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The Performance Stability of Ophthalmic Material with UV-Block Effect Containing Hydroxyl Benzophenone Group and Tungsten Nanoparticles

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ABSTRACT. In this study, the functional hydrogel ophthalmic lens containing tungsten oxide nanoparticles, 2,4-dihydroxy benzophenone and 2-hydroxy-4-(methacryloyloxy) benzophenone were manufactured. HEMA (2-hydroxyethyl methacrylate), MMA (methyl methacrylate), AA(acrylic acid), the cross-linker EGDMA (ethylene glycol dimethacrylate), the initiator AIBN (azobisisobutyronitrile) and the functional additives including tungsten oxide nanoparticles, 2,4-dihydroxy benzophenone, and 2-hydroxy-4-(methacryloyloxy) benzophenone were used respectively. The measurements of water content and refractive index of the sample was decreased and increased, respectively. And also, the UV transmittance of produced lens containing 2,4-dihydroxy benzophenone, 2-hydroxy-4-(methacryloyloxy) benzophenone and tungsten oxide nanoparticles was measured. Based on the results of this study, it is judged that the performance improvement increased over time when 2-hydroxy-4-(methacryloyloxy) benzophenone was used as an additive, while the use of tungsten oxide nanoparticles influenced on blue-ray-blocking effect of the hydrophilic lens.

Key words: 2,4-Dihydroxy benzophenone, 2-Hydroxy-4-(methacryloyloxy) benzophenone, Nano particle, Tungsten oxide, UV-Block

INTRODUCTION

One of the most frequently found air contaminants, ozone is an allotrope of oxygen composed of three oxygen atoms. It is also naturally generated in the air by sunlight.[1] When airborne, it accounts for the majority of photo-oxidants, inflicting serious damage to plants as well as to humans.[2,3] Ozone also makes up the ozone layer in the stratosphere, which blocks the ultraviolet rays. The ozone layer, however, has been thinning out of late with the advancement of industry not only in South Korea but elsewhere in the world.[4,5] Due to the aforementioned property of ozone, numerous studies are being conducted in an effort to come up with products that could protect people from ultraviolet (UV) rays, including sunscreen, clothes, and glasses[6–8] as well UV-ray-blocking substances used for ophthalmic lenses.[9–11] In addition, other studies on the required properties of ophthalmic lenses, such as gas permeability, high water content, and antibiotic activity, are being conducted.[12–16]

The substances that are used for hydrophilic lenses include 2-hydroxyethylmethacrylate (HEMA) and methylmethacrylate (MMA), which have excellent optical functionality; acrylic acid (AA), which is a hydrophilic substance, and ethylene glycol dimethacrylate (EGDMA), which is used mainly as a crosslinking agent. Few studies have been conducted, however, on the polymerization reaction of 2,4-dihydroxybenzophenone, which is used as an additive to impart the UV-ray-blocking property to substances, and according to Kim *et al*.,[17] not many studies have been conducted on the elution of the said substance. Based on this understanding, multiple lens samples were made in this study using different substances, such as 2-hydroxy-4-(methacryloyloxy)benzophenone, which is part of the benzophenone family; 2,4-dihydroxybenzophenone, which is used mainly as a sunscreen; and tungsten oxide,[17] which is drawing attention as a promising hydrogel optical lens material due to its hardness and excellent wetting and UV-ray-blocking properties. The physiological and optical characteristics of each lens sample were first measured, and the same measurement was done again 14 days later to detect any potential change in the samples respective material properties by comparing two different sets of measurement.

EXPERIMENTAL METHOD

Materials

For the hydrogel lens materials, HEMA, a popular material for hydrophilic lenses, and AIBN (azobisisobutyronitrile), an initiator, were used while AA by JUNSEI and MMA by Crown Guaranteed Reagents were both used as well. EGDMA was used as a crosslinking agent; 2,4-dihyroxybenzophenone and 2-hydorxy-4-(methacryloyloxy)benzophenone were

used as additives to impart the UV-ray-blocking property; and tungsten oxide made by Sigma-Aldrich was also used.

