자외선 흡수제를 첨가한 고분자 중합 및 안 의료용 소재로의 적용

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UV Absorbent-added Polymerization and its Application as Ophthalmological Material

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요 약. 본 연구는 자외선 흡수제로 사용되는 benzophenone계(group) 및 높은 굴절률과 화학적, 물리적으로 매우 안정한 물질로 알려진 TiO_2 를 기존의 재료에 첨가하여 자외선 차단 기능을 가진 고분자 재료를 중합하였다. 중합 결과 생성된 고분자의 자외선 흡수 정도를 기존의 재료들과 비교하였으며, 제조된 콘택트렌즈의 함수율, 굴절률 및 광투과율 등의 기본적인 물성을 측정하였다. 측정 결과, 자외선 흡수제를 첨가한 콘택트렌즈의 굴절률과 함수율은 각각 1.430~1.440, 35.0~45.0의 값들로 나타나 기존의 콘택트렌즈와 비슷한 결과를 나타내었다. 또한 각 파장대별 광투과율에서는 자외선 흡수제를 넣지 않은 콘택트렌즈에서는 UV-A, UV-B, 가시광선 투과율이 각각 89%, 88%, 89%로 나타나 자외선 투과율이 매우 높았으나, 2-hydroxy-4-methoxy-benzophenone와 2,4-dihydroxy-benzophenone을 첨가한 콘택트렌즈의 경우, 각각 UV-A 0%, UV-B 6%의 투과율을 나타내어 자외선 차단 효과가 있는 것으로 나타났다. 또한 TiO_2 를 첨가한 콘택트렌즈의 경우, 각각 UV-A 6%, UV-B 51%의 투과율을 나타내어 자외선 차단 효과가 다소 있는 것으로 나타났다. 가시광선 투과율은 모두 77~89%로 콘택트렌즈의 가시광선 투과율의 조건에 만족함을 알 수 있었다.

주제어: 자외선 흡수제, 굴절률, 가시광선 투과율, 고기능성 고분자

ABSTRACT. This study was done for the preparation of macromolecular material with UV-blocking features by adding the benzophenone group that is commonly used as a UV-absorbent and TiO_2 which is known to be a very stable material in chemical and physical aspects. Also, we compared the level of UV absorbency of the polymer produced from polymerization with previous materials and measured basic properties such as water content, refractive index and optical transmittance of produced contact lenses. The results of the measurement showed that the refractive index and water content of the contact lens with added UV-absorbent was 1.430~1.440 and 35.0~45.0% respectively, which was similar to that of previous contact lenses. Also, for optical transmittances of each wave length, contact lenses without the UV-absorbent was 89%, 88% and 89% respectively for UV-A, UV-B and visible light, indicating that the UV transmittance is very high though contrary with cases of contact lenses with added 2-hydroxy-4-methoxy-benzophenone and 2,4-dihydroxy-benzophenone which showed transmittances of 0% and 6% respectively for UV-A and UV-B showing a UV-blocking effect. Meanwhile, contact lenses with added TiO_2 showed transmittance of 6% and 51% respectively for UV-A and UV-B also showing a UV-blocking effect. The visible transmittance was 77~89% showing that it satisfies the visible transmittance required for ophthalmological materials.

Keywords: UV absorbent, Refractive index, Visible transmittance, High performance polymer

INTRODUCTION

Currently due to the increase of global pollution caused by mankind's reckless development and industrial advancement, public interest in environmental pollution is increasing. Among environmental pollution, the destruction of the ozone layer was first reported by a British Antarctica expedition team which raised concerns that the depleted ozone layer may lead to serious outcomes. Since then,

there have been active studies on the ozone layer which provided more in-depth understanding of the importance of the ozone layer and its effects on mankind.¹

The light emitted by the sun is an electromagnetic wave of various wavelengths. Among the light, the ultraviolet ray which has a short wavelength is known to be very harmful to humans and plants. The ozone layer absorbs, reflects and filters this harmful ray. However, if the ozone layer becomes thinner or even destroyed, the layer cannot

play such a protective role, and as UV rays reach the earth's surface, it can cause various diseases such as skin cancer and eye disease. Also, UV rays can inhibit the growth of plants and crops, and can cause a variety of problems. Not only that, but it can also discolor clothes and products.²⁻⁴

