

Comparative Study of Physical Properties of Functional Ophthalmic Hydrogel Lens Using Photo and Thermal Polymerization

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Abstract

In this study, HEMA, MMA, AA, and EGDMA were used as basic combinations for manufacturing hydrophilic lenses for ophthalmic applications. In addition, AIBN (thermal polymerization initiator), 2H2M (photo polymerization initiator), and 3-hydroxypyridine (additive) were used to manufacture hydrophilic ophthalmic lenses through thermal polymerization and photo polymerization before their physical properties were measured. The results showed that when ophthalmic lenses were prepared via thermal polymerization and photo polymerization using 3-hydroxypyridine as an additive, their optical and physical properties and surface structures were different in each case, but they all satisfied the physical properties required for ophthalmic lenses.

Keywords: Photo Polymerization, Thermal Polymerization, Hydrogel Lens, UV-block

1. Introduction

Photo polymerization through ultraviolet band irradiation can be utilized for a variety of applications by using numerous monomer combinations, making it ideal for a wide range of applications, including special coating and adhesive, because the polymerization is very fast compared to the thermal polymerization rate^[1,2]. Since recently, studies on the potential application of photo polymerization to biomaterials have been actively conducted because photo polymerization can be applied to a wide range of functional monomers. Furthermore, polymers copolymerized via photo polymerization exhibit a high degree of crosslinking property^[3-5]. Thermal polymerization is currently being used mainly for the manufacture of hydrophilic lenses for medical use. Ever since free-radical polymerization via thermal initiation was discovered by Gomberg in the 1990s, various studies on free radicals have been vigorously conducted, including studies employing peroxide functional groups, those using radical polymers initiated by photo degradation reactions, and other studies using radical polymers initiated by ther-

mal reactions^[6-11]. The irradiation of UV-A, which covers an ultraviolet ray band, is known to increase the probability of cancer outbreak in the human skin^[12-14]. In addition, oxidative damage to the lens protein and nucleic acid is known to induce turbidity in the orbitofrontal cortex and lens epithelium owing to the influence of ultraviolet rays on the eyeball^[15]. In the case of endogenous pyridinium compounds, the photo-oxidation mechanism of UV-A sensitization in the skin cells has been reported, and 3-hydroxypyridine derivatives have also been found to act as UV-A sensitizers^[16]. Extensive studies have been performed of late on ophthalmic lenses. Various studies, including those on high oxygen permeability^[17], high wettability^[18,19], antimicrobial activity^[20], and the ultraviolet ray blocking function^[21,22], which are all important physical properties required for hydrophilic lenses, have been carried out, but most of them have elected to use the free-radical polymerization method incorporating the thermal initiation mechanism. In this study, hydrophilic ophthalmic lenses were prepared via free-radical polymerization employing a photo initiator and the thermal polymerization method. In addition, 3-hydroxypyridine was used as an additive to enhance the ultraviolet shielding function of the lenses, before the basic physical properties, optical properties, and surface properties of each lens sample were measured, compared, and then analyzed.

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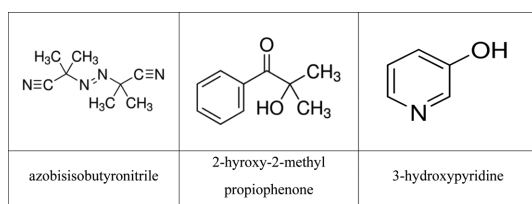


Fig. 1. Chemical structures of initiators and functional additive

2. Methods

2.1. Reagents and Materials

HEMA (2-hydroxyethyl methacrylate), AA (acrylic acid), MMA (methylmethacrylate), and AIBN (azobisisobutyronitrile), the main ingredients of the ophthalmic hydrophilic lenses that were used in this experiment, were manufactured by JUNSEI. 2-hydroxy-2-methylpropiophenone (photo initiator), ethylene glycol dimethacrylate (EGDMA, crosslinking agent), and 3-hydroxypyridine (3HP, additive) were all manufactured by SIGMA-ALDRICH. The molecular structures of the thermal initiator, photo initiator, and additives that were used in this experiment are shown in Fig. 1.

