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〈Research Paper〉

Effect of Coloration on the Hydrophilicity and Swelling Properties of Poly-HEMA Hydrogels

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Abstract— Photopolymerization of 2-hydroxyethyl methacrylate(HEMA), in the presence of ethyleneglycol dimethacrylate(EGDMA) and 1-Hydroxycyclohexyl phenyl ketone as crosslinker and photoinitiator, respectively, produced crosslinked poly-HEMA hydrogels. The hydrogels were colored by the exhaustion of vinylsulphone-type reactive dyes. Good colorfastness to laundering was achieved when colored with C.I. Reactive Black 5. We investigated that the effect of coloration on the hydrophilicity and swelling properties of the films. More hydrophilic gel-surfaces were generated with an increase in coloration and crosslinking. Higher surface energy was observed with higher crosslinking level. The more rapid and higher water swellability of poly-HEMA gels after coloration may be resulted from a more opened gel structure by the easier hydration of the hydrophilic sulphonic acid groups of the reacted dyes in water.

Keywords: *poly-HEMA hydrogel, hydrophilicity, reactive dye, dyeability, swellability*

1. Introduction

Poly HEMA(2-hydroxyethyl methacrylate) is a hydrophilic hydrogel capable of absorbing large amount of water while maintaining a three-dimensional network structure which has good biocompatibility and biological inertness[1)].

The poly-HEMA hydrogels have been extensively studied in biomedical and pharmaceutical industries for making contact lenses, biosensors, membranes, artificial organs, and carriers for drug delivery system[2,3)]. Poly-HEMA hydrogel is used as a hydrophilic air-permeable membrane film which has low surface tension and high water absorbency in a water-rich environment. Particularly large amount of poly HEMA, crosslinked with ethyleneglycol dimethacrylate(EGDMA) or diethyleneglycol dimethacrylate(DEGMA), is utilized in the soft contact lens industry due to its advantages over hard contact lenses such as less irritation, convenient fit, longer lifetime as well as its excellent oxygen permeability and hydrophilic properties[4)].

Recently the coloration of soft contact lenses has been increasingly adopted because consumers become more interested in the aesthetic properties of lenses, such as the color of the iris and the apparently enlarged size of the eyes with the colored lenses, rather than their inherent properties, such as the correction of vision deficiency or the medical treatment of certain eye diseases.

Several dyes and pigments have been already approved for use in soft contact lenses by the FDA(Food and Drug Administration). They include C.I. Reactive Black 5, C.I. Solvent Blue 246, C.I. Vat Orange 1, C.I. Pigment Violet 23, Iron oxide, and Titanium dioxide. Conventional colored contact lenses are manufactured by coating or printing the pigment formulation of high tinctorial strength containing fixable binders on the outer lens surface.

Some inevitable problems that are associated

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with the pigmented systems include a higher surface hydrophobicity and a lower oxygen permeability, an incompatibility with the cornea of the eye, the durability of the pigment layer to cleaning and wearing, and adverse effects on optical properties, which results from the larger size and more hydrophobic character of pigments and the chemical binder systems in use.

Therefore new binder-free coloration without hydrophobic pigments have been developing for the commercial contact lens. Coloration with water-soluble dyes can be an alternative to the pigment-based system because coloration with dyes could give better optical properties such as a higher transmittance due to the smaller particle size of dyes in the colored poly-HEMA hydrogels as well as avoiding the usage of fixable binders in question. However, high colorfastness must be met because cosmetic lenses are always in contact with water environments of tear or cleaning solution. Among the dye classes capable to use in contact lenses, reactive dyes seem to be promising in terms of higher fastness to the wet environment because of the possible covalent bond formation between hydroxy groups in poly-HEMA gels and reactive groups in the dyes. However few studies have been done on the colored soft contact lenses in spite of the rapidly developing market of the colored lenses[5-9].

This study investigates the dyeability of poly-HEMA hydrogel via the exhaustion method using FDA-approved reactive dyes and evaluates the color fastness of the colored gels. In addition, this study investigates the effect of coloration and crosslinking on the hydrophilicity and swellability of the colored poly-HEMA hydrogel, which can replace the conventional pigment-based coloring system for soft contact lenses.

