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Hydrogel Contact Lens Materials with Improved UV Blocking Effect

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Abstract

HEMA, AA, MMA, and EGDMA as crosslinking agent and AIBN as an initiator, and 2,4-dihydroxybenzophenone, 2-ethylhexyl-trans-4-methoxy-cinnamate, 2-hydroxy-4-(methacryloyloxy)benzophenone as additives at 0.1-1.0% ratios were used to manufacture hydrophilic ophthalmic lenses through thermal polymerization before their physical properties were measured. The results showed that the samples containing of 2,4-dihydroxybenzophenone and 2-ethylhexyl-trans-4-methoxy-cinnamate resulted in a decrease of the UV blocking performance after high-pressure sterilization whereas the sample containing 2-hydroxy-4-(methacryloyloxy)benzophenone showed no change in the UV blocking performance. It is judged that this is induced by presence or absence of an acyl functional group in benzophenone.

Keywords : Benzophenone Group, Thermal Polymerization, Ophthalmic Hydrogel Lens, UV-block, Autoclaving

1. Introduction

Blue light refers to a band of blue color and short wavelength in the visible-light region with a 380-495 nm wavelength. And also, blue light has high energy in the visible-light region. Recent studies have shown that blue light suppresses the secretion of the melatonin hormone, disrupting the vital rhythm and causing sleep disturbances[1,2]. In addition, it was proven through a lab experiment that rats suffered a reduction of the potassium conductance of the Muller cells in their retinas when they were exposed to blue light[3]. UV (ultraviolet) rays have greater energy than blue light, causing ocular diseases when they are irradiated directly at the eyes[4-6]. For this reason, various studies have been carried out on the glasses and ophthalmic hydrogel lenses that are used to prevent direct UV ray contact with the eyes[7-9]. Recently, studies have been performed on the application of UV ray screening agents to ophthalmic hydrogel lenses as well as on the desirable properties of ophthalmic lenses, such as high water content, high wettability, high oxygen permeability, and antimicrobial activity[10-14]. Benzophenone material has been studied in the past as a prospective additive with a UV ray blocking function, but Kim et al.[15]. He stated that there is no satisfactory solution that is currently available for the problem of elution occurring during the lens manufacturing process. In this study, 2-ethylhexyl-trans-4-methoxy-cinnamate with a blue-light blocking function and 2,4-dihydroxybenzophenon, which is commonly used as a UV ray blocking agent, were used as functional additives in the manufacture of ophthalmic hydrogel lenses, along with MMA (methylmethacrylate) with biocompatibility and a high optical function and 2-hydroxy-4-(methacryloyloxy)benzophenone, a benzophenone group material. The produced hydrogel lenses were then hydrated for 24 hours before their physical and optical properties were measured. After the sterilization of the lenses at 121°C for 15 minutes, the changes in their physical and optical properties were measured, and the results were compared and evaluated to determine the suitability of the test ingredients as ophthalmic hydrogel lens materials.

2. Experiment Method

2.1. Reagents and Materials

HEMA (2-hydroxyethyl emthacrylate), the main ingredient of the hydrogel ophthalmic lenses manufactured by JUNSEI, was used, along with MMA (methylmethacylate), AA (acrylic acid), EGDMA (ethyleneglycol dimethacrylate), AIBN (azobisisobutyronitirle), 2,4-

