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Study on the Preparation and Characterization of Ophthalmic Polymer with High and Low-Water Content

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ABSTRACT. This study was planned considering the chain length, hydrophilicity, and hydrophobicity of the additives to be used in the polymerization, while various ophthalmic lenses that use various additives with similar water contents were manufactured before their optical and physical properties were compared and analyzed. With regard to the additives required for manufacturing high-, medium-, and low-water content lens groups, HEA (hydroxyethyl acrylate), PVP (polyvinylpyrrolidone), and NMV(N-methyl-N-vinylacetamide) were used as additives for preparing the high-water content lens group, HEMA(2-hydroxyethyl methacrylate), HPMA(hydroxypropyl methacrylate) and BD(1,4-butanediol) were used for the medium-water content lens group. For the low-water content lens group, BMA(buthyl methacrylate), BDDA(1,4-butanediol diacrylate), and Bis-GMA(bisphenol A glycerolate diacrylate) were used, respectively. The average water content of HEA was 40.14%; that of PVP, 39.63%; and that of NMV, 40.52%. The mean of water content was 35.92% for HEMA, 35.74% for BD, and 34.62% for HPMA. For the low-water content lens group, the mean of water content was 26.69% for BMA, 27.76% for BDDA, and 26.14% for Bis-GMA. With regard to the results of the water content measurement using a moisture analyzer, the average water content of the high-water content lens group was 41.34% for HEA, 42.62% for PVP, and 42.73% for NMV. Finally, for the low-water content lens group, the average water content was 28.62% for BMA, 28.82% for BDDA, and 28.32% for Bis-GMA. The measurements of the water contents of the lenses using the two methods showed that the water content and refractive index of the lenses were similar in all the lens groups. The measurements of the contact angles, however, showed a different wettability value for each lens with a similar water content. Also, the change tendency of the lens curvature according to the change of time showed that the change amount became larger and the recovery time became longer from the lens samples with a lower water content to those with a higher water content. Based on these results that will be helpful for the study of ophthalmic lenses.

Key words: High-water content group, Medium-water content group, Low-water content group, Wettability, Base curvature

INTRODUCTION

Remarkable progress has been made in the research on the optical and physical properties of lenses, along with the progress in the research on lens materials for medical use. In the case of hydrophilic lenses, researches on hydrogel lenses based on HEMA have been actively conducted considering the wearer convenience (e.g., the water content and wettability of the lenses) ever since Otto Wichterle and Drahoslav of Czechoslovakia developed the hydrophilic polymer PHEMA (polyhydroxyethyl methacrylate) in 1955.[1–8] Generally a water-soluble polymer, PVP is widely known as a polymer with low protein deposition and that increases the dissolution rate of hydrophobic compounds. Thanks to such property, the polymer is being used in diverse medical fields either as a dressing or for treating skin ulcers and other diseases.[4,5,9,10] NMV is used as a monomer that improves the surface hydrophilicity of materials such as films. Also a polar monomer with excellent biocompatibility, NMV imparts desirable properties to lenses, such as blood compatibility and a hydrophilic surface. It has also been reported that a hydrophilic monomer such as NMV can increase the electric conductivity at 37.1 °C.[11–13] BD is used in various fields either as a moisturizer or as a flexible material, or as a material to compensate for wettability, the property that is absent in other hydrophobic monomers, such as polyethylene terephthalate. In a study conducted by Cho et al., the change in the water content was not significant, and the contact angle decreased as the BD addition amount increased.[6] BDDA is used as a hydrophobic monomer because acrylate is attached to both ends of BD. It is also used as a crosslinking agent because it accelerates the radical reaction of an acrylic monomer.[14,15] BMA is a monomer with high tensile strength but strong hydrophobicity and poor wettability.[7] Bis-GMA is also used for restoring dental resin because it shows relatively low hardening shrinkage while the double bond at both ends of the molecule produce a highly cross-linked network polymer. Moreover, the viscosity of the resin is very high because a hydrogen bond is formed due to the hydroxyl groups present in the molecule.[16] Examples of monomers with a similar structure as HEMA, the basic monomer that comprises hydrogel ophthalmic lenses, are HEA and HPMA. According to related researches, hydrophilic monomer has been reported to have hydrophilic and hydrophobic physical properties depending on the chain length of the hydrophilic polymer monomers.[8] The experiment that was performed in this study was planned considering the chain length, hydrophilicity, and hydrophobicity of the additives to be used in the polymerization, while various ophthalmic lenses that use various additives with similar water contents were manufactured before their optical and physical properties were compared and analyzed. The water content, the water evaporation rate and the contact angle of the contact lens affect the feeling of wearing, and the curvature change is related to the variation of the lens power when worn, and the light transmittance in the visible light region affects the image clarity.

