensive research using nanotechnology in relation to "bio,"[2,3] and since recently, nanotechnology research has been conducted to pursue various functionalities of ophthalmic contact lenses directly connected to the eye.[4,5] Contact lenses are generally used regardless of age for vision correction, beauty, and treatment purposes. Thus, there is a growing interest in functional lenses that can alleviate the discomfort associated with wearing contact lenses and can protect eye health. The eyes are more vulnerable to UV rays than the skin tissues, and the importance of UV protection, which is a major cause of eye diseases, is increasing.[6] Therefore, nano materials are added to the main material of contact lenses so they would absorb light in a specific wavelength range, and so they could be used as a material for blocking UV rays.[7,8] The materials that are mainly used for UV protection include gold, silver, platinum, and cerium,[9-11] and nanomaterials have not only UV protection but also antimicrobial properties, so their research and application are expanding.[12,13] The physical properties of contact lenses include the water content, refractive index, wettability, oxygen transmissibility, and strength. To improve these physical properties, hydrophilic materials are mainly used. The use of such materials increases the water content, wettability, and oxygen transmissibility, but as the water content increases, the refractive index and the strength associated with the durability of the lens decrease.[14,15] Therefore, it is necessary to study the material so that the damage to the lens can be minimized without losing the lens's original shape, by maintaining the hydrophilic properties and improving the durability at the same time. In this study, ophthalmic contact lenses were fabricated using cerium iron hydroxide nanoparticles, employed as a sunscreen, as an additive, to evaluate the physical properties of the fabricated lenses. In addition, the physical properties of the lenses fabricated by adding 4-chlorostyrene at different ratios to add functionality to the lenses and to improve their durability were evaluated.

Department of Optometry & Vision Science, Daegu Catholic University, Gyeongsan

†Corresponding author : say123sg@hanmail.net
(Received : February 5, 2020, Revised : March 9, 2020, Accepted : March 14, 2020)

2. Experiment Method

2.1. Reagents and Materials Used

For 2-hydroxyethyl methacrylate (HEMA) and azobisisobutyronitrile (AIBN), an initiator, the products of Junsei were used. For N-vinylpyrrolidone (NVP), 4-chlorostyrene, ethylene glycol dimethacrylate (EGDMA, a crosslinking agent), and cerium iron hydroxide (CI, a nanoparticle), the products of Sigma-Aldrich were used.

2.2. Polymerization

For polymerization, a mixture of HEMA, EGDMA, AIBN, and NVP was used as a basic combination, and CI was used as an additive. After adding CI at different ratios, it was evenly dispersed for about 30 minutes using an ultrasonic disperser (Branson 2510). In addition, one combination of CI was selected, and 4-chlorostyrene was mixed with the basic combination, followed by stirring with a vortex for about 1 hour. After thermal polymerization using the respective mixed monomers, the physical properties of the fabricated contact lenses were measured. The fabricated contact lens samples were named Ref, CI05, CI1, and CI2, respectively, according to the amount of CI added. CI2 was selected and classified into CI2-S1, CI2-S3, CI2-S5, CI2-S7, and CI2-S10, according to the amount of 4-chlorostyrene added. Table 1 shows the mixing ratios of the samples that were used in the experiment.

3. Results and Discussion

3.1. Thermal Properties according to Initiator Condition

To compare the degree of polymerization according to the initiator, the differential scanning calorimetry