2.2. Polymerization

HEMA, MMA, AA, and EGDMA were used as a basic combination to manufacture ophthalmic hydrophilic lenses. Next, 3HP was mixed to the basic combination at a ratio of 1~10%, before stirring each sample for about 30 minutes. For the thermal polymerization of the samples, polymer was polymerized at 100°C for about 1 hour, and a 463 nm wavelength was irradiated for about 15 minutes to initiate a photo polymerization reaction. The prepared ophthalmic lens samples were then hydrated in a sterile saline solution for 24 hours before their physical properties (e.g., spectral transmissibility, refractive index, and water content) were evaluated. The surface structure of the lens fabricated using scanning electron microscopy (SEM) was then analyzed. With regard to the naming of the lens samples, the basic combinations copolymerized via thermal polymerization were named “Th-1,” “Th-5,” and “Th-10,” respectively, according to the ratio of Th-Ref and 3-hydroxypyridine added to the mixture. The basic combinations copolymerized via photo polymerization were named “Ph-1,” “Ph-5,” and “Ph-10,” respectively,

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

Sample	HEMA	MMA	AA	EGDMA	3-HP ⁺
Th-Ref.	94.79	2.84	1.90	0.47	-
Th-1	93.90	2.82	1.88	0.47	0.94
TH-5	90.50	2.71	1.81	0.45	4.52
TH-10	86.58	2.60	1.73	0.43	8.66
Ph-Ref.	94.79	2.84	1.90	0.47	-
Ph-1	93.90	2.82	1.88	0.47	0.94
Ph-5	90.50	2.71	1.81	0.45	4.52
Ph-10	86.58	2.60	1.73	0.43	8.66

3-HP⁺ : 3-hydroxypyridine

according to the ratio of Ph-Ref and 3-hydroxypyridine added to the mixture. The mixing ratios of the ophthalmic lenses that were used in the experiment are shown in Table 1.

2.3. Instruments and Analysis

All the hydrophilic lens specimens that were used in the experiments were stored in a standard sterile saline solution at room temperature for 24 hours before the test. A spectral transmittance meter (Cary 60 UV-vis, Agilent Technologies) was used to measure the spectral transmissibility of UV-B, UV-A, and visible light, respectively, and the obtained values were then expressed as percentages. The water contents of the samples were measured using the gravimetric method, and the refractive indices were measured using an ABBE refractometer (NAR 1T, ATAGO, Japan).

3. Results and Discussion

3.1. Polymerization and Manufacturing

All the combinations were thermally polymerized or photo polymerized to produce transparent ophthalmic hydrophilic lenses. After 24-hour hydration in a sterile saline, ophthalmic lenses with overall transparency and high flexibility were obtained. In addition, the SEM measurement showed a structure with regular holes on the lens surface when the combinations were photo polymerized as opposed to being subjected to thermal polymerization, indicating that such structure was caused by the shrinkage differences between the surface layer and the bulk layer owing to the varying density of the acrylate group of the main material during the photo polymerization process^[23]. In the case of thermal

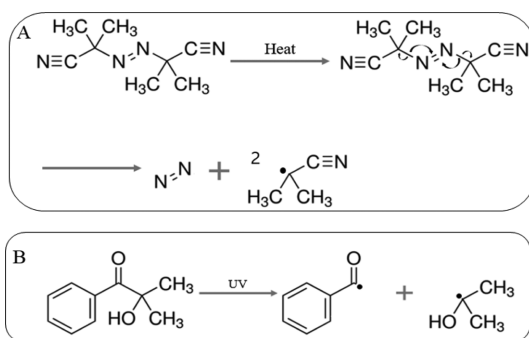


Fig. 2. Reaction mechanism of thermal and photo initiators. [(A) Thermal initiation mechanism. (B) Photo initiation mechanism]

polymerization, AIBN generates radicals at the initiation temperature, which again prompts the radical polymerization of the vinyl groups contained in the monomers to form a polymer. In the case of photo polymerization, on the other hand, the initiator 2H2M generates benzoyl and 2-hydroxyl-2-propyl radicals at the initiation wavelength band, which again imparts high reactivity, thereby facilitating easy polymerization. The initiation reaction mechanisms of thermal polymerization and photo polymerization are shown in Fig. 2, and photographs of the SEM measurement of each combination are shown in Fig. 3.