EXPERIMENTAL

Polymerization and Manufacturing

To fabricate ophthalmic lenses, HEMA, EGDMA (a crosslinking agent), and AIBN (an initiator) were gathered as a basic combination for copolymerization. With regard to the additives required for manufacturing high-, medium-, and low-water content lens groups, HEA, PVP, and NMV were used as additives for preparing the high-water content lens group, and HPMA and BD were used for the medium-water content lens group. For the low-water content lens group, BMA, BDDA, and Bis-GMA were used, respectively, at about 10%(wt %) ratios. The HEMA and AIBN that were used as additives were made by JUNSEI whereas the EGDMA, HEA, PVP, NMV, HPMA, BD, BMA, BDDA, and Bis-GMA were all made by Sigma-Aldrich. The lenses were polymerized at 100 °C for 1 hour using the cast mold method. The water content, optical transmittance, and refractive index of each polymerized contact lens sample were measured after hydration for 24 hours in a 0.9% saline solution. The water content of each prepared lens was measured with a microwave oven and a moisture analyzer (AND, MS-70) before the lenses were again compared with one another. The molecular formulas of the additives are shown in *Fig*. 1, and their mixing ratios by water content are shown in *Table* 1.

The water content of the ophthalmic lens was measured for the reference to differentiate by the water content of each lens. In this study, the water content of each fabricated ophthalmic lens was measured using the gravimetric method, and the measurement results were compared and analyzed with those that were obtained using a microwave oven and a moisture analyzer. For the microwave oven method, the weights of the oven-dried and hydrated samples were measured with a balance scale. In the case of the moisture analyzer method, the evaporation rate per minute and the water content were measured by placing and drying the moist samples on an MS-70 instrument (AND Corporation). By measuring the evaporation rate of water per minute of the manufactured ophthalmic lens, it is possible to predict the amount of evaporation when the ophthalmic lens is worn. The per-minute evaporation rate

