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Optical application of poly(HEMA-*co*-MMA) containing silver nanoparticles and N,N-dimethylacrylamide

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Abstract−High functional ophthalmic lens materials, poly(HEMA-*co*-MMA)s, were prepared by the copolymerization of HEMA, MMA, NVP, EDGMA, and N,N-dimethylacrylamide in the presence of silver nanoparticles. Silver nanoparticles have antimicrobial properties and a hydrophilic monomer N,N-dimethylacrylamide has excellent biocompatibility and oxygen transmissibility. The water content was in the range of 36.63-44.45%, indicating the characteristics of general water-content contact lenses, and the refractive index was measured to be in the range of 1.423-1.435. Meanwhile, the oxygen transmissibility ranged from 10.63×10^{-11} to 18.85×10^{-11} (cm^2/sec)(mlO_2/ml×mmHg) increasing with increasing the addition ratio of N,N-dimethylacrylamide. The polymeric materials satisfied the basic characteristics required for ophthalmic contact lenses. The polymers can be used to fabricate antimicrobial hydrogel contact lenses with high oxygen transmissibility.

Key words: Silver Nanoparticle, N,N-dimethylacrylamide, Oxygen Permeability, Water Content, Antimicrobial Property

INTRODUCTION

Contact lenses have been used worldwide because the use of macromolecule materials enables them to become a popular means of correcting visible ability. The major physical characteristics of macromolecules used in hydrogel contact lenses include refractive index, optical transmittance, surface hydrophilic (or wettability), water content, permeability to oxygen and carbon dioxide, physical and chemical stability, biocompatibility and mechanical properties. Poly(methyl methacrylate) or poly(MMA) and poly(2-hydroxyethyl methacrylate) or poly(HEMA) have been extensively used in hydrogel contact lenses application. Various studies have been conducted on the macromolecular materials that not only have basic characteristics (such as optical properties, chemical and physical stability and biocompatibility), but also antimicrobial characteristics and UV-blocking capabilities [1-4]. Other macromolecules are already used for their application in contact lenses [5,6].

Among the physical characteristics required for a contact lens, oxygen permeability is an important property for the cornea which is supplied directly with oxygen through the air diffusion. Failure to supply sufficient amount of oxygen to the cornea can cause various adverse reactions such as corneal edema and angiogenesis [7,8]. PDMS (polydimethylsiloxane) and polyphosphazene with high oxygen permeability were also used for ophthalmic contact lenses [9]. However, these polymeric materials are extremely hydrophobic, inhibiting the contact lens wettability, and aggravate the comfort, which limits the ophthalmic application.

The eye is abundant with neurons and is composed of various forms of fibers. A fibric tissue that can easily be exposed to microbial infections at proper temperature and high humidity makes it vulnerable to acute disorders. In particular, the prevalence of ophthalmologic disorders is increasing due to adverse reactions caused by the use of contact lenses. Hart et al. [10] reported that 35% of soft contact lenses worn by people were contaminated. *E. coli*, fungi, pseudomonas aeruginosa and staphylococci are the most common bacterial pathogens related to the eye which can cause fungal corneal ulcer, pseudomonas corneal ulcer, acute catarrhal conjunctivitis, and chronic bacterial conjunctivitis [11-13]. Various studies are being conducted on antimicrobial contact lens materials using silver-gold nanoparticles and chitosan [14,15]. Although studies are being conducted on improving individual characteristics of materials used in contact lenses, there is still a lack of study of materials that satisfy the basic properties mentioned above.

Here we report ophthalmic hydrogel copolymers containing both silver nanoparticles (showing protective properties against pathogens due to their microbial and sterilizing characteristics) and N,N-dimethylacrylamide (having high hydrophilicity and biocompatibility). N,N-dimethylacrylamide is being used for adhesives, coating agents, enhancers for polyamide and epoxy resin, and protective agents for resins and paper [16,17]. We investigated the characteristics of the copolymers such as water content, refractive index, optical transmittance and oxygen transmissibility to test the validity of this material for use in contact lenses.

EXPERIMENTAL SECTION

1. Chemicals and Polymerization

HEMA (2-hydroxyethyl methacrylate), MMA (methyl methacrylate), NVP (N-vinyl-2-pyrrolidone), EGDMA (ethylene glycol dimethacrylate), AIBN (2,2-azobisiobutyronitrile), $AgNO_3$, and N,N-dimethylacrylamide were purchased from Aldrich. The vinyl monomers were distilled to remove radical inhibitor before use. A cast mould method was used to produce the contact lens where mixtures mixed at a constant ratio were injected into the contact lens mould and thermopolymerized at 110 °C for 2 hrs.