3.2. Water Content

For the water content of each of the prepared ophthalmic lenses, it was found to be 36.96% for the Th-Ref combinations. In the combinations of 3-hydroxypyridine and 3-hydroxypyridine, the water content was 37.54% for Th-1, 43.02% for Th-5, and 46.33% for Th-

10, suggesting that the water content of the lens increased as the hydroxyl group in the 3-hydroxypyridine molecule underwent hydrogen bonding with H₂O, and as the ratio of the additive increased. In the case of the combinations that were subjected to photo polymerization, the water content was 34.19% for the Ph-Ref. combination to which 3-hydroxypyridine was not added. The water content was 38.26% for Ph-1, 43.92% for Ph-5, and 48.01% for Ph-10 when 3-hydroxypyridine was added to the Ph-Ref. combinations according to their respective ratios, suggesting that the water content tends to increase with an increasing amount of additive in the case of photo polymerization. The water content was higher among the samples that were manufactured via photo polymerization than among those that were manufactured via thermal polymerization. From the analysis of the lens surfaces through SEM, it can be said that the surfaces of the lenses that were prepared after photo polymerization had relatively large holes that were distributed regularly. In the ophthalmic lenses that were produced via photo polymerization, the water content increase was larger than that in the lenses that were produced via thermal polymerization when pyridine was added to the lenses, suggesting that the water content increase stemmed from the synergistic effect of hydrogen bonding due to the hydroxyl group of the photo initiator 2H2M. The change in the water content for each combination is shown in Fig. 4.

3.3. Refractive Index

The refractive index of each sample was found to be 1.4361 for the Th-Ref. combinations. When 3-hydroxypyridine was added to the Th-Ref. in proportion to their respective ratios, the water content was 1.4347 for Th-

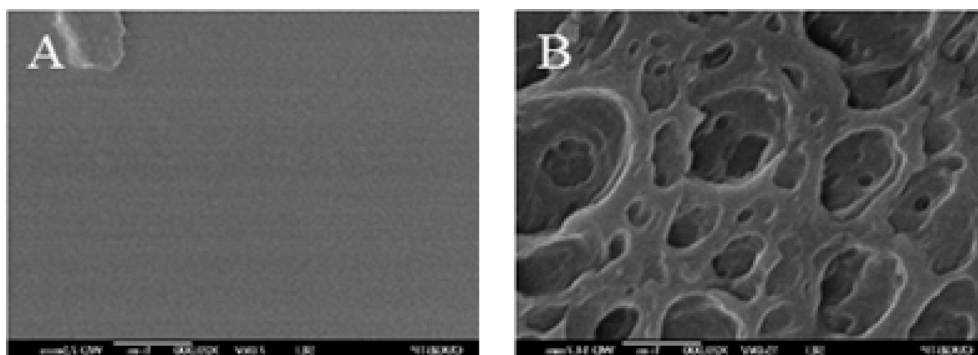


Fig. 3. Surface analysis of produced hydrogel lens sample by SEM [(A) Th-Ref. (B) Ph-Ref.].

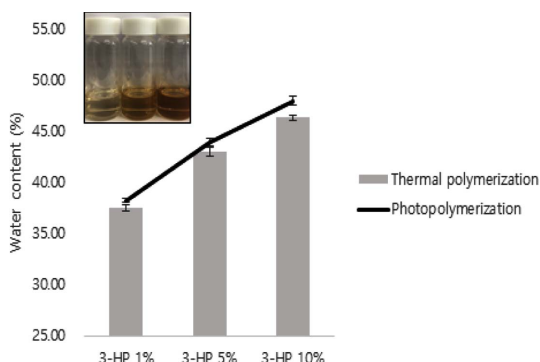


Fig. 4. Water content distribution of hydrophilic lens.