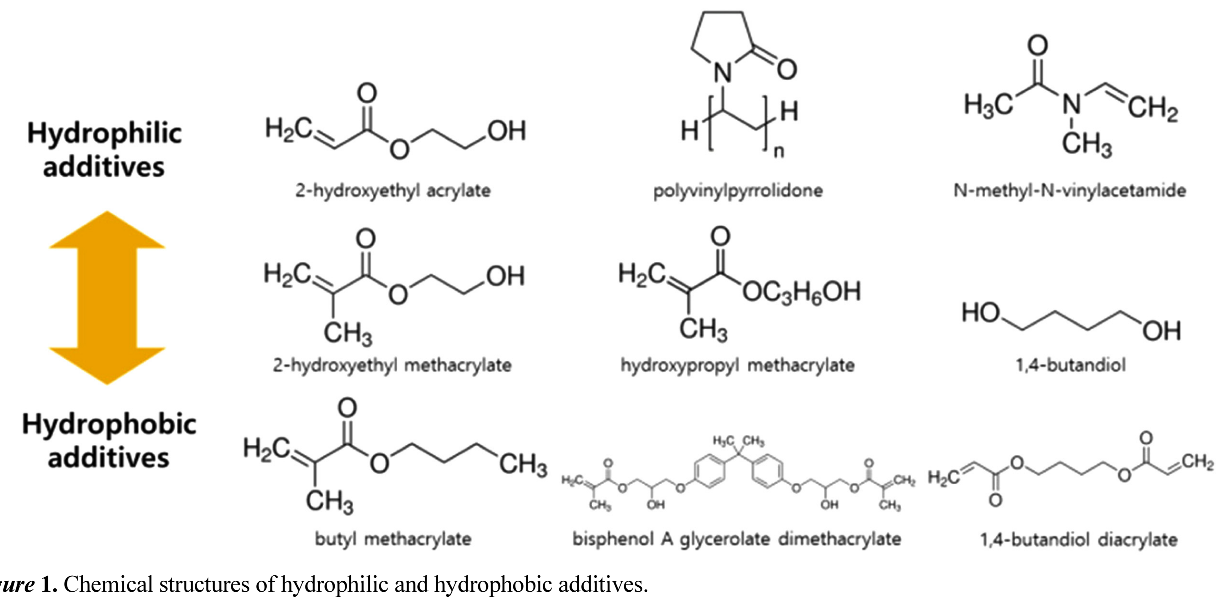

***Figure* 1.** Chemical structures of hydrophilic and hydrophobic additives.

***Table* 1.** Percent compositions of samples with water content of hydrogel polymer Unit : wt %

	Sample	HEMA	EGDMA	AIBN	HEA	PVP	NMV	SUM
High W.C.*	HEA	90.37	0.45	0.09	9.09	-	-	100.00
	PVP	90.37	0.45	0.09	-	9.09	-	100.00
	NMV	90.37	0.45	0.09	-	-	9.09	100.00
Medium W.C.*	Sample	HEMA	EGDMA	AIBN	HEMA	HPMA	BD	SUM
	HEMA	90.37	0.45	0.09	9.09	-	-	100.00
	HPMA	90.37	0.45	0.09	-	9.09	-	100.00
	BD	90.37	0.45	0.09	-	-	9.09	100.00
Low W.C.*	Sample	HEMA	EGDMA	AIBN	BMA	BDDA	Bis-GMA	SUM
	BMA	90.37	0.45	0.09	9.09	-	-	100.00
	Bis-GMA	90.37	0.45	0.09	-	9.09	-	100.00
	BDDA	90.37	0.45	0.09	-	-	9.09	100.00

*W.C. = water content

of each lens was converted by 1 minute for analysis. A contact angle instrument (Kruss GMBH, DSA30) was used to measure the wettability of the manufactured lenses. The contact angle was measured using the sessile drop method, in which the angle generated by dropping sterile physiological saline on the sample surface at room temperature was measured. With regard to the baseline of the sessile drop method, the contact angle calculated from the curvatures of the lens and the water droplet was determined as the final value, with the curved baseline as the baseline. The measurement of the curvature change of the manufactured ophthalmic lens can be used as a criterion for judging the recovery time when drying the lens according to the water content. The JCF of Optimec was used to measure the variation of the base curve according to the changing hydration time, while the measured temperature of the samples was maintained using a TC 20 temperature controller. As the measurement method, a completely dried lens sample was immersed in a 0.9% physiological saline solution set at 21°C to observe the changes in the curvature according to the hydration time. A spectrophotometer (Agilent, Cary 60 UV-Vis.) was used to measure the optical transmittance of the lenses, and the transmittance levels in the near-UV and visible-light regions were measured with the water removed from the lens surfaces.

RESULTS AND DISCUSSION

Polymerization and Manufacturing

For the production of the basic ophthalmic lens, HEMA, EGDMA as a crosslinking agent, and AIBN as an initiator were copolymerized. With regard to the additives required for manufacturing the high-, Medium-, and low-water content lens groups, HEA, PVP, and NMV were used as additives for preparing the high-water content lens group, and HPMA and BD were used for preparing the medium-water content lens group. For the low-water content lens group, BMA, BDDA, and Bis-GMA were used as additives for polymerization. It was confirmed that the basic lens shape appeared across all the lens group combinations after polymerization.

Optical and Physical Properties

A microwave oven and a moisture analyzer were used to measure the water contents of the ophthalmic lens samples. The average water content of HEA was 40.14%; that of PVP, 39.63%; and that of NMV, 40.52%. The mean water content was 35.92% for HEMA, 35.74% for BD, and 34.62% for HPMA. For the low-water content lens group, the average water content was 26.69% for BMA, 27.76% for BDDA, and 26.14% for Bis-GMA. With regard to the results of the water content measurement using a moisture analyzer, the average water content in the high-water content lens group was 41.34% for HEA, 42.62% for PVP, and 42.73% for NMV. The mean water content was 39.33% for HEMA, 39.53% for BD, and 38.20% for HPMA. Finally, for the low-water content lens group, the average water content was 28.62% for BMA, 28.82% for BDDA, and 28.32% for Bis-GMA. In all the lens group combinations, the water content measured by the moisture analyzer was higher than that measured by the microwave oven, whereas the reproducibility of the measurements was somewhat lower. The change in the water content according to the aforementioned two measurement methods is shown in *Fig.* 2.