Polymerization

For the polymerization of hydrophilic lenses, the lens samples were made by using HEMA, MMA, AA, and EGDMA, which are crosslinking agents, and AIBN, a heat initiator. In addition, the additives 2,4-dihydroxybenzophenone and 2-hydroxy-4-(methacryloyloxy)benzophenone were added to the mixture at a 0.1~1.0% ratio, respectively. With regard to tungsten oxide, the mix made by adding 2,4-dihydroxybenzophenone and 2-hydroxy-4-(methacryloyloxy)benzophenone at a 1% ratio was added at a 0.5% ratio. The mixture was then stirred for 3 minutes using an agitator (Vortex GENIE2, Scientific Industries, USA) before its tungsten oxide nanoparticles content was separated using an ultrasonic device (JAC-4020, South Korea) for 20 minutes. The reagent, which was made via thermal polymerization, was hydrated for 24 hours at room temperature in a 0.9% saline solution before its surface was assessed using scanning electron microscopy (SEM) and atomic force microscopy (AFM). Then its basic physical characteristics, such as its refractive index and water content, were measured along with the assessment of its optical characteristics, such as its optical transmittance and absorbance. The reagents that were used in the experiment were named "24DB-1," "24DB-2," "24DB-3," "24DB-4," and "24DB-5," respectively, according to the ratio of the 2,4-dihydroxybenzophenone additive that was added to the basic combination was named "Ref.", whereas the combination that was made by adding tungsten oxide to 24DB-5 was named "24DB-T." Moreover, the groups that were made by adding 2-hydroxy-4-(methacryloyloxy) benzophenone in accordance with the respective given ratios were named "2H4M-1", "2H4M-2," "2H4M-3," "2H4M-4," and "2H4M-5," respectively, whereas the combination that was made by adding tungsten oxide to the 2H4M-5 combination was named "2H4M-T." The mixing ratios for the different mixes are shown in *Table* 1.

INSTRUMENTS AND ANALYSIS

Physical Properties

The water contents of the produced lens samples were measured using an ABBE refractometer (ATAGO NAR 1T, Japan) and in accordance with the weight measurement routine specified in ISO 18369-4:2006 (Ophthalmic optics - Contact lenses - Part 4: Physicochemical properties of contact lens materials). Moreover, an atomic force microscope (AFM; XE-100, Parks Systems) and a finite-element scanning electron microscope (FESEM; JSM-7500F+EDS, Oxford) were used to analyze the nanoparticles on the lens surfaces. All the tests were repeated three times before the measurements were averaged, to enhance the reliability of the experiment.

RESULTS AND DISCUSSION

Polymerization

The polymerization of lens materials showed that a transparent high-molecular substance was made when the Ref. combination and 2,4-dihydroxybenzophenone and 2-hydroxy-4-(methacryloyloxy)benzophenone were added, respectively. The final mixture, which was hydrated for 24

***Table* 1.** Percent composition of samples Unit: %

Sample	HEMA	AA	MMA	EGDMA	24DB[a)]	2H4M[b)]	Tung[c)]
Ref	93.90	4.69	0.94	0.47	-	-	
24DB-1	93.81	4.69	0.94	0.47	0.09	-	-
24DB-2	93.63	4.68	0.94	0.47	0.28	-	-
24DB-3	93.46	4.67	0.93	0.47	0.47	-	-
24DB-4	93.28	4.66	0.93	0.47	0.65	-	-
24DB-5	93.02	4.65	0.93	0.47	0.93	-	-
24DB-T	92.98	4.65	0.93	0.46	0.93	-	0.05
2H4M-1	93.81	4.69	0.94	0.47	-	0.09	-
2H4M-2	93.63	4.68	0.94	0.47	-	0.28	-
2H4M-3	93.46	4.67	0.93	0.47	-	0.47	-
2H4M-4	93.28	4.66	0.93	0.47	-	0.65	-
2H4M-5	93.02	4.65	0.93	0.47	-	0.93	-
2H4M-T	92.98	4.65	0.93	0.46	-	0.93	0.05

[a)]2,4-Dihydroxybenzophenone.
[b)]2-Hydroxy-4-(methacryloyloxy) benzophenone.
[c)]Tungsten oxide.