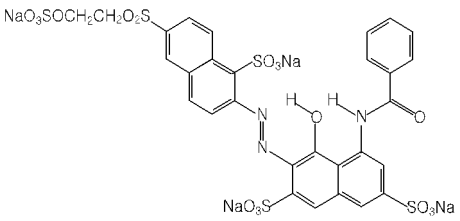
2. Experimental

2.1 Materials

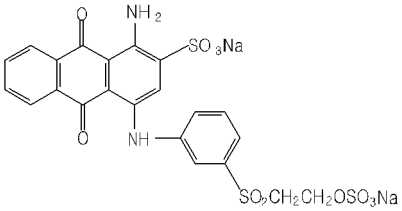
2-Hydroxyethyl methacrylate(HEMA) and ethyleneglycol dimethacrylate(EGDMA) were kindly provided by Geomedical Co. Ltd. and were used as a monomer and a crosslinker respectively. 1-Hydroxycyclohexyl phenyl ketone(Irgacure 184) was used as a free-radical photoinitiator.

The photopolymerized samples were colored using three Remazol dyes(C.I Reactive Red 180, C.I Reactive Blue 19, C.I Reactive Black 5) where the commercial dyes were not purified further. Glauber's salt and soda ash were used for dyeing auxilliaries.

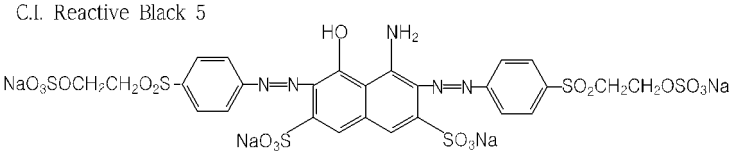
C.I. Reactive Red 180



C.I. Reactive Blue 19



C.I. Reactive Black 5



Scheme 1. Chemical structures of reactive dyes.

2.2 Photopolymerization and FT-IR analysis

A HEMA formulation mixed with 1%(w/w) photoinitiator was photopolymerized into a film form with a grid-type UV irradiator(H-bulb, Jelight Co.) using a UV energy of 10.8J/㎠ or less. The degree of gel crosslinking was adjusted by changing the molar ratio of the EGDMA to the monomer. The degree of cure was observed with a Jasco FT-IR 300E spectrophotometer.

2.3 Contact angle measurement and surface energy calculation

A static goniometer attached with a CCD camera(Phoenix 300, Ahtech) was used to measure the contact angles of water and diiodomethane on the polymerized samples by a sessile drop method under a constant temperature and humidity condition(25℃, 65%RH). Five measurements or more were averaged to obtain the contact angles on the samples. The surface energy was calculated using the contact angles of the three liquids. When a liquid wets on a solid surface, Young's equation and work of adhesion (W_a) are as follows:

$$\gamma_L(\cos\theta) = \gamma_S - \gamma_{SL} \quad (1)$$

$$W_a = \gamma_S + \gamma_L - \gamma_{SL} \quad (2)$$

where γ_S, γ_L and γ_{SL} are interfacial energies of solid/air, liquid/air and solid/liquid interfaces respectively. The total surface energy (γ_s^{TOT}) of a solid surface is the sum of the Lifshitz-van der Waals component (γ_s^{LW}) and the Lewis acid-base component(γ_s^{AB}) of which the latter is the geometric sum of the electron-withdrawing parameter (γ^+) and the electron-donating parameter (γ^-).

$$\gamma_s \quad (3)$$

$$\gamma_s^{AB} = 2\sqrt{\gamma^+\gamma^-} \quad (4)$$

Therefore the total surface energy of a solid can be calculated by the measured contact angles (θ) of the three liquids according to the following equation.

$$W_a = \gamma_L(1+\cos\theta) = 2\sqrt{\gamma_s^{LW}\gamma_L^{LW}} + 2\{\sqrt{\gamma_s^+\gamma_L^-} + \sqrt{\gamma_s^-\gamma_L^+}\} \quad (5)$$

2.4 Dyeability of poly-HEMA hydrogel

Poly-HEMA hydrogels were colored using the three reactive dyes according to the dyeing methods I and II using an infrared dyeing machine under the liquor to goods ratio of 30:1. In both dyeing methods, the dye liquor contained 30g/L of Glauber's salt together with the sample and dye. The dyeing temperature gradually increased from 20 ℃ to 50 ℃. At the temperature, 10g/L of soda ash was added into the dyebath and maintained for 60 minutes using method I, while the soda ash addition was made after a longer exhaustion period of 60 minutes at 50 ℃ using method II. The method II used 1%owf dye, while the different amount of dyes used in method I ranged from 0.25%owf to 1%owf.

After the dyeing processes, the colored poly HEMA were thoroughly soaped with a detergent (1g/L) at 85 ℃ for 30 minutes and subsequently rinsed with tap water. K/S at λ_{max} and % exhaustion, based on the remaining liquor, were evaluated with a reflectance spectrophotometer and a UV/VIS spectrophotometer, respectively.