The eye is one of the things that can be most sensitive to the harmfulness of UV rays. Unlike other organs, the human eye is exposed directly to light. While light is essential for the human brain to identify objects, parts of the eye such as the cornea, retina and lens can be damaged when exposed directly to an excessive amount of UV rays which may also cause various eye diseases such as cataract and macular degeneration.^{5,6} Therefore, there have been many attempts to protect the eyes and wearing glasses that can block UV rays is one of the methods. Spectacles with coated material on the surface of the lens can easily block UV rays but in the case of contact lenses, it is difficult to coat the surface and due to the characteristics of the material, many problems can occur in blocking UV.^{7,8} Due to these reasons, studies are currently in progress in order to enhance the potential of the materials used to make contact lenses, but there are fewer studies of materials for UV-blocking contact lenses. Also, due to the increased interest on aesthetic features and the inconveniences of spectacles, more people are preferring contact lenses over glasses and the user rate of contact lenses is increasing throughout the world.

Hence, studies on high-performance materials used to produce contact lenses are being actively conducted along with studies on water content which greatly affect comfortable wear.⁹⁻¹¹

Due to the present situation, in this study we added the benzophenone group which is used in films and bottles as a light-resistant stabilizer that absorbs UV rays in order to synthesize a polymer with a UV-blocking feature that can be used to produce contact lenses. Also, TiO_2 was used as another UV-absorbing additive. TiO_2 is known to be very stable in chemical and physical aspects and has the highest refractive index among white pigments and also has a well defined particle size and dispersibility. Also, TiO_2 decomposes organic compounds when activated with a photo-catalyst and there is a recent global trend of various applications of such characteristics in various fields. This study used TiO_2 as a material to absorb UV rays with a high visible transmittance and refractive index.

Therefore, we compared the UV absorbency of the polymer produced with the benzophenone group and TiO_2 with previous materials and measured the properties of the

produced contact lens in order to experiment whether the material is suitable for ophthalmic materials.

MATERIALS AND METHODS

Materials

The 2-hydroxy-4-methoxy-benzophenone and 2,4-dihydroxy-benzophenone used in this study were products from Aldrich and the SEM image taken in order to visualize the structure of TiO_2 is shown in Fig. 1. The ethylene glycol dimethacrylate (EGDMA) was procured from Acros while the 2-hydroxyethyl methacrylate (HEMA) and azobisisobutyronitrile (AIBN) was supplied by JUNSEI and used without any purification.

Methods

Refractive index and water content: The refractive index of the produced contact lens was measured with ATAGO NAR 1T. It can be seen in Fig. 2. The hydrated material refractive index (n_{wet}), dry material refractive index (n_{dry}) and standard saline solution (ISO 18369-3) refractive index (n_{std}) were measured. Formula (1) based on the refractive index method of the ISO 18369-4:2006,

Fig. 1. SEM image of TiO_2 .

Fig. 2. Abbe refractometer (ATAGO NAR 1T).

Fig. 3. Spectral transmittance meter (TOPCON TM-2).

Ophthalmic optics - Contact lenses - Part 4: Physicochemical properties of contact lens materials was used to measure to calculate the water content.

$$\phi H_2O = \frac{n_{dry} - n_{wet}}{n_{dry} - n_{std}} \times 100 \quad (1)$$

Optical transmittance: TOPCON TM. 2 and Hitachi Model U-4001 Spectrophotometer were used to measure the optical transmittance for visible light, UV-A and UV-B. It can be seen in Fig. 3. The average optical transmittance (τ) from wavelength λ_1 to λ_2 was calculated using Formula (2) and is shown as a percentage. The optical transmittance and the luminance transmittance of the produced contact lens were measured after hydrating for 24 hours in a 0.9% sodium chloride PBS solution.

$$\tau(\lambda_1, \lambda_2) = \frac{1}{\lambda_2 - \lambda_1} \int_{\lambda_1}^{\lambda_2} \tau(\lambda) d\lambda \quad (2)$$

Table 1. Composition ratio of each sample

Sample	HEMA	EGDMA	2-hydroxy-4-methoxy-benzophenone	2,4-dihydroxy-benzophenone	TiO ₂	Unit: %
Blank	99.54	0.46	-	-	-	
HMB	94.78	0.45	4.77	-	-	
DHB	94.78	0.45	-	4.77	-	
HDB	94.78	0.45	2.39	2.39	-	
TO	94.78	0.45	-	-	4.77	

Fig. 4. SEM image of HMB sample.