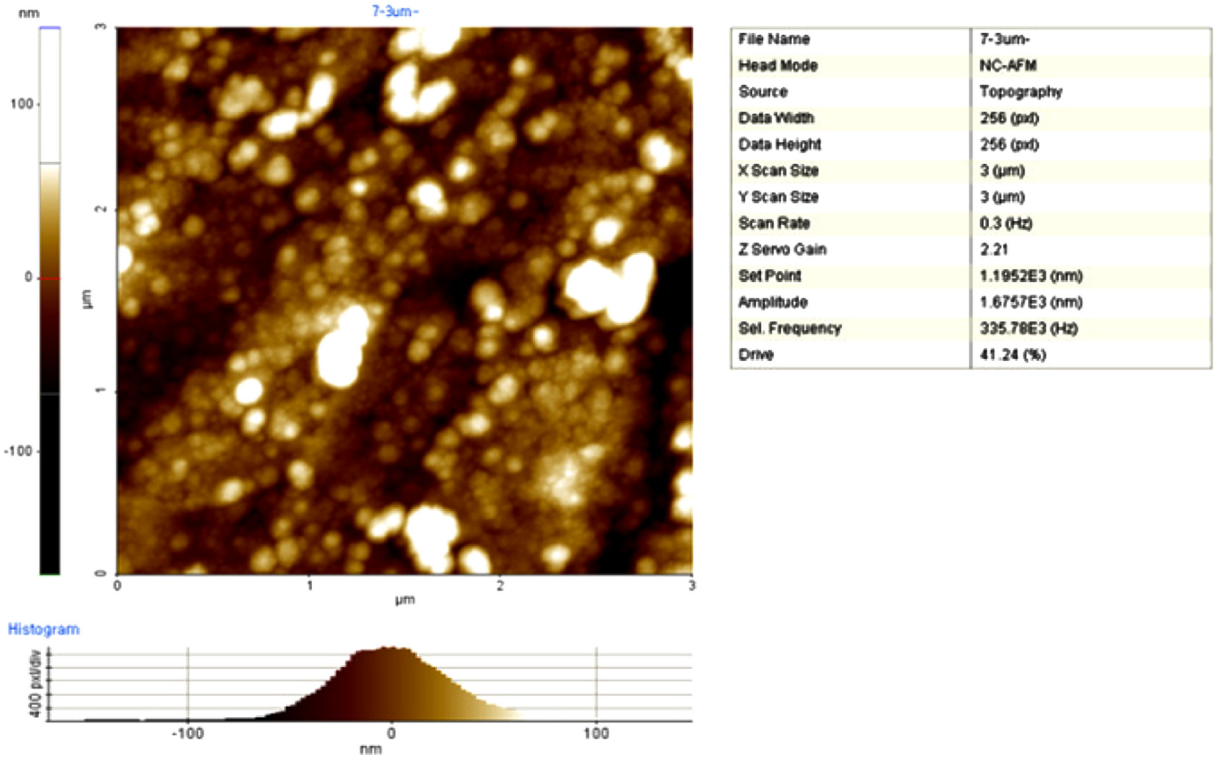

***Fig.* 1.** Surface analysis of lens sample by SEM (Inc. tungsten oxide nanoparticle).

hours in a saline solution containing 0.9% sodium chloride, showed that all the samples demonstrated flexibility.