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Table 1. Percent composition of samples Unit: %

	HEMA	MMA	NVP	EGDMA	$AgNO_3$	N,N-dimethylacrylamide
Ref.	93.90	0.94	4.69	0.47	-	-
Ag-1	93.02	0.93	4.65	0.47	0.93	-
AgDMA-1	92.17	0.92	4.61	0.46	0.92	0.92
AgDMA-3	90.50	0.90	4.52	0.45	0.90	2.71
AgDMA-5	88.89	0.89	4.44	0.44	0.89	4.44
AgDMA-7	87.34	0.87	4.37	0.44	0.87	6.11
AgDMA-10	85.11	0.85	4.26	0.43	0.85	8.51

To produce a contact lens with high oxygen permeability and antimicrobial properties, approximately 1 wt% MMA and 5 wt% NVP were mixed with HEMA, which is the main component of the hydrophilic contact lens, and 1 wt% $AgNO_3$ was added afterwards. In addition, N,N-dimethylacrylamide (0.92, 2.71, 4.44 and 8.51 wt%), 0.5% EGDMA were added along with 0.1% AIBN as the initiator. The samples used in this study were named as Ref., Ag-1, AgDMA-1, AgDMA-3, AgDMA-5, AgDMA-7 and AgDMA-9 based on the mixing ratio of $AgNO_3$ and N,N-dimethylacrylamide. The results are summarized in Table 1.

2. Characterizing Methods

The water content was measured according to the ISO 18369-4:2006 (Ophthalmic optics-Contact lenses-Part 4: Physicochemical properties of contact lens materials) using the gravimetric method. Oxygen permeability (Dk/t) was measured based on the ISO 18369-4:2006 (Ophthalmic optics-Contact lenses-Part 4: Physicochemical properties of contact lens materials, 4.4.3 Polarographic method). The entire system was maintained inside the general incubator with a temperature of 35±0.5 °C. The contact lenses used in this study were stored in standard saline solution for at least 24 hrs before measurements were taken and were placed at the experiment temperature for

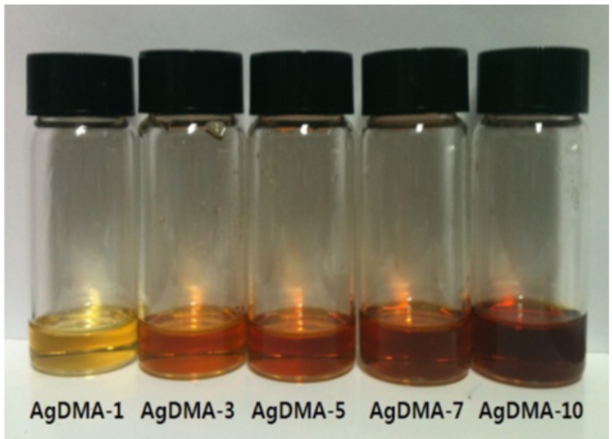

Fig. 1. Color change of mixed monomer samples.