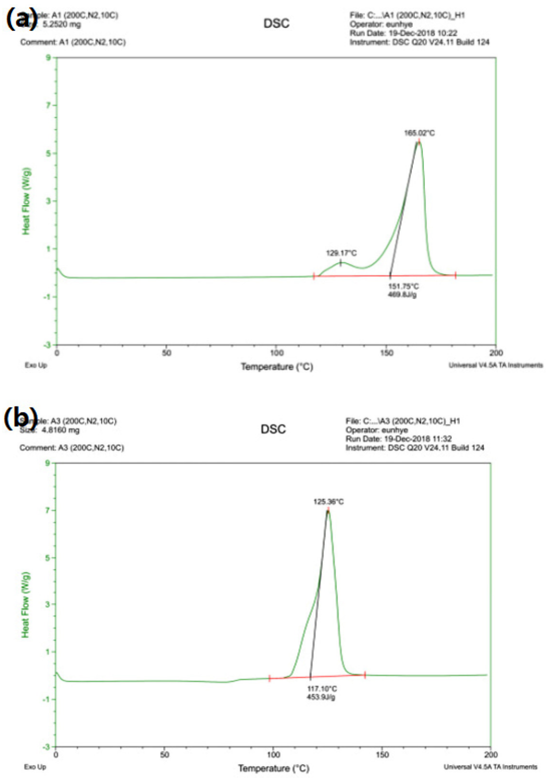

Fig. 1. Typical DSC thermogram analysis of the contact lens samples: (a) CI-AIBN0.1 and (b) CI-AIBN0.3.

(DSC) was measured by mixing AIBN (an initiator) at 0.1 and 0.3%, respectively, to CI among the fabricated contact lens samples. DSC can be used to analyze the thermal changes such as the decomposition, transition, and formation of new crystal phases according to the temperature of each sample. In addition, according to the amount of initiator used, the samples were named CI-AIBN0.1 and CI-AIBN0.3. The comparison of the

Table 1. Percent compositions of the CI samples (unit: wt%)

Sample	HEMA	EGDMA	AIBN	NVP	CEI	S
Ref	92.76	0.46	0.28	6.49	-	-
CI05	92.72	0.46	0.28	6.49	0.05	-
CI1	92.67	0.46	0.28	6.49	0.10	-
CI2	92.58	0.46	0.28	6.48	0.20	-
CI2-S1	91.66	0.46	0.27	6.42	0.20	0.99
CI2-S3	89.88	0.45	0.27	6.29	0.19	2.91
CI2-S5	88.17	0.44	0.26	6.17	0.19	4.76
CI2-S7	86.52	0.43	0.26	6.06	0.19	6.54
CI2-S10	84.16	0.42	0.25	5.89	0.18	9.09

glass transition temperatures (Tg) of primary and secondary heating showed 66.7 and 74°C, respectively, for CI-AIBN0.1, and 88.2 and 98°C, respectively, for CI-AIBN0.3. The temperatures were slightly higher in CI-AIBN0.3 than in CI-AIBN0.1. As the initiator amount increased, the Tg also increased, indicating a higher crosslinking degree. Moreover, as shown in Fig. 1, CI-AIBN0.3 had a lower heat capacity than CI-AIBN0.1, indicating that it had a high degree of crosslinking with low heat capacity. CI-AIBN0.1 was found to have had two peaks, indicating that the degree of polymerization was somewhat incomplete. As such, CI-AIBN0.3 was selected for the experiment rather than CI-AIBN0.1.

3.2. Fabrication of Hydrogel Lenses Containing Cerium Iron Hydroxide Nanoparticles

To analyze the properties of cerium iron hydroxide nanoparticles included in the hydrogel lens, the optical and physical properties were measured according to the addition ratio based on the aforementioned results. Ref-N7 was renamed Ref, and CI-N7 was renamed CI05. The samples were named Ref, CI05, CI1, and CI2 according to the amount of CI added.

3.2.1. Optical Transmittance

For the results of the measurement of the spectral transmittance to identify the optical properties, a transparent lens was fabricated for the Ref without nanoparticles, showing 59.15% transmittance for UV-B, 82.20% for UV-A, and 88.28% for visible ray. According to the CI addition amount, the transmittance was 9-31% for UV-B, 35-64% for UV-A, and 85- 89% for visible ray, indicating that the UV blocking rate gradually increased with the CI addition ratio. Fig. 2 shows the measurement graph of each combination's optical transmittance. Moreover, the sample assumed a pale yellow color when Cl was added to it, and the colors of the copolymerized lenses are compared in Fig. 3.