The analysis of the produced lens surfaces using SEM confirmed that the surfaces were covered with 35~60 nm nanoparticles. The analysis of the nanoparticles by AFM confirmed that the nanoparticles were evenly distributed across the lens surfaces. Moreover, the lens samples containing

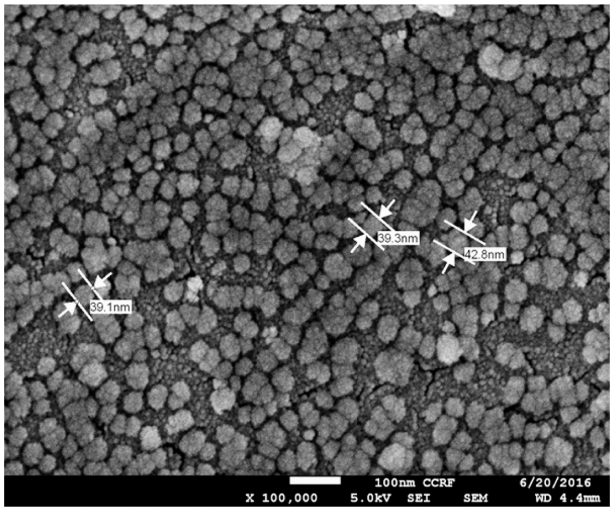

***Fig.* 2.** SEM image of lens sample (Inc. tungsten oxide nanoparticle).

2,4-dihydroxybenzophenone and 2-hydroxy-4-(methacryloyloxy) benzophenone were measured via SEM after 1- and 14-day hydration, respectively, and the results showed that the crystalline distribution was significantly reduced.

The AFM and SEM analysis results of the produced lens samples are shown in *Fig.* 1~4.

Physical Characteristics

The refractive indices of the produced lens samples after 24-hour hydration treatment were measured. The results showed that the refractive index of Ref was 1.4353 whereas the refraction indices were within the 1.4334-1.4353 range in the case of the combinations to which 2,4-dihydroxybenzophenone was added to the Ref mixture in accordance with the respective given ratios. In the case of the 24DB-T mix, to which 1% 2,4-dihydroxybenzophenone and 0.5% tungsten oxide were added, respectively, the refractive index of Ref was 1.4372. In the case of the group to which 2-hydroxy-4-(methacryloyloxy)benzophenone was added in accordance with the respective given ratios, the refractive indices were within the 1.4348-1.4401 range, whereas in the case of the 2H4M-T combination, to which 1% 2-hydroxy-4-(methacryloyloxy)benzophenone and 0.5% tungsten oxide were added, respectively, the refractive index was 1.4401. When the mix was measured after 14-day hydration, the