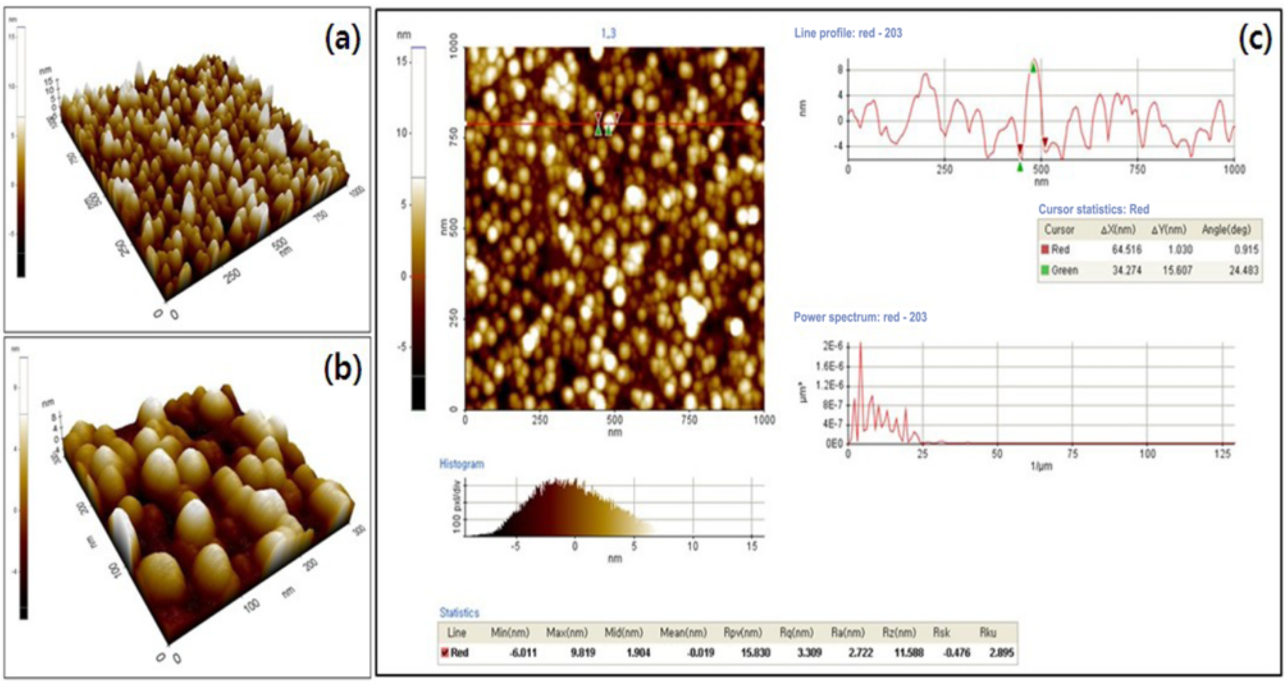

Fig. 2. AFM images of manufactured contact lens. (a) scan size: 1,000×1,000 nm, (b) scan size: 300×300 nm, (c) morphology of the hydrogel lens by AFM analysis.

at least 2 hrs to reach equilibrium. The thickness of the contact lens required to measure the oxygen permeability (Dk) was measured at the center of contact lens. The refractive index was measured three times using a ABBE refractometer according to the ISO 18369-4:2006 (Ophthalmic optics-Contact lenses-Part 4: Physicochemical properties of contact lens materials, 4.5. Refractive index) at a hydrated state and the mean of the three measurements was calculated.

RESULTS AND DISCUSSION

1. Polymerization

HEMA, MMA and NVP mixed at a constant ratio were polymerized in the presence of 0.1% AIBN (as initiator), 1% of $AgNO_3$ and 0.5% EGDMA (as cross-linking agent) to give a colorless transparent contact lens. A yellowish color developed with the increase of the adding ratio of N,N-dimethylacrylamide and silver nitrate. Contact lenses of all combinations showed flexible and soft characteristics after being hydrated for 24 hrs in standard saline solution. The changes in color (from pale yellow to pale brown) of each material are shown and compared in Fig. 1. Also, the AFM images and XPS spectrum of the produced contact lens samples are shown in Figs. 2 and 3.

2. Water Content Measurement

The water content was measured by using the gravimetric method to assess the water content of the produced macromolecule. The water content of Ref. without $AgNO_3$ and N,N-dimethylacrylamide is measured to be 39.40%. Ag-1 (with approximately 1% of $AgNO_3$) showed average water content of 37.51%, indicating that $AgNO_3$ reduces the water content. The mean water content of AgDMA-1 where N,N-dimethylacrylamide was added for each ratios was 36.63%, while the water content of AgDMA-3, AgDMA-6, AgDMA-7 and AgDMA-10 was 38.54%, 40.77%, 42.74% and 44.45%, respectively. The increase of N,N-dimethylacrylamide showed to be proportionally associated with the increase in water content. A comparison of the changes in water content of each combination is shown in Fig. 4.