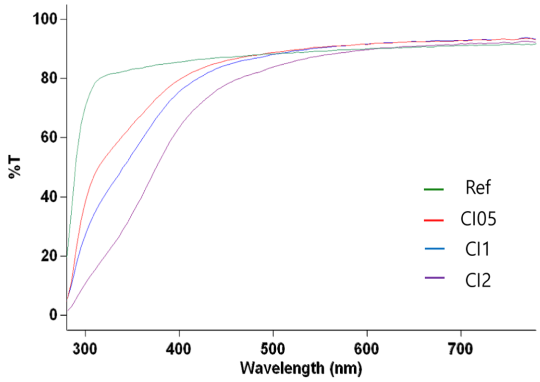

Fig. 2. Spectral transmittance of the contact lens samples.

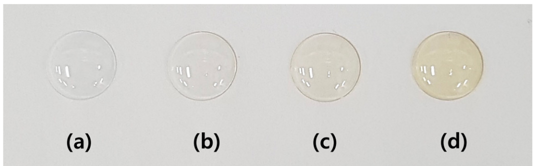

Fig. 3. Produced hydrogel lens samples: (a) Ref; (b) CI05; (c) CI1; and (d) C2.

3.2.2. Water Content and Refractive Index

The water content and refractive index were measured based on ISO 18369-4:2006, using the gravimetric method and an ABBE refractometer (ATAGO NAR 1T, Japan), respectively. The measurement results were similar to those of the Ref regardless of the addition of CI. As a result, CI was found not to change the physical properties like water content and refractive index. The water content and refractive index results are summarized in Table 2.

3.2.3. Wettability

The wettability of the fabricated lenses was evaluated through the contact angle, and was measured using the sessile drop method. The contact angle was 70.45° for the Ref without nanoparticles, 66.87° for CI05, 65.54° for CI1, and 62.50° for CI2. As a result, the contact angle slightly decreased with an increasing amount of CI, indicating that the wettability increased. The contact angle measurement images are compared in Fig. 4.

As a result, the addition of CI did not change the physical properties of the water content and the refrac-

Table 2. Physical properties of the contact lens samples with nanoparticles

	Ref	CI05	CI1	CI2
Refractive index	1.4261	1.4255	1.4260	1.4256
Water content (%)	41.45	41.62	41.47	41.55

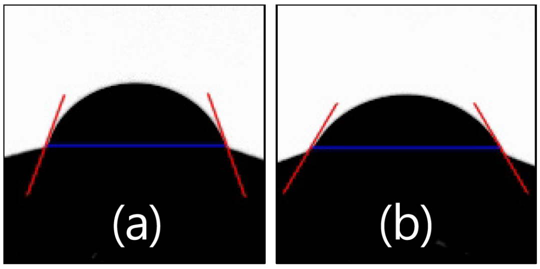

Fig. 4. Wettability of samples: (a) Ref. (b) CI2.

tive index, but slightly increased the wettability and at the same time showed excellent UV protection. CI2 was selected based on these results, and 4-Chlorostyrene that can increase durability was added at each ratio.

3.3. Hydrogel Lenses Containing Cerium Iron Hydroxide Nanoparticles and 4-Chlorostyrene

As a result of the copolymerization by adding 4-chlorostyrene at each ratio to CI2, the refractive index was 1.4256-1.4694 and the water content was 41.55-26.66%. This showed an inversely proportional change, in which the refractive index increased while the water content decreased due to the influence of 4-chlorostyrene. The contact angle was 62.50-85.09°, indicating that it gradually increased according to the increasing ratio of 4-chlorostyrene, decreasing the wettability. The breaking strength was 0.13326-1.67409 kgf, showing an overall increase, especially in CI2-S5. The spectral transmittance was not significantly affected by the addition of 4-chlorostyrene, and thus, there was no large difference from CI2 when 4-chlorostyrene was not added, showing that 4-chlorostyrene does not greatly affect the optical properties.

When 4-chlorostyrene was added, the refractive index and strength increased whereas the water content and wettability tended to decrease. In addition, 4-chlorostyrene did not have a great influence on the optical properties, like spectral transmittance. The refractive indicex and breaking strengths of the lenses with 4-chlorostyrene added to CI are summarized in Fig. 5.