Production method of the contact lens: The cast mould method was used in order to produce the contact lenses used in this study. The mixed materials were inserted in the mould and heated for 40 minutes at 70 °C, for 40 minutes at 80 °C and for 40 minutes at 100 °C for polymerization. Meanwhile, 0.1% (wt) AIBN (azobisisobutyronitrile) was used as an initiator.

RESULTS AND DISCUSSION

Polymerization and lens production

The crosslinking agent EGDMA and UV-absorbents (2-hydroxy-4-methoxy-benzophenone, 2,4-dihydroxy-benzophenone, TiO₂, etc.) were mixed with a certain amount of HEMA and other raw materials and the mixture was polymerized and measured for UV-blocking performance. The mixture ratio used in this study is shown in Table 1. In order to classify each reagent used in this study, the mixture of only HEMA and EGDMA is described as Blank while HMB indicates the addition of 2-hydroxy-4-methoxy-benzophenone to Blank and the addition of 2,4-dihydroxy-benzophenone to Blank is described as DHB. Also, the sample that is a mixture of 2-hydroxy-4-methoxy-benzophenone and 2,4-dihydroxy-benzophenone which are of the benzophenone group and Blank is described as HDB while the addition of TiO₂ to Blank is described as TO in order to compare the measurements on the refractive index, water content and the visible transmittance.

Table 2. Refractive index and water content of Blank

Sample	Refractive index		Water content (%)
	n_{dry}	n_{wet}	
Blank-1	1.501	1.434	39.88
Blank-2	1.501	1.435	39.29
Blank-3	1.500	1.434	39.52
Blank-4	1.501	1.434	39.88
avg.	1.501	1.434	39.64

The polymerization used in this study all resulted in colorless transparent macromolecules and the SEM image of the produced contact lens is shown in Fig. 4.

Properties of the polymer produced with the benzophenone group

Refractive index and water content: The n_{dry} of Blank which does not include any UV-absorbent was 1.501 while n_{wet} was 1.434 and the water content was calculated to be 39.64%. The refractive index and water content of Blank is summarized in Table 2.

Also, the n_{dry} of HMB which is 2-hydroxy-4-methoxy-benzophenone added to Blank was 1.503 and the n_{wet} was 1.434 while the water content was 40.41%, showing that the refractive index and water content are similar to that of Blank. In cases with DHB which is 2,4-dihydroxy-benzophenone added to Blank, the n_{dry} was 1.507 and the n_{wet} was 1.440. The water content was calculated to be 38.56% showing a higher refractive index compared to that of Blank but did not show any significant differences in water content. The n_{dry} of HDB which is 2-hydroxy-4-methoxy-

Table 3. Refractive index and water content (benzophenone)

Sample	Refractive index		Water content (%)
	n_{dry}	n_{wet}	
HMB-1	1.502	1.433	40.83
HMB-2	1.502	1.434	40.24
HMB-3	1.503	1.435	40.00
HMB-4	1.503	1.434	40.59
avg.	1.503	1.434	40.41
DHB-1	1.508	1.440	38.86
DHB-2	1.507	1.439	39.08
DHB-3	1.508	1.441	38.29
DHB-4	1.504	1.439	38.01
avg.	1.507	1.440	38.56
HDB-1	1.501	1.439	36.90
HDB-2	1.499	1.439	36.14
HDB-3	1.499	1.438	36.75
HDB-4	1.500	1.440	35.93
avg.	1.500	1.439	36.43

Fig. 5. Distribution of Water content results.

benzophenone and 2,4-dihydroxy-benzophenone added to Blank was 1.500 while the n_{wet} was 1.439, and the water content was 36.43% which was lower than that of Blank while the refractive index was similar to that of Blank. The refractive index and water content of the samples produced with the benzophenone group are summarized in Table 3. Also the distribution of water content is shown in Fig. 5.