1, 1.4244 for Th-5, and 1.4156 for Th-10, suggesting that the optical density decreased because the higher the 3-hydroxypyridine ratio is, the higher the water content, thereby decreasing the refractive index. In the case of photo polymerization, the water content was 1.4452 for the Ph-Ref. to which 3-hydroxypyridine was not added, whereas in the case of the combinations to which additives were added to the Ph-Ref combinations in proportion to their respective ratios, the water content was 1.4394 for Ph-1, 1.4268 for Ph-5, and 1.4175 for Ph-10, suggesting that the refractive index tends to decrease as the 3-hydroxypyridine ratio increases due to the influence of the water content. The variation tendency of the refractive index of each combination is shown in Fig. 5.

3.4. Spectral Transmittance

With regard to the spectral transmissibility of each

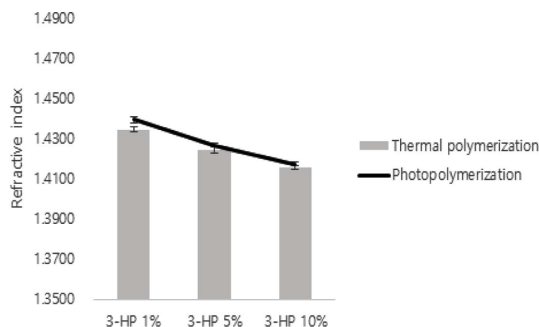


Fig. 5. Refractive index distribution of hydrophilic lens samples.

sample, the Th-Ref. thermal polymerization combinations showed 33.49% UV-B transmittance, 72.42% UV-A transmittance, and 85.01% visible-light transmittance, similar to the transmittance of the generic hydrogel lens, suggesting that there was no UV blocking property. The average spectral transmissibility values of the Th combinations with 3-hydroxypyridine added to the thermal polymerization combination by their respective 1-10% ratios were 31.35, 75.09, and 88.40% for UV-B, UV-A, and visible light, respectively, in the case of the Th-1 combination; 3.29, 45.82, and 89.22% in the case of the Th-5 combination; and 0.03, 30.89, and 87.63% in the case of the Th-10 combination. As the amount of 3-hydroxypyridine increased, the transmittance gradually decreased in the ultraviolet band, thereby demonstrating UV blocking capability. The Ph-Ref. of the photo polymerization combination showed 5.51% UV-B transmittance, 53.69% UV-A transmittance, and 86.27% visible-light transmittance. The transmittance in

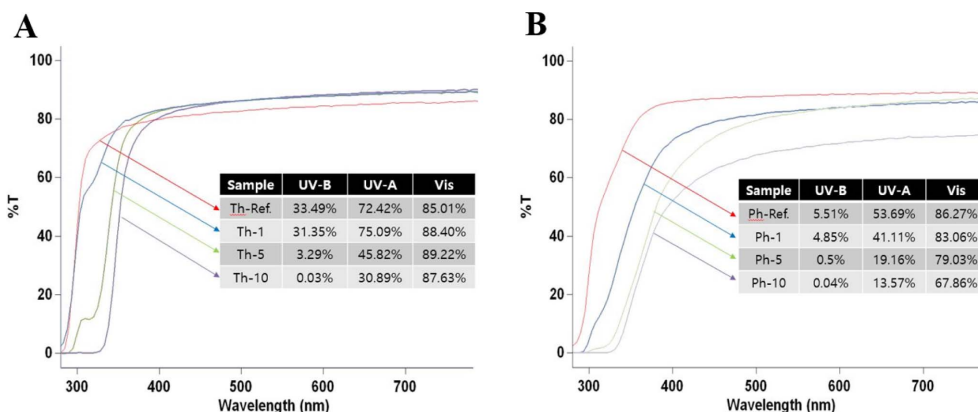


Fig. 6. Optical transmittance of produced lens sample [(A) Th group. (B) Ph group].