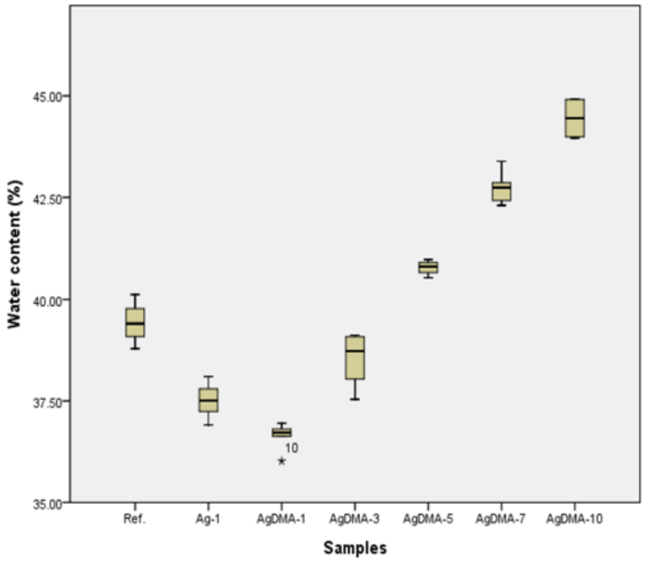

Fig. 4. Effect of $AgNO_3$ and N,N-dimethylacrylamide on water contents.

3. Refractive Index Measurement

Measurements of the refractive index of each sample showed that the refractive index of Ref. where $AgNO_3$ and N,N-dimethylacrylamide were not added is 1.431, while that of Ag-1 where approximately 1% $AgNO_3$ was added is 1.434, which indicates that $AgNO_3$ increases the refractive index. Meanwhile, the refractive indexes for AgDMA-1, AgDMA-3, AgDMA-5, AgDMA-7 and AgDMA-10 where N,N-dimethylacrylamide were added at each ratio were 1.434, 1.435, 1.430, 1.427 and 1.423, respectively. In general, the increase in N,N-dimethylacrylamide showed to be proportionally associated with the decrease in refractive index. The refractive index generally changes reciprocal to water content, and all combinations showed an identical tendency. The changes in refractive index for each refractive index and water content of each combination are shown in Fig. 5.

4. Optical Transmittance Measurement

The optical transmittance of Ref. for UV-B, UV-A and visual light was 82.25%, 87.50% and 91.00%, respectively. This satisfies the requirements for visual light transmittance in general contact lenses, although these measurements show that the material was

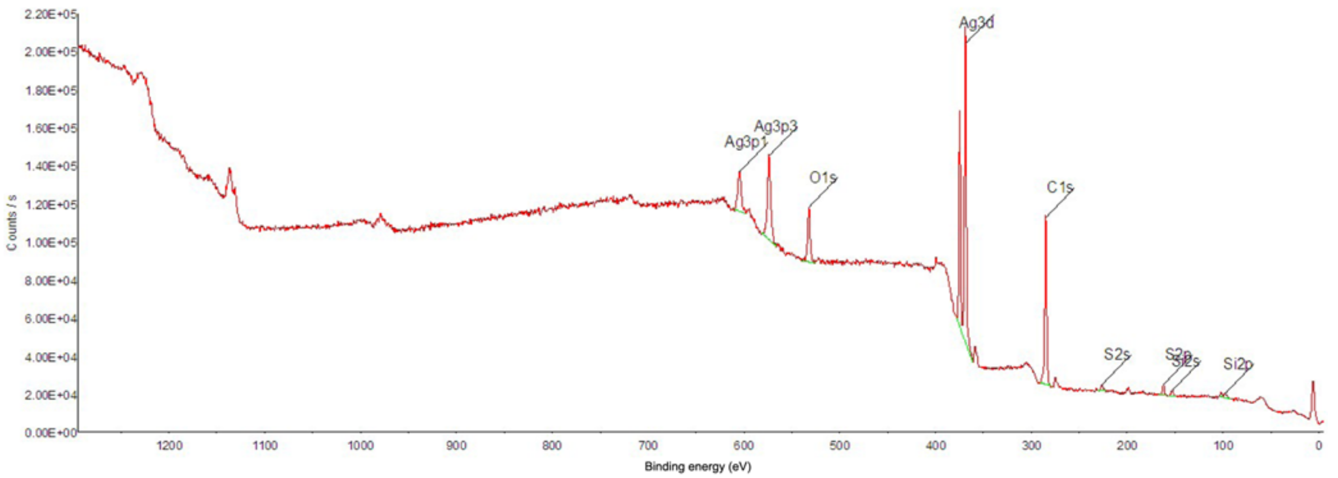

Fig. 3. XPS spectrum of manufactured contact lens.