The evaporation rate per minute of each sample was measured using a moisture analyzer, and the evaporation rate per minute was measured in units of 1-5 minutes for conversion. The measurement results showed that the HEA of the high-water content lens group was 1.10-0.27%; the

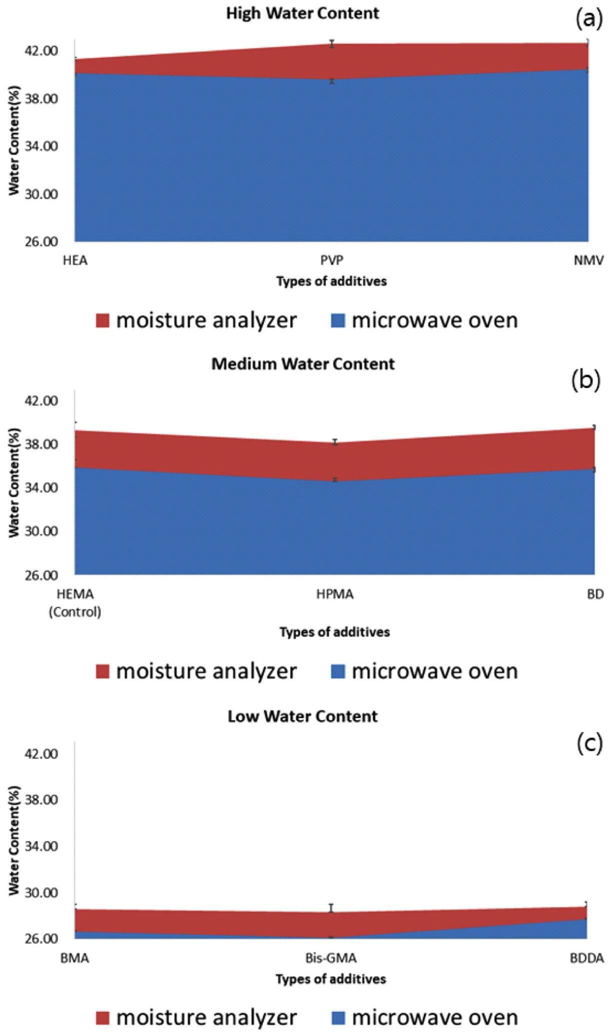

***Figure* 2.** Water content of samples (n=5) [(a): High water content, (b): Medium water content, (c): Low water content].

PVP, 1.21-0.28%; and the NMV, 1.23-0.26%, while the HEMA was determined to be 1.33-0.21%; the BD, 1.19-0.23%; and the HPMA, 1.20-0.21%. In the low-water content lens group, the BMA was 0.85-0.16%; the Bis-GMA, 0.86-0.16%; and the BDDA, 0.85-0.16%. The experiment showed that the water evaporation rate of the high-water content lens group was higher than that of the low-water content lens group. Both the high- and medium-water content lens groups showed evaporation rates that were significantly different from that of the low-water content lens group, thereby confirming that the larger the water content is, the higher the evaporation rate. In the study conducted by Her et al., more than half of the lens wearers experienced the side effect of dry eye syndrome, which is the second leading cause of complications.[17] Therefore, for patients suffering from ocular dryness and eye disease