Optical transmittance: The optical transmittance of Blank which is the standard sample was high for all wavelengths such as the UV-B wavelength (280~315 nm), UV-A wavelength (315~400 nm) and in the visible light range (400~750 nm). Meanwhile, the transparency calculated with Formula (2) was 89%, 88% and 89% for each wavelength. Therefore, considering that the sample Blank has high transparencies for all wavelengths of UV rays, Blank can be considered to be ineffective in blocking UV rays. Contrary to the above, the DHB's optical transmittance showed a higher UV-blocking performance in UV-B (315~400 nm) than UV-A (280~315 nm) and also showed a higher transparency in the visible light wavelength (400~750 nm). The transparencies calculated with Formula (2) were 8%, 21% and 74%. The HMB's optical transmittance showed a total UV-blocking performance in UV-B (280~315 nm) and also showed a high transparency in the visible light wavelength (400~750 nm). The transparencies calculated with Formula (2) were 0%, 4% and 80%. The results are shown in Fig. 6.

Comparing the transparencies of Blank with that of HDB, HDB showed much lower transparencies in UV-B (280~315 nm) and UV-A (315~400 nm) as can be seen in Fig. 7. The transparencies for Blank calculated with Formula (2) was 84% in UV-B and 88% in UV-A, and in cases with HDB, the transparencies were 0% in UV-B and 6% in UV-A. Based on this result, Blank and HDB all showed very high transparencies of 90% in the visible light range and in wavelengths between 400~750 nm showing that the contact lens' transparency is suitable to

Fig. 6. Optical transmittance of HMB(Ultraviolet rays).

Fig. 7. Optical transmittance of Blank and HDB.

Table 4. Optical transmittance of samples (Benzophenone)

Sample	UV-B (%)	UV-A (%)	Visible light (%)
Blank	89	88	89
DHB	8	21	77
HMB	0	4	80
HDB	0	6	89

visible light. The optical transmittances of each sample are summarized in Table 4.

Properties of the material using TiO₂

Refractive index and water content: The n_{dry} of TO with TiO₂ added to the standard sample Blank was 1.507 and the n_{wet} was 1.432 while the water content was calculated to be 43.09%. Also, TO showed the highest water content from all other samples.

The refractive index and water content of each sample of TO are shown in Table 5.

Optical transmittance: Comparing the transparencies of Blank with that of TO, TO showed lower transparencies in all wavelengths of UV-B (280~315 nm) and UV-A (315~400 nm) as can be seen in Fig. 8. The transparencies

Table 5. Refractive index of TO sample

Sample	Refractive index		Water content (%)
	n_{dry}	n_{wet}	
TO-1	1.507	1.433	42.53
TO-2	1.507	1.433	42.53
TO-3	1.506	1.430	43.93
TO-4	1.506	1.431	43.35
avg.	1.507	1.432	43.09

Fig. 8. Optical transmittance of Blank and TO.

for Blank calculated with Formula (2) was 89% in UV-B and 88% in UV-A, and in cases with TO, the transparencies were 6% in UV-B and 51% in UV-A. Blank and HDB all showed high transparencies of 89% and 81% respectively in the visible light range (400~750 nm) showing that the contact lens' transparency is suitable to visible light.

CONCLUSION

In this study we polymerized macromolecule material that can block UV rays by adding 2-hydroxy-4-methoxy-benzophenone, 2,4-dihydroxy-benzophenone and TiO₂ to HEMA which is commonly used to produce contact lenses and measured the transparencies for visible light and UV rays. Also, by comparing the values with those of previous contact lenses, we tried to verify the effects of the materials used to block UV rays and its application to ophthalmological contact lenses.

As a result, we discovered that the contact lenses produced with UV-blockers are basically similar in water content and refractive index with previous lenses showing that there are no problems in applying the ophthalmological materials. Also, for optical transmittances of each wave length, the contact lens without the UV-absorbent was 89%, 88% and 89% respectively for UV-A, UV-B and visible light, indicating that the UV transmittance is

very high though contrary to cases with contact lenses with added 2-hydroxy-4-methoxy-benzophenone and 2,4-dihydroxy-benzophenone which showed transmittances of 0% and 6% respectively for UV-A and UV-B showing a UV-blocking effect. And in cases with contact lenses with added TiO₂, they showed transparencies of 6% and 51% respectively for UV-A and UV-B showing that they have UV-blocking effects. The visible transmittances were between 77~89%, showing that it satisfies the visible transmittance condition required for ophthalmological contact lenses.

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