the ultraviolet region was lower than that of the general hydrogel lens, suggesting that the hydrogen atoms of the hydroxyl group of 2H2M absorb ultraviolet light due to the hydrogen bonding with the oxygen in the molecule. This result also showed the same tendency as that in the study of Seo *et al.*^[24]. The average spectral transmissibility values of the Ph combinations with 3-hydroxypyridine added to the photo polymerization combination by their respective 1-10% ratios were 4.85, 41.11, and 83.06%, respectively, for UV-B, UV-A, and visible light. The transmittance in the ultraviolet region decreased as the amount of 3-hydroxypyridine increased. In the case of the Th-5 combination, it was 0.5, 19.16, and 79.03%, and in the Th-10 combination, 0.04, 13.57, and 67.86%, indicating that the larger the amount of 3-hydroxypyridine additive is, the lower the transmittance in the UV region. This suggests that the pyridine molecule structure absorbs ultraviolet light due to the hydrogen bonding between the hydrogen in the hydroxyl group and the nitrogen in the molecule. In addition, photo polymerization showed a higher UV blocking effect than thermal polymerization because the molecular structures of the photo initiator and pyridine that were used in the photo polymerization reaction induced hydrogen bonding in the molecules, thereby showing a synergistic effect of UV blocking. The spectral transmissibility of each combination is shown in Fig. 6.

4. Conclusions

HEMA, MMA, AA, and EGDMA were used as basic combinations for manufacturing hydrophilic lenses for ophthalmic applications. And also, 2H2M and 3-hydroxypyridine were used for hydrophilic lenses through thermal and photo polymerization. The experiment showed that when ophthalmic lenses were prepared via thermal polymerization and photo polymerization using 3-hydroxypyridine as an additive, their optical and physical properties and surface structures were different in each case, but they all had the physical properties required for ophthalmic lenses. In addition, a synergistic effect was observed in their water contents and spectral transmissibility when the lenses were prepared via photo polymerization using 2H2M as a photo initiator and 3-hydroxypyridine as the additive. The water content increased among those samples that were manufactured via photo polymerization compared to those that

were manufactured via thermal polymerization, while the UV blocking effect decreased when thermal polymerization was used. It is therefore concluded that if the materials that were used in this experiment are polymerized using the photo polymerization method, they can be used as ophthalmic hydrophilic lens materials with an ultraviolet shielding function and a high water content.

References

- [1] L. Lecamp, B. Youssef, C. Bunel, and P. Lebaudy, "Photoinitiated polymerization of a dimethacrylate oligomer: 1. Influence of photoinitiator concentration, temperature and light intensity", *Polymer*, Vol. 38, pp. 6089-6096, 1997.
- [2] W. D. Cook, "Thermal aspects of the kinetics of dimethacrylate photopolymerization", *Polymer*, Vol. 33, pp. 2152-2161, 1992.
- [3] P. E. M. Allen, D. J. Bennett, S. Hagias, A. M. Hounslow, G. S. Ross, G. P. Simon, D. R. G. Williams, and E. H. Williams, "The radical polymerization of dimethacrylate monomers—the use of NMR spectrometry to follow the development of network structure", *Eur. Polym. J.*, Vol. 25, pp. 785-789, 1989.
- [4] G. P. Simon, P. E. M. Allen, D. J. Bennett, D. R. G. Williams, and E. H. Williams, "Nature of residual unsaturation during cure of dimethacrylates examined by CPPEMAS carbon-13 NMR and simulation using a kinetic gelation model", *Macromolecules*, Vol. 22, pp. 3555-3561, 1989.
- [5] Y. Choe and B. K. Ryu, "Photopolymerization of reactive oligomers and Methacrylate/SBS blends", *Polymer (Korea)*, Vol. 27, pp. 421-428, 2003.
- [6] G. Smets, L. Convent, and X. Van der Borght, "Branching and graftcopolymerization of polyethyl- α -chloroacrylate", *Macromol. Chem. Phys.*, Vol. 23, pp. 162-174, 1957.
- [7] R. J. Ceresa, "The physico-chemical synthesis of block copolymers", *Polymer*, Vol. 1, pp. 397-399, 1960.
- [8] H. A. Dieu, "Etudes des solutions d'alcool polyvinyle", *J. Polym. Sci. A Polym. Chem.*, Vol. 12, pp. 417-438, 1954.
- [9] J. A. Hick and H. W. Melville, "A flow method for the synthesis of 'Block' copolymers", *Nature*, Vol. 171, pp. 300-301, 1953.
- [10] S. Yamago, K. Iida, M. Nakajima, and J.-I. Yoshida, "Practical protocols for organotellurium-mediated living radical polymerization by in situ generated