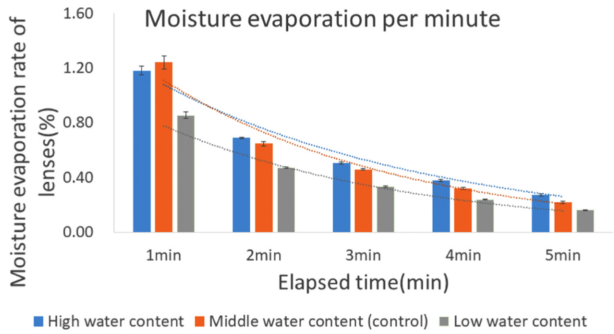

***Figure* 3.** Moisture evaporation according to elapsed time of hydrogel polymer (n=6).

***Table* 2.** Refractive index of samples (n=5), Unit : %

	Sample	Refractive index
High W.C.*	HEA	1.4275
	PVP	1.4254
	NMV	1.4294
Medium W.C.*	HEMA (control)	1.4339
	HPMA	1.4373
	BD	1.4373
Low W.C.*	BMA	1.4532
	Bis-GMA	1.4617
	BDDA	1.4465

*W.C. = water content

after wearing hydrogel lenses, it is desirable to wear low-water content lenses rather than high-water content lenses with high water evaporation rates. The water evaporation rate per minute for each lens is shown in *Fig*. 3.

For the results of the refractive index measurement, the average value for each lens is shown in *Table* 2.

In this study, the sessile drop method was employed to evaluate the wettability of the manufactured lenses. For the high-water content lens group, the wettability of HEA was determined to be 46.57°; that of PVP, 41.02°; and that of NMV, 39.42°. In the case of the medium-water content lens group, the wettability of HEMA was determined to be 61.06°; that of BD, 45.53°; and that of HPMA, 51.35°, while in the case of the low-water content lens group, the wettability of BMA was determined to be 64.94°; that of Bis-GMA, 62.49°; and that of BDDA, 61.58°. The experiment showed that the wettability was also changed by the additives in the samples with similar water contents. In the high-water content lens group, the wettability of PVP and NMV was high, suggesting that the nitrogen atom with the hydrophilic groups of PVP and NMV that were used in this study was located at the center of the molecule, thereby increasing the wettability of the lens surface. The contact

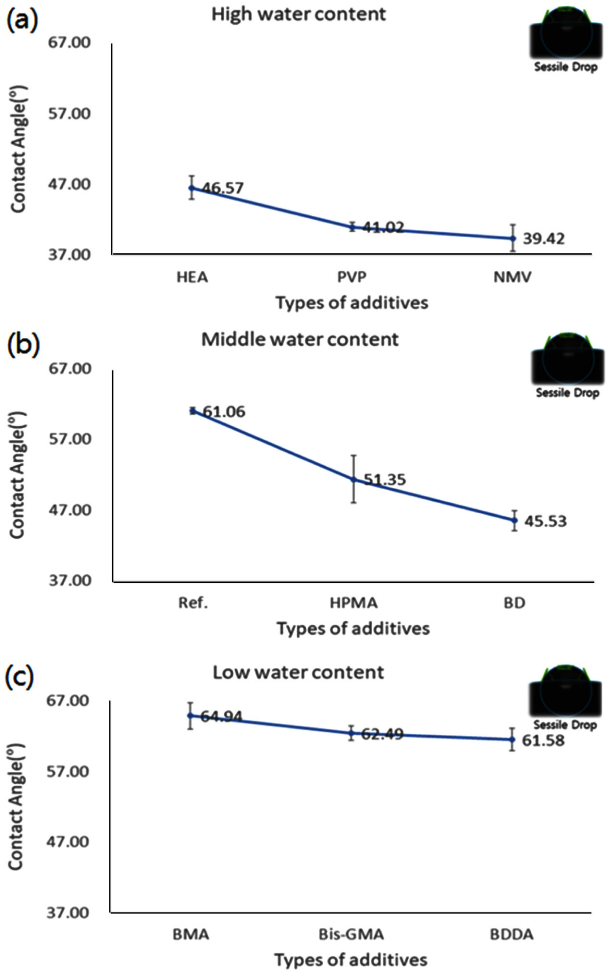

***Figure* 4.** Contact angle distribution of samples (n=5) [(a): High water content, (b): Medium water content, (c): Low water content].

angle changes of each group measured by the sessile drop method are shown in *Fig.* 4.