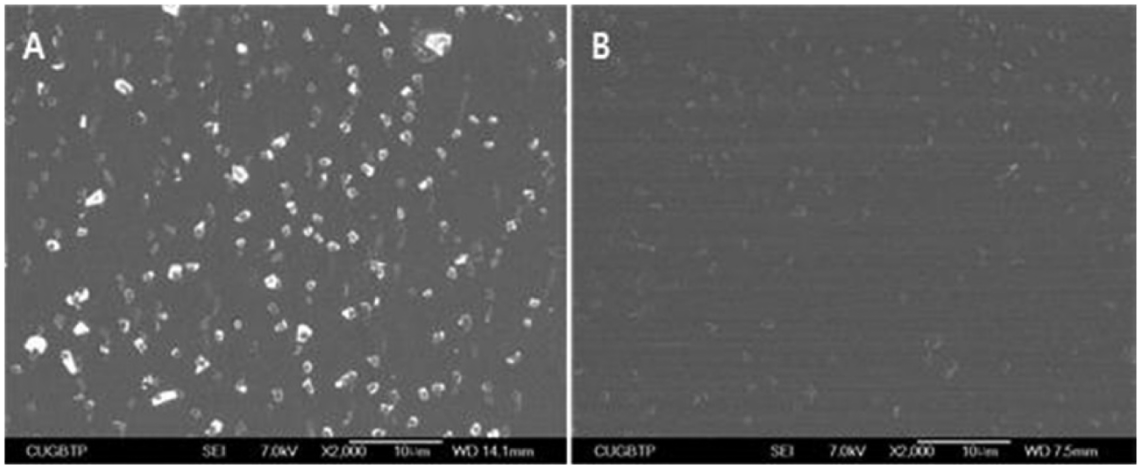

***Fig*. 3.** SEM image of the sample 24DB group over time (A: 1 day Hydration, B: 14 day Hydration).

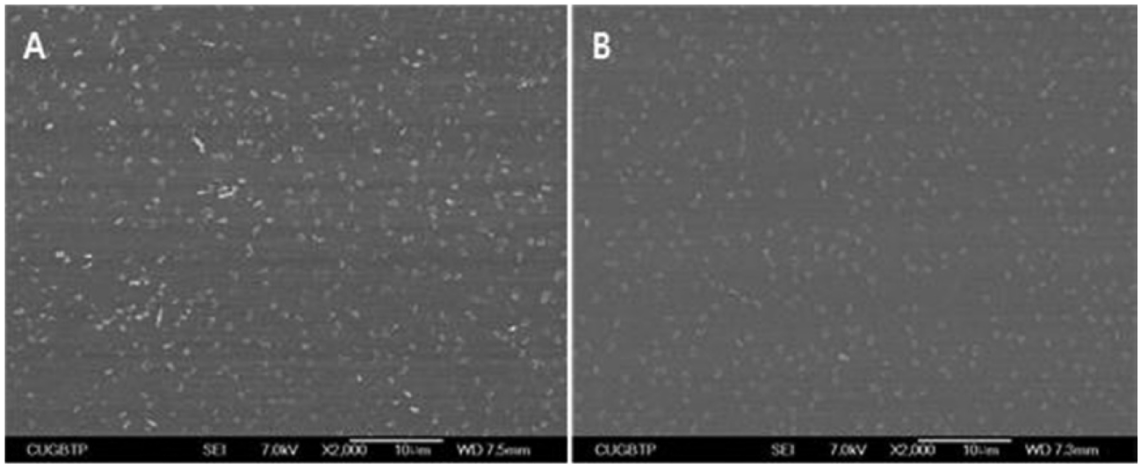

***Fig*. 4.** SEM image of lens sample 2H4M group by SEM (A: 1 day Hydration, B: 14 day Hydration).

refractive index of the Ref combination was 1.4354. In the case of the combination where 2,4-dihydroxybenzophenone was added to the Ref combination in accordance with the respective given ratios, the refractive indices were within the 1.4341-1.4363 range, whereas the refractive index was 1.4377 in the case of the 24DB-T combination. In the case of the combination to which 2-hydroxy-4-(methacryloyloxy) was added in accordance with the respective given ratios, the refractive indices were within the 1.4349-1.4397 range, whereas the refractive index was 1.4397 in the case of the 2H4M-T combination. To sum up, it was confirmed that the refractive index did not change significantly when 2,4-dihydroxybenzophenone, 2-hydroxy-4-(methacryloyloxy) benzophenone, and tungsten oxide were used as additives, respectively, while no significant change was observed either after 14-day hydration.

With regard to the water contents of the produced reagents measured after 24-hour hydration, the water content of Ref was 34.33% whereas water contents were within the 45.42-34.27% range in the combination where 2,4-dihydroxy-benzophenone was added to the Ref combination in accordance with the respective given ratios, and water content was 33.69% in the 24DB-T combination. In the case of the group to which 2-hydroxy-4-(methacryloyloxy)benzophenone was added in accordance with the respective given ratios, the water contents were within the 34.08-32.63% range, and the water content was 32.28% in the 2H4M-T combination. When the mix was measured after 14-day hydration, the water content of the Ref combination was 34.63% whereas the water contents were within the 35.97-34.62% range in the case of the combination where 2,4-dihydroxybenzophenone was added to the Ref combination in accordance with the respective given ratios, while it was 33.765% in the case of the 24DB-T combination. In the case of the combination to