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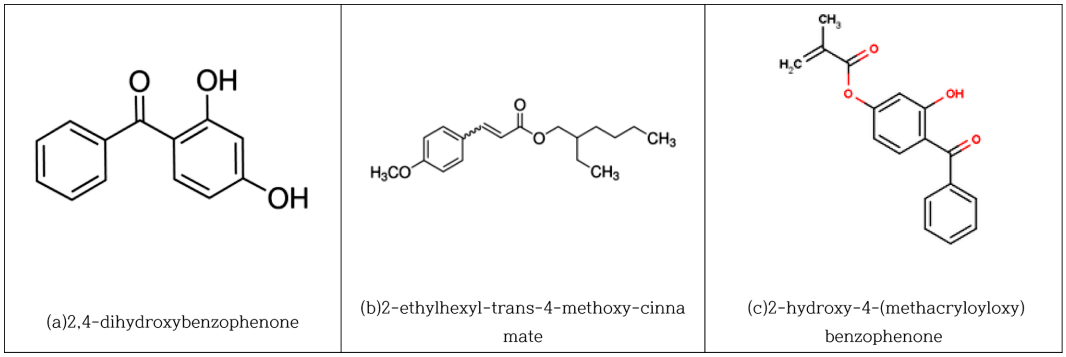

(a)2,4-dihydroxybenzophenone (b)2-ethylhexyl-trans-4-methoxy-cinnamate (c)2-hydroxy-4-(methacryloyloxy) benzophenone

Fig. 1. Chemical structures of the additives for this study.

Table 1. Percent composition of the samples (unit: %)

Sample	HEMA	AA	MMA	EGDMA	24DB[a)]	2E4M[b)]	2H4M[c)]
Ref.	93.90	4.69	0.94	0.47	-	-	
24DB-1	93.81	4.69	0.94	0.47	0.09	-	-
24DB-2	93.46	4.67	0.93	0.47	0.47	-	-
24DB-3	93.02	4.65	0.93	0.47	0.93	-	-
2E4M-1	93.81	4.69	0.94	0.47	-	0.09	-
2E4M-2	93.46	4.67	0.93	0.47	-	0.47	-
2E4M-3	93.02	4.65	0.93	0.47	-	0.93	-
2H4M-1	93.81	4.69	0.94	0.47	-	-	0.09
2H4M-3	93.46	4.67	0.93	0.47	-	-	0.47
2H4M-5	93.02	4.65	0.93	0.47	-	-	0.93

a): 2,4-dihydroxybenzophenone
b): 2-ethylhexyl-trans-4-methoxy-cinnamate
c): 2-hydroxy-4-(methacryloyloxy)benzophenone

dihydroxybenzophenone, 2-ethylhexyl-trans-4-methoxy-cinnamate, and 2 hydroxy-4-(methacryloyloxy)benzophenone, all of which are additives for blocking UV rays made by Sigma-Aldrich. The chemical structures of the additives that were used in the experiments are shown in Fig. 1.

2.2. Polymerization

The basic combination was prepared by mixing HEMA, AA, MMA, and EGDMA as crosslinking agents and AIBN as an initiator, and by adding 2,4-dihydroxybenzophenone, 2-ethylhexyl-trans-4-methoxy-cinnamate, and 2-hydroxy-4-(methacryloyloxy)benzophenone as additives at 0.1-1.0% ratios. The mixture was then stirred for 3 minutes using a stirrer (Vortex GENIE 2, Scientific Industries, USA), and then for 30 minutes at room temperature, before it was thermal polymerized using the cast mold method. The prepared samples were hydrated in a physiological saline solution containing 0.9% sodium chloride at room temperature for 24 hours before their physical and optical properties (i.e., their refractive indices, water contents, and light transmittance and absorbance values) were measured and evaluated. After their sterilization using the high-pressure steam method at 121°C for 15 minutes, they were measured again for the same criteria shown above. The samples containing 2,4-dihydroxybenzophenone were named “24DB-1,” “24DB-2,” and “24DB-3,” respectively. In case of 2E4M, they were named “2E4M-1,” “2E4M-2,” and “2E4M-3”; and the samples containing 2-hydroxy-4-(methacryloyloxy)benzophenone were named “2H4M-1,” “2H4M-2,” and “2H4M-3.” The mixing proportions of the hydrogel lens samples that were used in the experiment are shown in Table 1.