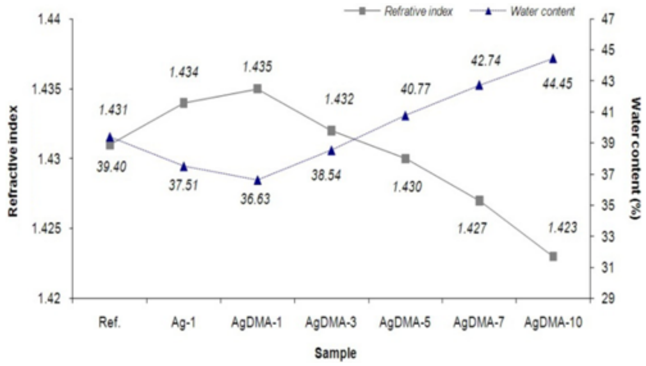

Fig. 5. Change of refractive index with water content of samples.

Table 2. Optical transmittance of samples

Sample	UV-B (%)	UV-A (%)	Visible (%)
Ref.	82.25	87.50	91.00
Ag-1	72.55	77.50	78.25
AgDMA-1	70.75	73.75	74.50
AgDMA-3	64.00	71.50	72.25
AgDMA-5	58.25	68.25	70.25
AgDMA-7	55.75	64.00	65.00
AgDMA-10	53.25	65.50	63.25

not able to block ultraviolet wavelengths of UV-B and UV-A. Meanwhile, Ag-1 where approximately 1% $AgNO_3$ was added showed optical transmittance of 72.55%, 77.50% and 78.25% for UV-B, UV-A and visual light, respectively. Although the lens failed in blocking UV light, it exhibited a very low transmittance for wavelengths below 300 nm. The drop in overall transmittance for visual light is estimated to have been caused by the reduced transmittance for 200 nm and 500 nm wavelengths due to the color of the lens. In general, the optical transmittance showed to decrease as the ratio of N,N-dimethylacrylamide increased, which is estimated to be caused by the decrease in transmittance in all wavelengths as the color of the lens becomes thicker. The optical transmittance of all combinations is shown in Table 2, while the optical transmittance of each sample where N,N-dimethylacrylamide were added by 1%, 5% and 7% are compared with that of the Ref. where approximately 10% N,N-dimethylacrylamide was added is shown in Fig. 6.

5. Oxygen Permeability (Dk) Measurement

The oxygen permeability (Dk), which is a unique characteristic of a material, was calculated with consideration of the measured central thickness of the lens, and the results show that the oxygen permeability of Ref. which does not contain $AgNO_3$ and N,N-di-