***Table* 2.** Refractive index and Water contents of samples 24DB group

Hydration 1day			Hydration 14 day		
Sample	Refractive index	Water contents (%)	Sample	Refractive index	Water contents (%)
Ref.	1.4353	34.43	Ref.	1.4354	34.63
24DB-1	1.4334	35.42	24DB-1	1.4341	35.97
24DB-2	1.4343	34.82	24DB-2	1.4346	35.31
24DB-3	1.4343	34.31	24DB-3	1.4349	34.94
24DB-4	1.4350	34.76	24DB-4	1.4350	35.04
24DB-5	1.4353	34.27	24DB-5	1.4363	34.62
24DB-T	1.4372	33.69	24DB-T	1.4377	33.76

***Table* 3.** Refractive index and Water contents of samples 2H4M group

Hydration 1day			Hydration 14 day		
Sample	Refractive index	Water contents (%)	Sample	Refractive index	Water contents (%)
Ref.	1.4353	34.43	Ref.	1.4354	34.15
2H4M-1	1.4348	34.08	2H4M-1	1.4349	34.95
2H4M-2	1.4360	33.61	2H4M-2	1.4362	34.73
2H4M-3	1.4371	32.86	2H4M-3	1.4372	32.89
2H4M-4	1.4379	32.85	2H4M-4	1.4383	32.55
2H4M-5	1.4394	32.63	2H4M-5	1.4397	33.29
2H4M-T	1.4401	32.28	2H4M-T	1.4397	34.01

which 2-hydroxy-4-(methacryloyloxy)benzophenone was added in accordance with the respective given ratios, the water contents were within the 34.95-32.55% range, and the water content was 34.01% in the case of the 24DB-T combination. To sum up, it was confirmed that the water content did not change significantly when 2,4-dihydroxybenzophenone, 2-hydroxy-4-(methacryloyloxy)benzophenone, and tungsten oxide were used as additives, respectively, while no significant change was observed either after 14-day hydration. The refractive index and water content of each combination are shown in *Table* 2~3.

Optical Characteristics

The optical transmittances of the produced lens samples showed that the transmittance ratios of Ref. was UV-B 87.33% and UV-A 96.02%, respectively, whereas the transmittance ratio of the visible rays was 99.25%. The average transmission ratios of the reagents to which 2,4-dihydroxybenzophenone was added in accordance with the respective given ratios were within the 50.21~0.34% and 76.44~22.73% ranges in the UV-B and UV-A bands, respectively, and within the 99.24~98.49% range in the visible-ray band, whereas the average beam transmission ratios were 0.07, 15.99, and 93.97%, respectively, in the 24DB-T combination. They were determined to be 51.35~.37, 74.52~20.28, and 99.15~99.06%, respectively, in the case of the 2-hydroxy-4-(methacryloyloxy) combination, 1.80, 19.09, and 94.10%, respectively, in the case of the 2H4M-T combination. The measurement of the light transmission ratios after 14-day hydration showed that the Ref combination had UV-B 87.99% and UV-A 95.17%, respectively, and 98.79% in the visible-ray band. In addition, the average transmission ratios of the reagents to which 2,4-dihydroxybenzophenone was added in accordance with the respective given ratios were 65.18~5.08, 84.54~37.23, and 99.39~98.88%, respectively, in the UV-B, UV-A, and visible-ray bands whereas they were 2.34, 28.20, and 95.12%, respectively, in the 24DB-T combination. In the case of the 2-hydroxy-4-(methacryloyloxy) benzophenone combination, they were 1.25, 17.38, and 93.68%, respectively, whereas they were 1.25, 17.38, and 93.68%, respectively, in the case of the 2H4M-T combination. The UV-ray-blocking performance of the produced lens samples reduced across all the combinations after 14-day hydration in the case of the 2,4-dihydroxybenzophenone combination.