2.3. Instruments and Analysis

The water contents of the prepared lenses were measured using the gravimetric method according to ISO 18369-4:2006 (Ophthalmic optics, Contact lenses, Part 4: Physicochemical properties of contact lens materials), while the refractive index was measured using an ABBE refractometer (ATAGO NAR 1T, Japan) according to ISO 18396-4:2006 (Ophthalmic optics, Contact lenses, Part 4: Physicochemical properties of contact lens materials, 4.5 Refractive index). The light transmittance and absorbance values of the lenses were measured and analyzed using Cary 60 UV-vis (Agilent Technologies, United States). Finally, FESEM (field emission scanning electron microscope, JSM-7500F+ EDS, Oxford) was used for the surface analysis of the prepared hydrogel lens.

3. Results and Discussion

3.1. Polymerization

The polymerization results of the hydrophilic lens materials in this study showed that a colorless transparent polymer was formed when the Ref. combination and 2,4-dihydroxybenzophenone, 2-ethylhexyl-trans-4-methoxy-cinnamate, and 2-hydroxy-4-(methacryloyloxy)benzophenone were added to the mixture. In addition, the transparency was maintained across all the samples as a result of the hydration of the samples in a saline solution containing 0.9% sodium chloride for about 24 hours.

3.2. Sterilization Process and Physical Properties

The refractive index of each sample after 24-hour hydration was found to be 1.4350 for the Ref. sample. The samples to which 2,4-dihydroxybenzophenone was added to the Ref. sample according to the given proportions, the refractive index of 24DB-1 was 1.4343, that of 24DB-2 was 1.4357, and that of 24DB-3 was 1.4361. Regarding the samples to which 2-ethylhexyl-trans-4-methoxy-cinnamate was added according to the given proportions, the refractive index of 2E4M-1 was 1.4347, that of 2E4M-2 was 1.4352, and that of 2E4M-3 was 1.4352. In the samples to which 2-hydroxy-4-(methacryloyloxy)benzophenone was added according to the given proportions, the refractive index of 2H4M-1 was 1.4353, that of 2H4M-2 was 1.4378, and that of 2H4M-3 was 1.4399. To identify any change in the physical properties, the refractive indices of the samples were measured after high-pressure steam sterilization. The results showed that the refractive index of the Ref. sample was 1.4352 while in the samples to which 2,4-dihydroxybenzophenone was added to the mix according to the given proportions, the refractive index of 24DB-1 was 1.4347, that of 24DB-2 was 1.4365, and that of 24DB-3 was 1.4371. In the samples to which 2-ethylhexyl-trans-4-methoxy-cinnamate was added according to the given proportions, the refractive index of 2E4M-1 was 1.4352, that of 2E4M-2 was 1.4366, and that of 2E4M-3 was 1.4366. In the samples where 2-hydroxy-4-(methacryloyloxy)benzophenone was added according to the given ratios, the refractive index was 1.4353 for 2H4M-1, 1.4383 for 2H4M-2, and 1.4399 for 2H4M-3, suggesting that the refractive index increased slightly depending on the amount added before and after the high-pressure steam sterilization process. This is confirmed to indicate that the surface area of the crystals on the lens surface increased after the sterilization, thereby triggering entanglement among the crystals and increasing the refractive indices of the lenses. The water content of the Ref. sample measured after 24-hour hydration was 35.66%. As for the samples to which 2,4-dihydroxybenzophenone was added according to the given proportions, the water content of 24DB-1 was 35.90%, that of 24DB-2 was 35.43%, and that of 24DB-3 was 33.64%. For the samples to which 2-ethylhexyl-trans-4-methoxy-cinnamate was added according to the given proportions, the water content of 2E4M-1 was 34.52%, that of 2E4M-2 was 34.50%, and that of 2E4M-3 was 34.67%. For the samples to which 2-hydroxy-4-(methacryloyloxy)benzophenone was added according to the given proportions, the water content of 2H4M-1 was 34.49%, that of 2H4M-2 was 34.09%, and that of 2H4M-3 was 33.12%. The measurement after the high-pressure steam sterilization process showed that the water content of the Ref. sample was 34.36%. As for the samples to which 2,4-dihydroxybenzophenone was added according to the given proportions, the water content of 24DB-1 was 34.53%, that of 24DB-2 was 33.02%, and that of 24DB-3 was 32.25%. For the combinations to which 2-ethylhexyl-trans-4-methoxy-cinnamate was added according to the given proportions, the refractive index of 2E4M-1 was 34.91%, that of 2E4M-2 was 32.16%, and that of 2E4M-3 was 31.4%. For the combinations to which 2-hydroxy-4-