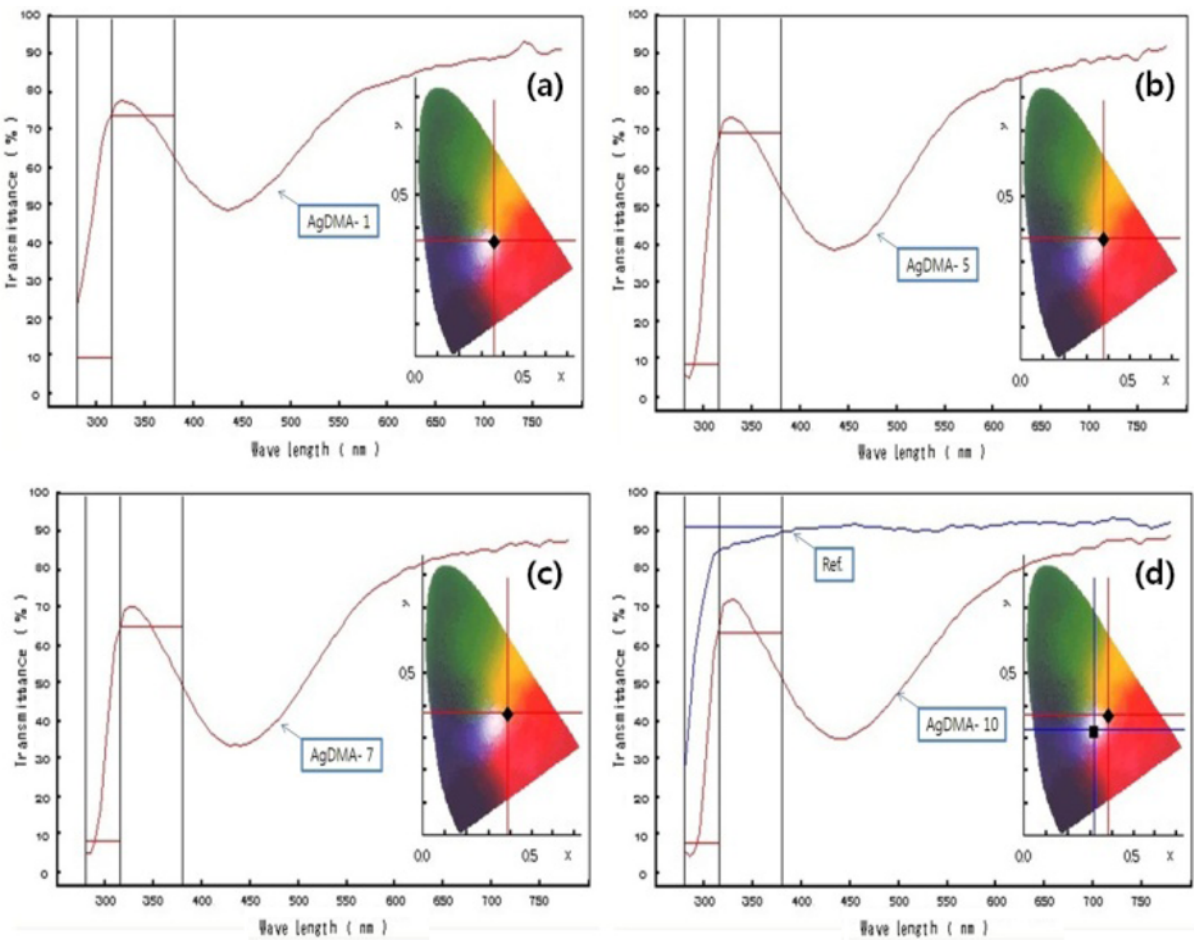

Fig. 6. Optical transmittance of samples. (a) AgDMA-1, (b) AgDMA-5, (c) AgDMA-7, (d) Ref. and AgDMA-10.

Table 3. Oxygen permeability of samples

Sample	Central thickness (μm)	Current (nA)	Oxygen Transmissibility (Dk/t)[a]	Oxygen permeability (Dk)[b]
Ref.	0.284	1.62	4.8114	13.66438
Ag-1	0.252	1.42	4.2174	10.62785
AgDMA-1	0.290	1.54	4.5738	13.26402
AgDMA-3	0.259	1.88	5.5836	14.46152
AgDMA-5	0.289	1.82	5.4054	15.62161
AgDMA-7	0.243	2.33	6.9201	16.81584
AgDMA-10	0.259	2.45	7.2765	18.84614

[a]Dk/t: $\times 10^{-9}$ (cm/sec)(mlO_2/ml$\times$mmHg)
[b]Dk: $\times 10^{-11}$ (cm^2/sec)(mlO_2/ml$\times$mmHg)

methylacrylamide is 13.66×10^{-11} (cm^2/sec)(mlO_2/ml×mmHg), which is similar to that of general hydrogel contact lens. In general, the oxygen permeability (Dk) increased proportionally with the increase in N,N-dimethylacrylamide, which is estimated to have been affected by the increase in water content. However, in cases with AgDMA-1 and AgDMA-3, the water content was lower than that of Ref., although the oxygen permeability was similar or higher, which indicates that N,N-dimethylacrylamide increases oxygen permeability. The oxygen permeability of each combination is summarized in Table 3.

6. Changes in N,N-dimethylacrylamide with Adding Silver Nanoparticles

The physical properties of DA-1, DA-3, DA-5 and DA-10 that do not contain $AgNO_3$, although having identical composition as AgDMA-1, AgDMA-3, AgDMA-5 and AgDMA-10, were investigated in order to compare the effects of the macromolecules produced with silver nanoparticles. The average water content of DA-1, DA-3, DA-5 and DA-10 was determined to be 38.23%, 36.78%, 39.63% and 42.05%, respectively [18]. In general, the increase in