3.3.1. Stability Analysis

The absorbance, pH, and extractables were measured to evaluate the stability of the produced lens polymer. The absorbance values were compared by measuring the hydrated solution after 1-, 5-, and 10-day hydration, and the pH and extractables were measured after the prepared lenses were heated at 70°C for 24 hours.

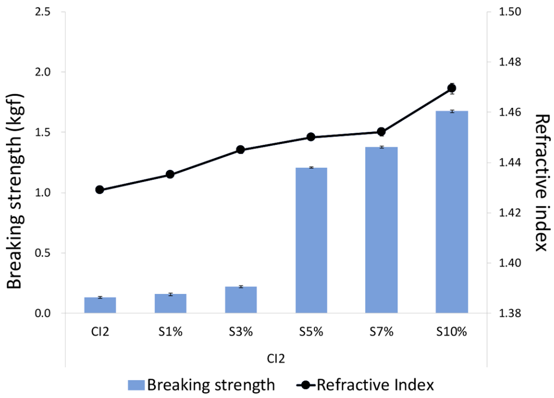

Fig. 5. Refractive indices and breaking strengths of the contact lens samples.

3.3.2. Absorbance Analysis

In the measurement results of the absorbance after 1-, 5-, and 10-day hydration, it was found to be 0.2633-0.4483 for the Ref without nanoparticles, 0.1230-0.1723 for CI2, 0.0398-0.0705 for CI2-S1, and 0.0450-0.1096 for CI2-S10. Compared to Ref, the addition of CI (the nanoparticles) improved the polymerization stability. It increased more when 1% 4-chlorostyrene was added rather than 10%. Fig. 6 shows the absorbance results on day 10.

3.3.3. pH Analysis

When the pH results of the control and experimental groups were compared, Ref, CI2, CI2-S1, and CI2-S10 all showed pH differences of 0.02-0.03. As the pH dif-

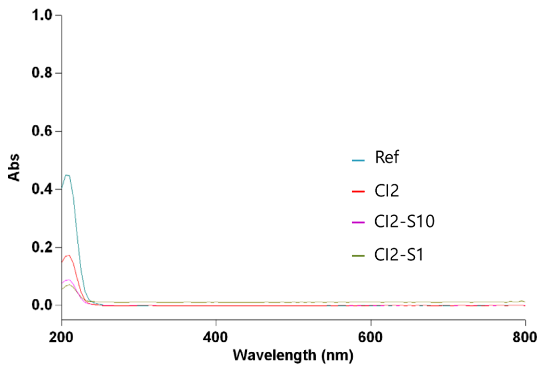

Fig. 6. Absorbance values of the contact lens samples after 10 days.

ferences in all the groups were less than 1.5, which is very small, the stability is considered excellent overall.

3.3.4. Analysis of the Extractables

For the measurement results of the difference in extractables between the control and experimental groups using distilled water as a control, it was 5.2 ml for Ref, 4.6 ml for CI2, 2.7 ml for CI2-S1, and 3.2 ml for CI2-S10. There was a difference depending on the presence or absence of nanoparticles and the ratio of 4-chlorostyrene, and a tendency similar to that of absorbance was shown.

The comparison of the samples showed that the pH difference was very low, and all of them showed excellent polymerization stability for hydrogen ions. In the case of the absorbance and extractables, the addition of CI showed higher polymerization stability compared to the Ref without nanoparticles, and the stability was slightly higher when 1% 4-chlorostyrene was added than when 10% was added. Therefore, if 4-chlorostyrene is used as an additive, 1% addition is considered stable.