Table 2. Refractive indices and water contents of the samples

Physical characteristics / Sample	Before autoclaving		After autoclaving	
	Refractive index	Water content	Refractive index	Water content
Ref.	1.4350	35.66%	1.4352	34.36%
24DB-1	1.4343	35.90%	1.4347	34.53%
24DB-2	1.4357	35.43%	1.4365	33.02%
24DB-3	1.4361	33.64%	1.4371	32.25%
2E4M-1	1.4347	34.52%	1.4352	34.91%
2E4M-2	1.4352	34.50%	1.4366	32.16%
2E4M-3	1.4352	34.67%	1.4366	31.60%
2H4M-1	1.4353	35.49%	1.4355	32.27%
2H4M-2	1.4378	34.09%	1.4383	31.06%
2H4M-3	1.4399	33.12%	1.4399	30.90%

Table 3. Optical transmittance values of the samples

Light transmittance / Sample	Before autoclaving			After autoclaving		
	UV-B	UV-A	Vis	UV-B	UV-A	Vis
Ref.	84.28%	93.59%	98.46%	81.54%	91.24%	98.22%
24DB-1	46.55%	71.77%	98.97%	51.76%	74.36%	98.20%
24DB-2	1.38%	27.39%	98.35%	4.36%	33.90%	95.98%
24DB-3	0.37%	20.50%	98.62%	0.77%	24.43%	97.60%
2E4M-1	46.55%	71.77%	98.97%	51.76%	74.36%	98.20%
2E4M-2	1.38%	27.39%	98.35%	4.36%	33.90%	95.98%
2E4M-3	0.37%	20.50%	98.62%	0.77%	24.43%	97.60%
2H4M-1	48.71%	71.10%	97.86%	44.39%	68.73%	98.85%
2H4M-2	6.87%	30.17%	98.57%	5.96%	29.04%	97.81%
2H4M-3	1.44%	19.04%	98.19%	1.93%	20.05%	97.15%

(methacryloyloxy)benzophenone was added according to the given proportions, the water content of 2H4M-1 was 35.49%, that of 2H4M-2 was 34.09%, and that 2H4M-3 was 33.12%, suggesting a slight decrease in the water content in the case of the samples that were subjected to high-pressure steam sterilization. These results also indicate that the surface areas of the crystals slightly increased, resulting in a decrease in their water content. Table 2 summarizes the changes in the refractive index and water content of each sample before and after the sterilization.

3.3. Sterilization Process and Optical Properties

The measurement of the light transmittance after the 24-hour hydration of the hydrogel lenses showed that in the case of the Ref. sample, the UV-B transmittance was 84.28%, the UV-A transmittance was 93.59%, and the visible-light transmittance was 98.46%. The average transmittance of the sample to which 2,4-dihydroxybenzophenone was added according to the given proportions were UV-B, 46.55-0.37%; UV-A, 71.77-20.50%; and visible light, 98.97-98.35%. In the 2E4H combinations, they were 38.58-0.03%, 73.64-23.52%, and 97.20-89.64%, respectively, and in the 2H4M combinations, 48.41-1.44%, 71.10-19.04%, and 98.57-97.86%. The measurement of the Ref. sample after high-pressure steam sterilization showed the following values; UV-B transmittance, 81.54%; UV-A transmittance, 91.24%; and visible-light transmittance, 98.22%. The average transmittance values of the samples to which 2,4-dihydroxybenzophenone was added according to the given proportions were 51.76-0.77%, 74.36-