- initiators from AIBN and ditellurides”, *Macromolecules*, Vol. 36, pp. 3793-3796, 2003.
- [11] S. Washiro, M. Yoshizawa, H. Nakajima, and H. Ohno, “Highly ion conductive flexible films composed of network polymers based on polymerizable ionic liquids”, *Polymer*, Vol. 45, pp. 1577-1582, 2004.
- [12] K. Scharffetter-Kochanek, M. Wlaschek, P. Brenneisen, M. Schauen, R. Blaudschun, and J. Wenk, “UV-induced reactive oxygen species in photocarcinogenesis and photoaging”, *Biol. Chem.*, Vol. 378, pp. 1247-1258, 1997.
- [13] E. Kvam and R. M. Tyrrell, “Induction of oxidative DNA base damage in human skin cells by UV and near visible radiation”, *Carcinogenesis*, Vol. 18, pp. 2379-2384, 1997.
- [14] F. R. de Gruijl, “Photocarcinogenesis: UVA vs UVB”, *Methods Enzymol.*, Vol. 319, pp. 359-366, 2000.
- [15] W. S. Duke-Elder, “The pathological action of light upon the eye”, *The Lancet*, Vol. 207, pp. 1137-1141, 1926.
- [16] G. T. Wondrak, M. J. Roberts, M. K. Jacobson, and E. L. Jacobson, “3-hydroxypyridine chromophores are endogenous sensitizers of photooxidative stress in human skin cells”, *J. Biol. Chem.*, Vol. 279, pp. 30009-30020, 2004.
- [17] A. Y. Sung, T. H. Kim, and J. I. Kong, “Polymerization of hydrogel contact lens with high oxygen transmissibility”, *Journal of Korean Ophthalmic Optics Society*, Vol. 11, pp. 49-53, 2006.
- [18] S. A. Cho, S. Y. Park, T. H. Kim, and A. Y. Sung, “Characterization of physical properties of hydrogel contact lens materials containing 1,4-butanediol and (\pm)-1,2,4-butanetriol for wettability improvement”, *The Korean Journal of Vision Science*, Vol. 14, pp. 69-76, 2012.
- [19] M. J. Lee, A. Y. Sung, and T. H. Kim, “Influence of wetting agents on physical properties of soft contact lens”, *Journal of Korean Ophthalmic Optics Society*, Vol. 19, pp. 43-49, 2014.
- [20] D. H. Kim, A. Y. Sung, and T. H. Kim, “Antibacterial and characterization of high performance soft contact lens using fluoro- and carboxy-substituted pyridine as additive”, *Korean J. Vis. Sci.* Vol. 16, pp. 89-97, 2014.
- [21] T. H. Kim, K. H. Ye, and A. Y. Sung, “UV-Blocking effect of ophthalmic material containing benzophenone”, *Journal of the Korean Chemical Society*, Vol. 53, pp. 391-394, 2009.
- [22] D. H. Kim and A. Y. Sung, “Application of hydroxyl-substituted benzophenone group for UV-block soft contact lens”, *The Korean Journal of Vision Science*, Vol. 17, pp. 1-12, 2015.
- [23] Y. Gan, J. Yin, and X. Jiana, “Self-wrinkling induced by the photopolymerization and self-assembly of fluorinated polymer at air/liquid interface”, *J. Mater. Chem. A*, Vol. 2, pp. 18574-18582, 2014.
- [24] Y. S. Suh and S. H. Kim, “UV-cut effects of cotton fabrics treated with UV absorbents”, *J. Korea Society of Clothing and Textiles*, Vol. 18, pp. 622-627, 1994.