4. Conclusion

This study determined the combination of 2-hydroxyethyl methacrylate (HEMA, mainly used as a hydrogel material), ethylene glycol dimethacrylate (EGDMA, a crosslinking agent), N-vinylpyrrolidone (NVP, a hydrophilic monomer), and azobisisobutyronitrile (AIBN, an initiator) as a basic combination. The nanoparticle, cerium iron hydroxide (CI), was used as an additive for the fabrication of ophthalmic polymers, and their physical properties were measured. The experiment results showed that the UV blocking rate increased with the CI addition ratio, the contact angle slightly decreased, and the physical properties like the refractive index and water content were not affected. In addition, in the case of the polymers fabricated by adding 4-chlorostyrene to increase the durability, the refractive index and the breaking strength significantly increased as the amount of 4-chlorostyrene added increased. According to the CI addition amount, the degree of polymerization increased, and the polymerization stability increased more when 1% 4-chlorostyrene was added rather than 10%. This study revealed that CI has an excellent UV protection effect, and that 4-chlorostyrene as an additive can be used as an ophthalmic material to increase the refractive index and strength and to improve the polymerization stability.

References

[1] C. S. Yoon, "Consideration of Nano-Measurement Strategy", Korean Journal of Environmental Health Sciences, 37(1), 73-79, 2011.

[2] O. V. Salata, "Applications of nanoparticles in biology and medicine" Journal of nanobiotechnology, 2(1), 3, 2004.

[3] K. Cho., X. U. Wang., S. Nie. And D. M. Shin, "Therapeutic nanoparticles for drug delivery in cancer", Clinical cancer research, 14(5), 1310-1316, 2008.

[4] C. F. Lai, J. S. Li, Y. T. Fang, C. J. Chien and C. H. Lee, "UV and blue-light anti-reflective structurally colored contact lenses based on a copolymer hydrogel with amorphous array nanostructures", RSC advances, 8(8), 4006-4013, 2018.

[5] B. S. F. Bazzaz, B. Khameneh, M. M. Jalili-Behabadi, B. Malaekeh-Nikouei and S. A. Mohajeri, "Preparation, characterization and antimicrobial study of a hydrogel (soft contact lens) material impregnated with silver nanoparticles", Contact Lens and Anterior Eye, 37(3), 149-152, 2014

[6] R. P. Gallagher and T. K. Lee, "Adverse effects of ultraviolet radiation: a brief review", Progress in biophysics and molecular biology, 92(1), 119-131, 2006.

[7] T. H. Kim and A. Y. Sung, "Copolymerizaton and application of hydrogel lens materials containing titanium (IV) isopropoxide and tungsten (VI) oxide nanoparticles", The Korean Journal of Vision Science, 15(4), 427-438, 2013.

[8] S. Gause and A. Chauhan, "Nanoparticle-loaded UV-blocking contact lenses", Journal of Applied Polymer Science, 132(37), 2015.

[9] M. J. Lee and A. Y. Sung, "Polymerization and Preparation of High Functional Ophthalmic Lens Material Containing 2-Fluoro Styrene with Si and Ag Nanoparticles", Science of Advanced Materials, 12(3), 427-434, 2020.

[10] M. J. Lee, S. M. Shin and A. Y. Sung, "Preparation and Characterization of Functional Ophthalmic Polymer Containing Nanoparticles Using Heat Treatment Method After Polymerization", Journal of nanoscience and nanotechnology, 19(8), 4495-4502, 2019.

[11] M. Aklalouch, A. Calleja, X. Granados, et al., "Hybrid sol–gel layers containing CeO2 nanoparticles as UV-protection of plastic lenses for concentrated photovoltaics", Solar energy materials and solar cells, 120, 175-182, 2014.

[12] M. Montazer and S. Seifollahzadeh, "Enhanced self-cleaning, antibacterial and UV protection properties of nano TiO2 treated textile through enzymatic pretreatment", Photochemistry and photobiology, 87(4), 877-883, 2011.

[13] M. M. AbdElhady, "Preparation and characterization of chitosan/zinc oxide nanoparticles for imparting antimicrobial and UV protection to cotton fabric", International journal of carbohydrate chemistry, 2012.

[14] M. J. Lee and A. Y. Sung, "Analysis of Physical Properties of Hydrogel Lenses Polymer Containing Styrene and PVP", Korean journal of materials research, 26(7), 399-407, 2019.

[15] Brennan, N.A., "A simple instrument for measuring the water content of hydrogel lenses", International Contact Lens Clinic, 10, 357-361, 1983.