2.5 Swellability of poly-HEMA hydrogel

In order to investigate the effect of crosslinking and coloration on the water swellability of the hydrogel, vacuum-dried samples were immersed in distilled water for 30 minutes and excess water was removed by blotting it with filter paper. Percent swelling was calculated according to the following equation by weighing the samples after certain time duration:

$$Swelling\ (\%) = \frac{W_s - W_d}{W_d} \times 100 \quad (6)$$

where W_s and W_d respresent the weights of wet and dry samples, respectively.

3. Results and discussion

3.1 Photopolymerization of poly-HEMA

The swelling and mechanical properties of poly-HEMA hydrogel can be modified by adjusting crosslinking density using crosslinkers, such as ethyleneglycol dimethacrylate (EGDMA). Poly-HEMA can be synthesized by various polymerization techniques, such as thermal, oxidation-reduction, or UV irradiation[5]. UV polymerization is the most commonly applied system due to its distinct advantages of low temperature, fast polymerization rate, in-line production and low energy requirement[10,11]. In this study, ethyleneglycol dimethacrylate (EGDMA) was mixed with the HEMA formulation and the degree of crosslinking in the hydrogels was assumed to be dependent on the molar ratio of EGDMA to HEMA. Fig. 1 shows the FT-IR spectra of photopolymerized HEMA crosslinked with EGDMA. In the spectrum of the poly HEMA, C=C stretching bands located at 1637cm^{-1} of the unpolymerized HEMA or EGDMA alone are diminished due to photopolymerization of the monomers. In addition the CH_2 stretching bands at 2890 and 2957cm^{-1} increased due to the presence of EGDMA in the hydrogel.

3.2 Dyeability and color fastness of poly-HEMA hydrogels

It has been known that the increased crosslinking density of hydrogels results in decreased absorption capability and water swellability due to lower accessibility of crosslinked gel pores as well as increased mechanical strength of the gels.

Coloration of poly HEMA with three reactive dyes according to dyeing method II were summarized in Fig. 2 and 3. As expected, the hydrogels were successfully colored with the reactive dyes, which is presumably due to the nucleophilic addition of hydroxy groups in the poly HEMA to the vinylsulfone reactive groups in the dyes. However the higher crosslinking of poly-HEMA decreased both percent exhaustion and colour yield with increasing EGDMA concentrations in the photoactive formulations, and the trend was more pronounced in the case of the larger red and black dyes compared with the smaller blue dyes.

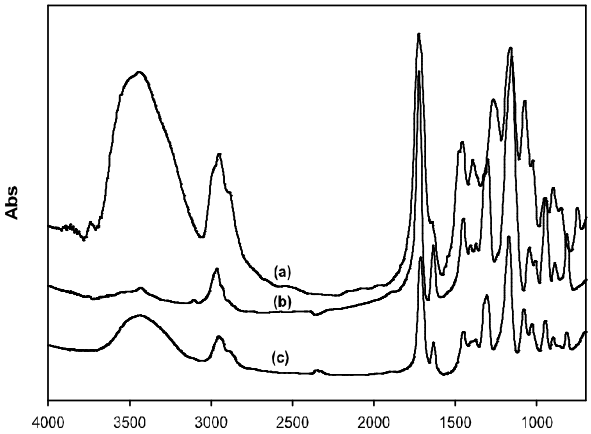


Fig. 1. FTIR spectra of polymerized HEMA with EGDMA(a), EGDMA(b), and HEMA(c).

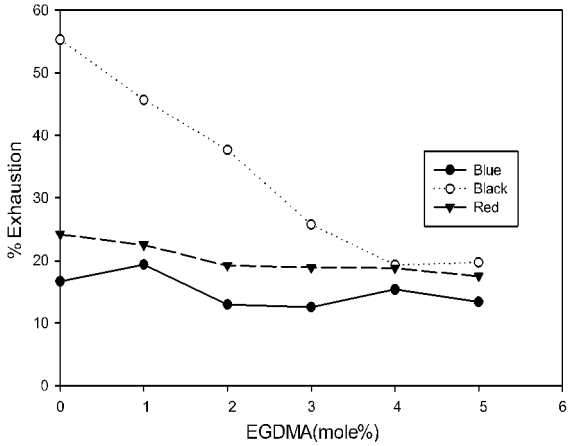


Fig. 2. Percent exhaustion of colored poly-HEMA(dyeing method II).