For the measurement of base curvature using the moisture analyzer, dried lens was placed in a saline solution, and the degree of change of base curvature according to the flow of time was measured using a radius gauge over a

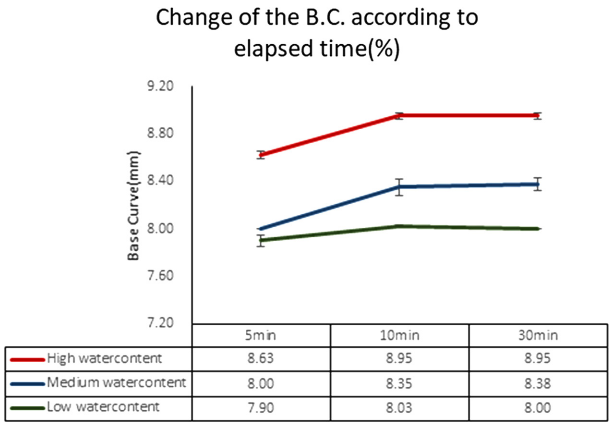

***Figure* 5.** Change of the base curve according to elapsed time (n=6).

period of 5-30 minutes. The base curve changed from 8.00 to 8.38 mm in the high-water content lens group, from 8.63 to 8.95 mm in the medium-water content lens group, and from 7.90 to 8.00 mm in the low-water content lens group, thereby confirming that the variation in the lens curvature increases from the low-water content lens group to the high-water content lens group. This is probably related to the increase of the swelling rate according to the water content, as was the case with the results of the aforementioned examples. The change of curvature over time is shown in Figure 5.

The near-UV and visible-light transmittance of each sample was 76.26% for HEA, 57.93% for PVP, 74.09% for NMV, 74.13% for HEMA, 76.61% for HPMA, 75.95% for BMA, 70.07% for BMA, 69.13% for Bis-GMA, and 70.56% for BDDA. The transmittance in the visible-light range was 91.17% for HEA, 86.27% for PVP, 89.58% for NMV, 88.39% for HEMA, 90.61% for HPMA, 89.71% for BD, 84.61% for BMA, 89.39% for Bis-GMA, and 85.69% for BDDA. The experiment showed that PVP blocked some of the near-UV and visible-light regions, and that Bis-GMA had 0.03% light transmittance at 280-290 nm, com-

***Table* 3.** Optical transmittance of samples (n=5), Unit: %

	Sample	280~290 nm	near-UV (280~380)	Vis (380~800)
High W.C.*	HEA	21.06	76.26	91.17
	PVP	13.59	57.93	86.27
	NMV	21.52	74.09	89.58
Medium W.C.*	HEMA (control)	23.69	74.13	88.39
	HPMA	24.75	76.61	90.61
	BD	25.05	75.95	89.71
Low W.C.*	BMA	21.23	70.07	84.61
	Bis-GMA	0.03	69.13	89.39
	BDDA	21.73	70.56	85.69

*W.C. = water content

pletely blocking the UV-B region. Thus, in the case of the combination including Bis-GMA, it is possible to prevent the diseases that may occur in the UV-B region by completely blocking some regions of UV-B. *Table* 3 shows the optical transmissibility measurement results across all the lens group combinations.

CONCLUSION

Ophthalmic lenses with high, medium, and low water contents were fabricated using various additives in the basic ophthalmic lens combination. The measurements of the water contents of the lenses using the two aforementioned methods showed that the water content and refractive index of the lenses were similar in all the lens groups. It is believed that such results are closely related to the inverse relationship between the water content and the refractive index. The measurements of the contact angles, however, showed a different wettability value for each lens with a similar water content. It can be concluded based on these resu1lts that various wettability values can be obtained when various additives are used with the same water content. Also, the change tendency of the lens curvature according to the change of time showed that the change amount became larger and the recovery time became longer from the lens samples with a lower water content to those with a higher water content. The optical transmissibility of the manufactured lens samples satisfied the basic hydrogel lens conditions in all the lens group combinations, and Bis-GMA had 0.03% transmittance at 280-290 nm, completely blocking part of the UV-B region. It is believed that the bonding of the hydrogen atoms with the oxygen atoms in the benzene ring has a strong correlation with the theory of ultraviolet ray absorption.[1-2] Based on the results of the experiment that was performed in this study, in which the optical and physical properties of the lenses in the high-, medium-, and low-water content lens groups were analyzed using various additives, it can be concluded that various physical properties were shown with similar water contents, results that will be helpful for the study of ophthalmic lenses.

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