The measurement of the absorbance after 14-day hydration showed that the absorbance was 0.0100 in the Ref combination, and 0.0312-0.3262 in the group to which 2,4-dihydroxy-benzophenone was added in accordance with the respective given ratios, whereas it was 0.3608 in the case of the 24DB-T combination. In the case of the group to which 2-hydroxy-4-(methacryloyloxy)benzophenone was added in accordance with the respective given ratios, the optical absorbances were 0.0033~0.0071 whereas the absorbance was 0.0084

***Table* 4.** Optical transmittance of samples 24DB group Unit: %

Hydration 1 day				Hydration 14 day			
Sample	UB-B	UV-A	VIs	Sample	UB-B	UV-A	VIs
Ref.	87.33	96.02	99.25	Ref.	87.99	95.17	98.73
24DB-1	50.21	76.44	99.24	24DB-1	65.18	84.54	99.39
24DB-2	15.68	50.62	99.23	24DB-2	35.92	66.50	99.18
24DB-3	6.56	39.44	98.90	24DB-3	22.22	55.86	98.50
24DB-4	2.11	31.04	98.33	24DB-4	12.85	47.16	98.52
24DB-5	0.34	22.73	98.49	24DB-5	5.08	37.23	98.88
24DB-T	0.07	15.99	93.97	24DB-T	2.34	28.20	95.12

***Table* 5.** Optical transmittances of samples 2H4M group Unit: %

Hydration 1 day				Hydration 14 day			
Sample	UB-B	UV-A	VIs	Sample	UB-B	UV-A	VIs
Ref.	87.33	96.02	99.25	Ref.	87.99	95.17	98.73
2H4M-1	51.35	74.52	99.15	2H4M-1	49.28	71.68	97.49
2H4M-2	20.97	48.52	99.43	2H4M-2	20.68	47.93	98.97
2H4M-3	10.27	36.22	98.76	2H4M-3	9.65	35.13	98.95
2H4M-4	5.82	29.54	98.60	2H4M-4	6.62	30.36	98.12
2H4M-5	1.37	20.28	99.06	2H4M-5	1.73	21.22	98.20
2H4M-T	1.80	19.09	94.10	2H4M-T	1.25	17.38	93.68

***Table* 6.** Absorbance of samples 24DB and 2H4M group Unit: %

Hydration 14 day		Hydration 14 day	
Sample	Absorbance	Sample	Absorbance
Ref.	0.0100	Ref.	0.0100
24DB-1	0.0312	2H4M-1	0.0033
24DB-2	0.0953	2H4M-2	0.0041
24DB-3	0.1471	2H4M-3	0.0049
24DB-4	0.2426	2H4M-4	0.0049
24DB-5	0.3262	2H4M-5	0.0071
24DB-T	0.3608	2H4M-T	0.0084

in the case of the 2H4M-T combination. These results showed that the absorbance increased along with the rising ratio of 2,4-dihydroxybenzophenone when it was used as an additive, whereas the absorbance in accordance with the changing ratio of the additives 2-hydroxy-4-(methacryloyloxy) benzophenone and tungsten oxide was similar to that of Ref. A brief look at the SEM measurement results shown in *Fig.* 3 and 4 would show that 2,4-dihydroxybenzophenone molecules decreased over time in the case of 2,4-dihydroxybenzophenone whereas the initial number was sustained in the case of 2-hydroxy-4-(methacryloyloxy)benzophenone, suggesting that it may be due to the fact that the additive 2,4-dihydroxybenzophenone did not completely combine with the main chain of the polymer, a result corroborated by the increased absorbance in the solution after 14-day hydration, as shown in *Table* 4. The measurements of the optical transmission and absorbance