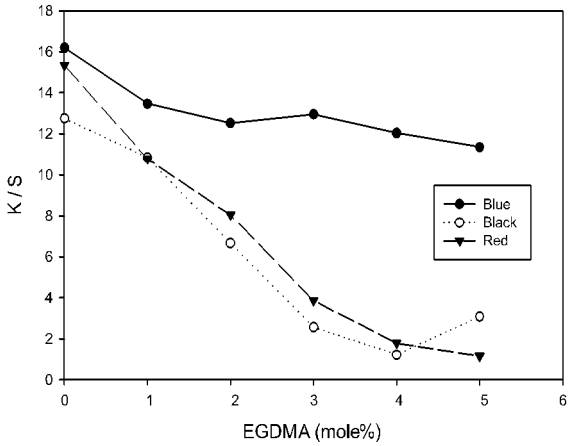


Fig. 3. K/S of colored poly-HEMA(dyeing method II).

Table 1. Color fastness to laundering of colored poly(HEMA)

Reactive dyes	K/S	Shade change	Staining					
			4-5	Acryl	Nylon	Silk	Rayon	Wool
Black 5	12.8	4-5	4-5	4-5	4	4	3-4	2-3
Red 180	15.3	3-4	2-3	4	3-4	2-3	1-2	2-3
Blue 19	16.2	2	3	4	1	1	2	1

Table 1 shows the colorfastness of the colored hydrogels to laundering for 30 minute at the boil. Although the sample colored with the bifunctional black dye of two vinylsulfone reactive groups gave the best fastness ratings in both shade change and staining, the other mono-functional dyes showed inferior ratings maybe indicating the presence of hydrolyzed reactive dyes in the samples. The larger red dyes had better ratings than the small blue dye.

3.3 Hydrophilicity and surface energy of poly-HEMA hydrogels

The hydrophility of poly-HEMA gels was assessed with the contact angle of water on the film(Fig. 4). Surprisingly, coloration with 1%owf red dye brought about a more hydrophilic surface, as indicated in the decreased water contact angle from 63.5° to 49.7°. It may be resulted from the fact that the anionic charges present in the dye contributed to the observed hydrophilicity. Similar hydrophilic effect by coloration was noticeable in the crosslinked poly HEMA. In addition, the EGDMA crosslinking itself resulted in an increased surface hydrophilicity in spite of higher crosslinking in the bulk probably due to the more polar nature of EGDMA compared to the poly HEMA.

Surface energy was calculated according to the method of van Oss *et al*[12] based on the contact angles of three liquids(Fig. 5). The total surface energy (γ^{TOT}) of the uncolored poly-HEMA gel was 39.5 mN/m consisting of a nonpolar component (γ^{LW}) and a polar component (γ^{AB}) having 35.9 and 3.7 mN/m respectively, where acid (γ^{+}) and base(γ^{-}) parameters are 27.5 and 0.1 mN/m respectively.

While significant γ (40.4mN/m) change was not observed because of combined effect of slightly increased γ^{LW} (38.6mN/m) and decreased γ^{AB} (1.8mN/m) when colored with the 1%owf red dye, higher crosslinking increased γ^{TOT} (47.2mN/m) remarkably due to the significantly increase in γ^{AB} (7.7mN/m) which was contributed from increased γ^{-} (58.5mN/m) rather than γ^{+} (0.3mN/m) at 3% mole ratio.

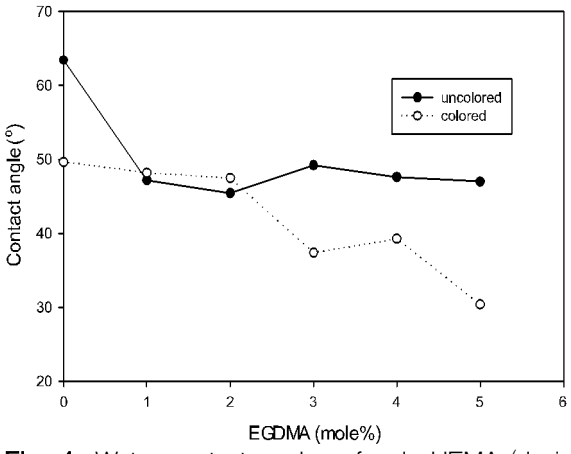


Fig. 4. Water contact angles of poly-HEMAs(dyeing method I, 1%owf Reactive Red 180).