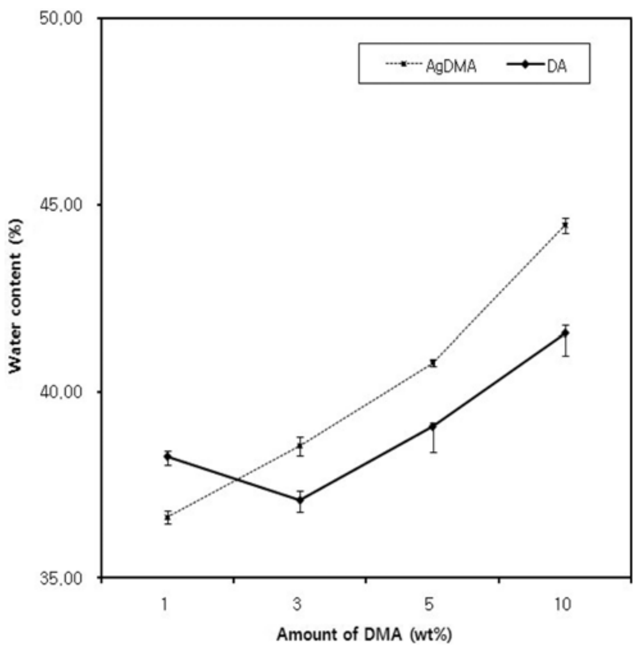

Fig. 7. Effect of N,N-dimethylacrylamide on water content.

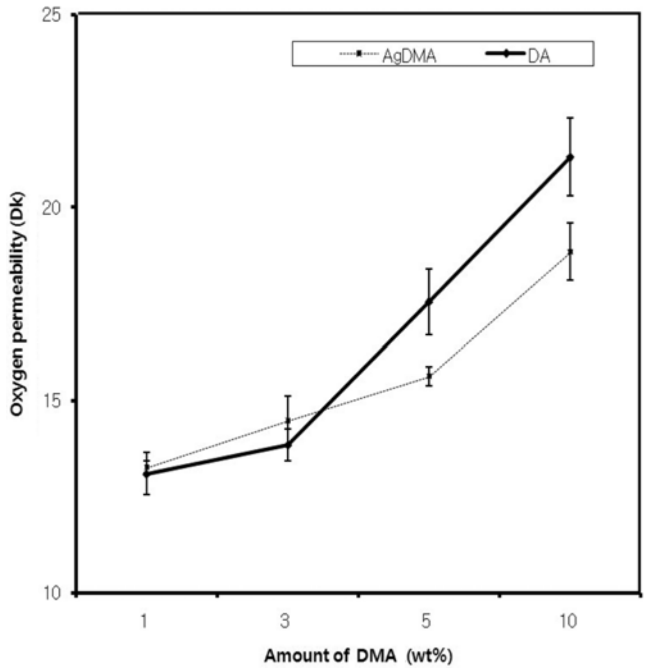

Fig. 8. Effect of N,N-dimethylacrylamide on oxygen permeability.

N,N-dimethylacrylamide was associated with the increase in water content. Meanwhile, the oxygen permeability was found to be 13.093 $\times10^{-11}$, 13.830×10^{-11}, 17.535×10^{-11}, and 21.288×10^{-11} (cm^2/sec) (mlO_2/ml×mmHg), respectively, for DA-1, DA-3, DA-5 and DA-10 which do not contain $AgNO_3$ [18], showing that oxygen permeability (Dk) significantly increases as the ratio of DMA increases. The combinations added with silver nanoparticles showed to have lower Dk when N,N-dimethylacrylamide was added at the same ratio. This indicates that the Dk is low even when the water content is higher because of silver nanoparticles mitigating oxygen transport. The changes in water content and oxygen permeability upon the addition of silver nanoparticles and the ratio of N,N-dimethylacrylamide are shown in Figs. 7 and 8.

CONCLUSION

High functional ophthalmic lens materials, poly(HEMA-*co*-MMA)s, were prepared by the copolymerization of HEMA, MMA, NVP, EDGMA, and N,N-dimethylacrylamide in the presence of silver nanoparticles. The water content was in the range of 36.63-44.45%, indicating the characteristics of general water-content contact lenses, and the refractive index was measured to be in the range of 1.423-1.435. Meanwhile, the oxygen transmissibility ranged from 10.63×10^{-11} to 18.85×10^{-11} (cm^2/sec)(mlO_2/ml×mmHg) increasing with increasing the addition ratio of N,N-dimethylacrylamide. The polymeric materials satisfied the basic characteristics required for contact lenses. Furthermore, the polymers have antimicrobial properties and excellent oxygen permeability.

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