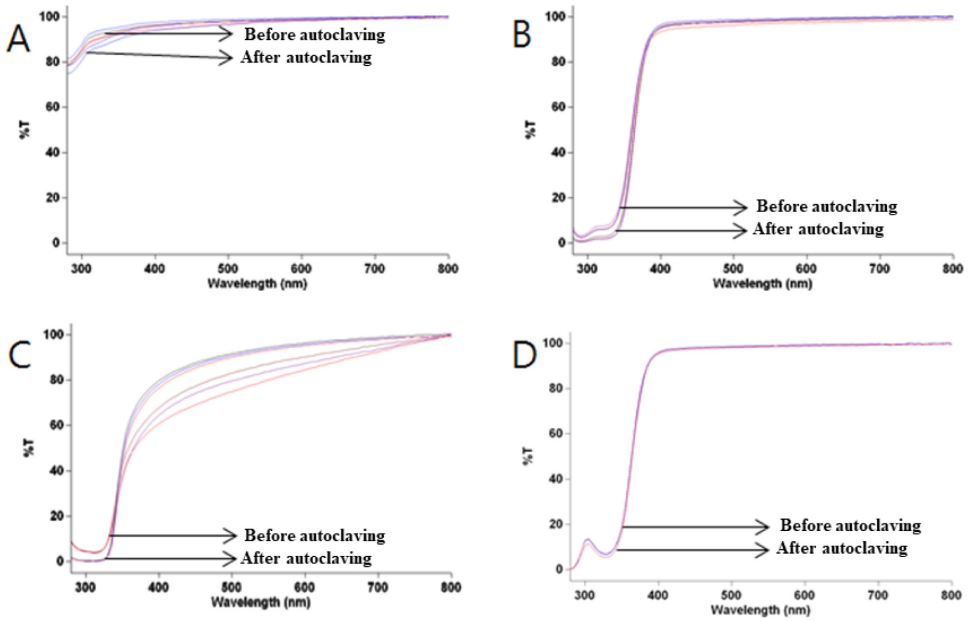

Fig. 2. Optical transmittance values of the samples (A: Ref.; B: 24DB-2; C: 2E4M-2; D: 2H4M-2).

24.43%, and 98.20-95.58% in the UV-B, UV-A, and visible-light regions, respectively, while in the 2E4H combinations, they were 44.57-1.13%, 75.05-18.44%, and 96.69-80.74%, and in 2H4M combinations, 44.39-1.93%, 68.73-20.05%, and 98.85-97.15%. The measurement of the absorbance of the solution after sterilization showed that it was 0.0136 for the Ref. sample, 0.0946-0.9429 for the 24DB combinations, 0.0117-0.0143 for the 2E4M combinations, and 0.0279-0.0426 for the 2H4M combinations. From the above results, the 4DB, 2E4M, and 2H4M combinations each showed UV ray blocking performance whereas the 2E4M combinations showed blocking performance in the blue-light region. The light transmittance values after high-pressure steam sterilization showed that the 24DB and 2E4M combinations each showed decreased UV ray blocking performance whereas the 2H4M combination did not show any decreased UV ray blocking performance. In addition, the measurements of the absorbance values of the samples after sterilization showed that the 24DB combination had higher absorbance than the Ref. sample, thereby confirming the reliability of the light transmittance values. The light transmittance and absorbance values of each sample are shown in Table 3 and Fig. 2 and 3, respectively.

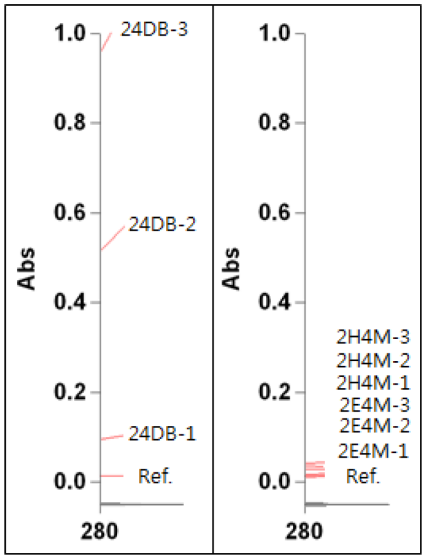

Fig. 3. Absorbance values of the samples in the 24DB, 2E4M, and 2H4M groups.