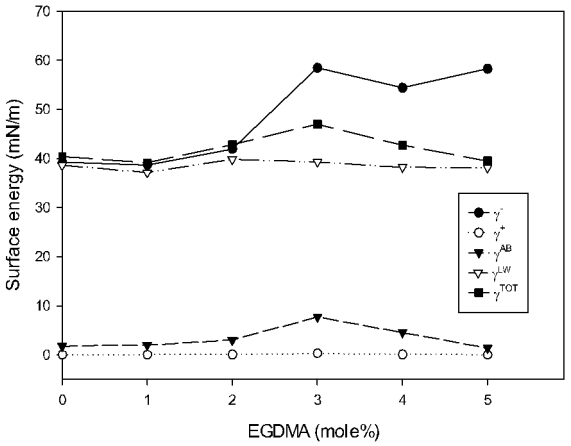


Fig. 5. Surface energies of colored poly-HEMA(dyeing method II, 1%owf Reactive Blue 19).

3.4 Swelling property of poly-HEMA hydrogels

Poly-HEMA hydrogels equilibrate in water at a room temperature of 40% or more hydration. Fig. 6 shows the effect of crosslinking on the percent swelling of the uncolored poly-HEMA. Unsurprisingly water swelling decreased with an increase in crosslinking density, where 2 mole% EGDMA was sufficient to reduce water swelling to half of the uncrosslinked hydrogel.

On the contrary, coloration increased substantially the swelling behavior of the uncrosslinked poly-HEMA gel as shown in Fig. 7. The preferential water absorption of boned anionic dyes in the colored hydrogel may cause the poly-HEMA network to stretch the gel structure, which is attributable to the rapid intake of water and higher swelling capacity. Also the enhanced swelling effect of coloration was observed in the colored and crosslinked gel systems, even though it was not included. Therefore the coloration of the HEMA-based soft contact lenses can be a beneficial technique in increasing the hydrophilic and swelling behavior by influencing both the surface and bulk structures of the poly-HEMA gels.

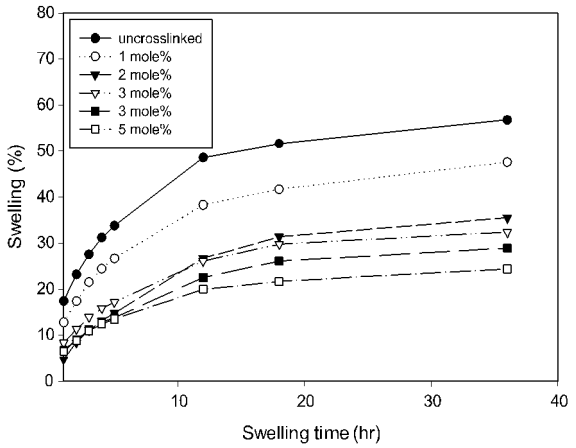


Fig. 6. Percent water swelling of uncolored poly-HEMA.

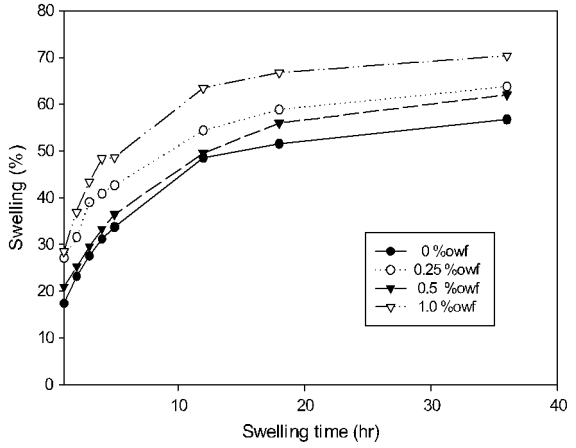


Fig. 7. Effect of dye concentration on percent swelling of colored poly-HEMA. (dyeing method I, Reactive Red 180)

4. Conclusions

Poly-HEMA hydrogels were produced via the UV-irradiated polymerization of HEMA with a different amount of EGDMA as a crosslinker. The dyeability to vinylsulfone reactive dyes and color fastness of the crosslinked gels were assessed, and the effects of coloration on hydrophilicity, surface energy and swellability of the colored gels were investigated. Three reactive dyes were able to color the hydrogels successfully and the colorfastness of the colored gels were good in case of the black dye. The difference in colorfastness may originate from a high fixation of the bifunctional reactive dye. The dyeability of the poly HEMA to reactive dyes decreased with an increasing crosslinker concentration because of the lower dye accessibility of the crosslinked gels. The coloration treatment caused the hydrogels more hydrophilic and increased equilibrium water hydration with increasing dye concentration. The surface energy of the hydrogels increased with increased crosslinking. The higher swellability of the colored gels may be resulted from the fact that the preferential hydration of the anionic sulphonic acid groups in the covalently-bonded dye in gels encourage the opening of the gel structure and hence increase the rapid intake of water and swelling capacity.

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