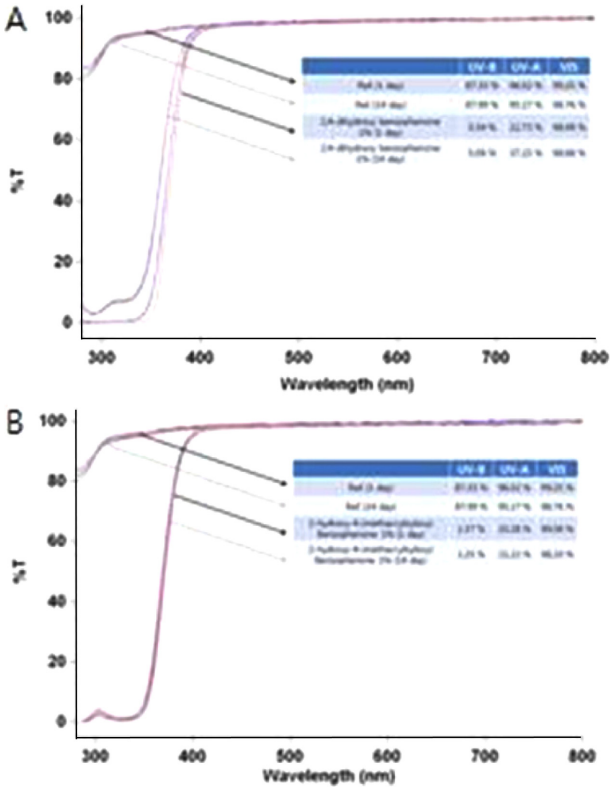

***Fig.* 5.** Optical transmittances of samples (A: 24DB group, B: 2H4M group).

of each combination are shown in *Table* 4~6 and *Fig.* 5,6, respectively.

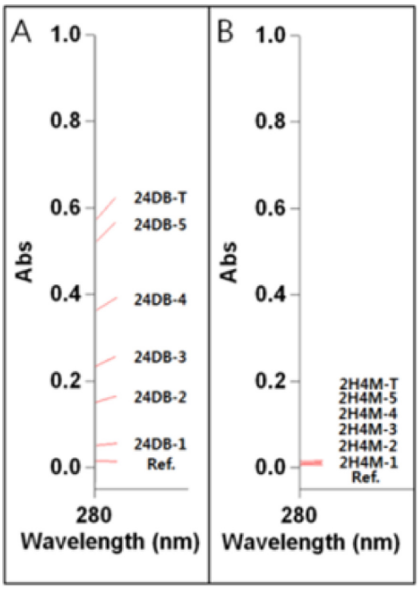

***Fig*. 6.** Absorbances of samples 24DB and 2H4M group.

CONCLUSION

In this study, 2,4-dihydroxybenzophenone, 2-hydroxy-4-(methacryloyloxy) benzophenone, and tungsten oxide were added to the mixture in accordance with their appropriate density before the physiological and optical characteristics of the produced lens samples were measured after 1-day hydration and 14-day hydration, respectively. The experiment results showed that the physical characteristics, such as their water contents and refractive index, did not change significantly in all the combinations. As for the optical characteristics of the produced lens samples, the ultraviolet-(UV)-ray-blocking performance and visible-ray transmission ratio of the two lens samples that were produced with either 2,4-dihydroxybenzophenone or 2-hydroxy-4-(methacryloyloxy) benzophenone were both high after 24-hour hydration. The UV-ray-blocking performance deteriorated in all the combinations, however, after 14-day hydration in the case of the lens sample to which 2,4-dihydroxybenzophenone was added, whereas no such deterioration was observed in the case where 2-hydroxy-4-(methacryloyloxy)benzophenone was added to the mix as an additive. It is judged that 2-hydroxyethylmethacrylate (HEMA), methylmethacrylate (MMA), acrylic acid (AA), and ethylene glycol dimethacrylate (EGDMA), the key materials for hydrogel lenses that perform acryl polymerization, did not reduce out even after an extended period because the acryl in 2-hydroxy-4-(methacryloyloxy) benzophenone triggers definitive polymerization. In addition, the UV-ray-blocking performance of the lens samples improved when tungsten oxide nanoparticle was used as an additive. Although their visible-ray transmission ratio reduced, they still demonstrated blue-ray-blocking performance due to the significant reduce in the 400 nm band. Based on the results of this study, it is judged that the performance improvement increased over time when 2-hydroxy-4-(methacryloyloxy) benzophenone was used as an additive, while the use of a small amount of tungsten oxide nanoparticle may trigger a blue-ray-blocking effect of the hydrophilic lens.

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