3.4. The Change of Surface Properties after Sterilization

SEM (scanning electron microscopy) analysis was performed to confirm the surface characteristics of the manufactured lenses. The Ref. sample showed a smooth

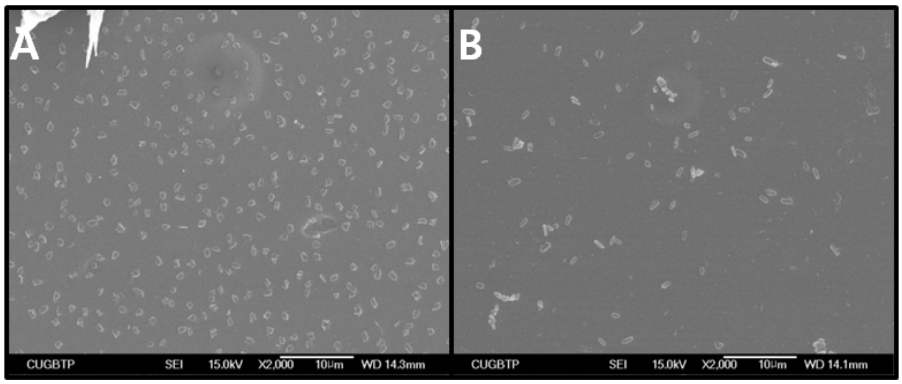

Fig. 4. Surface analysis of the 24DB group samples via SEM (A: before autoclaving; B: after autoclaving).

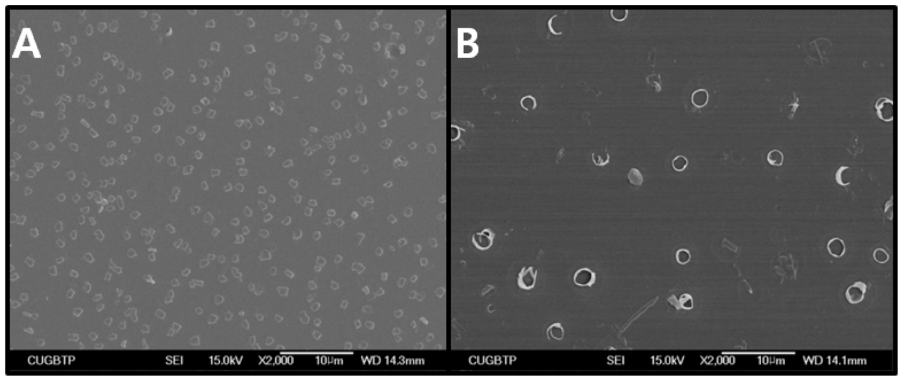

Fig. 5. Surface analysis of the 2E4M group samples via SEM. (A: before autoclaving; B: after autoclaving).

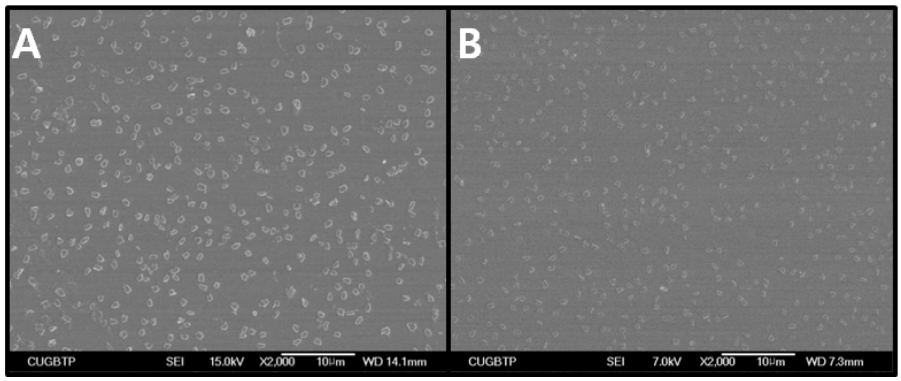

Fig. 6. Surface analysis of the 2H4M group samples via SEM (A: before autoclaving; B: after autoclaving).

surface, but when 2,4-dihydroxybenzophenone, 2-ethylhexyl-trans-4-methoxy-cinnamate, and 2-hydroxy-4-(methacryloyloxy)benzophenone were used as additives, 600-800 nm crystals were generated and distributed evenly across the lens surfaces. Furthermore, the studies conducted by Prativa Mazumdar et al.[16], Gregory Kuzmanich et al.[17], and Nan Zhang et al.[18] showed the same crystallization phenomenon when they used the benzophenone group. After high-pressure steam sterilization, the crystal ratio of the 2,4-dihy-

droxybenzophenone combination slightly increased, and the crystal formation of the 2-ethylhexyl-trans-4-methoxy-cinnamate combination also changed. No significant change in the ratio of the crystals appeared, however, in the case of 2-hydroxy-4-(methacryloyloxy)benzophenone. As discussed earlier, polymerization did not completely occur in the case of 2,4-dihydroxybenzophenone, 2-ethylhexyl-trans-4-methoxy-cinnamate, and 2-hydroxy-4-(methacryloyloxy)benzophenone due to the absence of an acrylic group, a result that is adjudged to have arisen from the complete binding with the main chain. The SEM analysis results of all the samples are shown in Fig. 4-6.

4. Conclusions

In this study, hydrogel lenses were prepared using the UV ray blocking agents 2,4-dihydroxybenzophenone, 2-ethylhexyl-trans-4-methoxy-cinnamate, and 2-hydroxy-4-(methacryloyloxy)benzophenone as additives before their physical and surface properties were measured. To determine the stability of the manufactured lenses, the same criteria were measured after high-pressure steam sterilization treatment at 121°C for 15 minutes, after which the results were compared. The results showed that the physical properties (water content, refractive index) changed significantly when 2,4-dihydroxybenzophenone, 2-ethylhexyl-trans-4-methoxy-cinnamate, and 2-hydroxy-4-(methacryloyloxy)benzophenone were used as additives. With regard to the optical property, all the three combinations to which 2,4-dihydroxybenzophenone, 2-ethylhexyl-trans-4-methoxy-cinnamate, and 2-hydroxy-4-(methacryloyloxy)benzophenone were added as optical additives, respectively, showed a high UV ray blocking rate, whereas the 2-ethylhexyl-trans-4-methoxy-cinnamate combination showed a high UV blocking rate in the wavelength range of 400-600 nm, confirming its excellent blue-light blocking performance. The 2,4-dihydroxybenzophenone and 2-ethylhexyl-trans-4-methoxy-cinnamate combinations, however, resulted in a decrease in the UV blocking performance after high-pressure sterilization whereas the 2-hydroxy-4-(methacryloyloxy)benzophenone combination showed no change in the UV blocking effect. This may be because of either the presence or absence of an acyl functional group in benzophenone. In other words, it is believed that 2-hydroxy-4-(methacryloyloxy)benzophenone does not exhibit a decrease in UV blocking performance even when it is sterilized through polymerization with other monomers, due to the acryl group in the molecule. Therefore, when the absorbance of the solution was measured in this study after sterilizing the manufactured lens, it was confirmed that the absorbance value of the 24DB combination significantly increased. It is concluded, therefore, that 2-hydroxy-4-(methacryloyloxy)benzophenone can be used as an additive to impart UV blocking capability to hydrogel lenses that does not significantly alter the physical properties and is not affected by sterilization.

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