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Study on the Novel Materials Containing Nanoparticles and Isocyanate Group for Strength Improvement of Hydrogel Ophthalmic Lens

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Abstract

This study was planned to prepare the high strength hydrogel ophthalmic lens containing isocyanate group and nanoparticles. HDI with carbon nanoparticles were used as additives for the basic combination of HEMA, MA and MMA, and the materials were copolymerized with EGDMA as the cross-linking agent and AIBN as the initiator. The mixture was heated at 100°C for an hour to produce the high performance hydrogel ophthalmic lens by cast mold method. Measurement of the physical characteristics of the produced material showed that the refractive index was in the range of 1.4027~1.4600, water content 25.21~44.01%, contact angle 54.18~72.94°, visible light transmittance 53.03~92.09%, and tensile strength 0.1024~0.2359 kgf and breaking strength was 0.0872~0.2825 kgf. The results showed an increase of refractive index while the decrease in water content. And also, the breaking strength was highest when the addition ratio of HDI was 5%(wt). As a result of the absorbance measurement, no significant difference was observed in all the samples, so it can be judged that the stabilization of nanoparticles in the polymer was maintained.

Keywords: Carbon Nanoparticles, Hexamethylene Diisocyanate, Tensile Strength, Breaking Strength, Light Transmittance

1. Introduction

The hydrogel for ophthalmic lenses is a hydrophilic polymer manufactured mainly by adding a crosslinking agent to a monomer, and can contain water molecular up to several thousand times as much as the weight of a hydrogel in a dry state. Hydrogels are widely applied to products such as eye drops and soft lenses, as well as biomaterials and drug release media. A hydrogel lens has been developed by copolymerizing molecules such as AA (acrylic acid), NVP (N-vinylpyrrolidone), MMA (methyl methacrylate), and MA (methacrylic acid) with HEMA (2-hydroxyethyl methacrylate), a material of the conventional soft ophthalmic lenses[1-3]. Siloxane-based hydrogel materials, which increase the oxygen permeability and maintain the comfortable fit of the conventional HEMA lenses, have been developed of late[4]. These materials played a major role in reducing the refusal to wear ophthalmic lenses by improving the fit condition while satisfying the wettability, flexibility, and water content requirements as well as allowing the lens to have durability, which led to the popularization of ophthalmic hydrophilic lenses. To evaluate the fit condition, the wettability is mainly assessed by measuring the contact angle[5]. The overall wettability of the material is important because the ophthalmic lens becomes placed on the tear film surface when the lens is already worn out[6]. It is known that ophthalmic lenses have different surface treatment methods by manufacturing method, and there is a difference in surface roughness or coloration by part even in the same lens. In other words, the properties of the interface that is the surface of the hydrogel lens are known to affect the physical properties of the hydrogel lens[7-9]. Therefore, attempts to improve the biocompatibility of lenses through surface modification in the production of ophthalmic lenses have been made[10]. The forces exerted by the repeated wearing and removal as well as the persistent blinking of the eyes cause shape changes and rupture of the ophthalmic lens hydrogel. Also, in the long term, this may result in a non-smooth surface, thereby making the lens lose its fundamental optical correction function and producing serious side effects on the cornea[11-13]. The development of ophthalmic lens materials has been consistently attempted to reduce

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these side effects and foreign body sensation. The most basic properties that ophthalmic lenses should have are comfortable fit and wettability, which greatly affect the ophthalmic side effects. Ophthalmic lenses can be evaluated based on their basic physical and optical properties, such as their water content, light transmittance, wettability, and oxygen permeability. The property of maintaining the tear layer as a primary requirement of the lens for the physiological adaptation of the eye is called "wettability." To improve the wettability, a method of increasing the water content is mainly used, which causes problems such as reduction of the refractive index and strength[14]. Moreover, a method of making the lens as thin as possible is being tried to improve the fit of the lens and to allow oxygen to easily pass through the lens to the cornea, but a thin lens may have decreased durability[15]. The durability of ophthalmic lenses can be evaluated based on the tensile and breaking strengths. In general, the tensile strength and water content are inversely proportional to each other; as such, research on materials that increase the tensile strength and wettability while minimizing the changes in the water content has been actively conducted. The modulus that explains the strength of the lens is the force per unit area required to create deformation. It is an important factor in evaluating the properties of ophthalmic lens materials. A lens with a high modulus is better in shape maintenance and handling than a conventional hydrogel lens, but it has the disadvantage of discomfort when first worn because it causes the eye to feel very dry. Therefore, research is needed to improve the durability while maintaining the lens thickness. Carbon nanoparticles have no cytotoxicity and have excellent impact and abrasion resistance due to their excellent physical and chemical properties, thereby enhancing the strength and elasticity. Furthermore, it is known that the wettability level of the material can be changed according to the chemical composition of the carbon surface. The roughness of the carbon surface is also known to greatly influence the wettability of the material; thus, the wettability can be improved through various surface treatments[16-18]. The isocyanate material that was used in this experiment is known to increase the degree of crosslinking and to improve the mechanical properties when it reacts with polyuria; thus, it is widely used as an adhesive, a hardener, and the like. In particular, HDI (hexamethylene diisocyanate) with two NCO groups tends to react easily with compounds that have active hydrogen atoms, and is used in various industries as a dental material, ophthalmic lens, and medical adsorbent[19]. This study thus considered that HDI containing carbon nanoparticles can be added to the hydrophilic monomer to increase the strength and durability and simultaneously increase the surface modification and wettability.

2. Experiment Details

2.1. Polymerization and Manufacturing

Copolymerization was done with HEMA used as a base material for hydrogel lenses; EGDMA (ethylene glycol dimethacrylate), a crosslinking agent; and AIBN (azobisisobutyronitrile), an initiating agent. Additionally, MA, a material showing hydrophilic characteristics, and MMA, which improves the strength, were utilized. The HEMA and AIBN used in the experiment were manufactured by JUNSEI while the EGDMA, HDI, and carbon nanoparticles (mesoporous, nanopowder, <500 nm) were manufactured by Sigma-Aldrich. The HEMA, EGDMA, AIBN, MA, and MMA samples were mixed at different ratios and were stirred with a stirrer (Vortex GENIE 2, Scientific Industries, USA) for about 1 hour. After that, additives were added at different ratios, and the samples were then stirred for about 1 hour. Then carbon nanoparticles were added, after which the samples were again stirred for about 1 hour using an ultrasonic stirrer. The ophthalmic lens was prepared through the cast molding method and was thermally polymerized at 100°C for 1 hour. The refractive index, water content, contact angle, light transmittance, and tensile and breaking strengths of the lens were measured after immersing the polymerized samples in a 0.9% normal saline solution for 24 hours. The molecular formula of HDI, which was used as an additive, is shown in Fig. 1, and the schematic diagram of the polymerization method is shown in Fig. 2.

To come up with a Ref., MA, MMA, EGDMA, and AIBN were added to HEMA, the base material for the hydrogel ophthalmic lenses. HDI was added to the Ref. at 1, 3, and 5% ratios, and the lenses were named HDI1, HDI3, and HDI5, respectively. In addition, polymeriza-

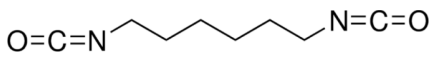


Fig. 1. Chemical structure of Hexamethylene diisocyanate.

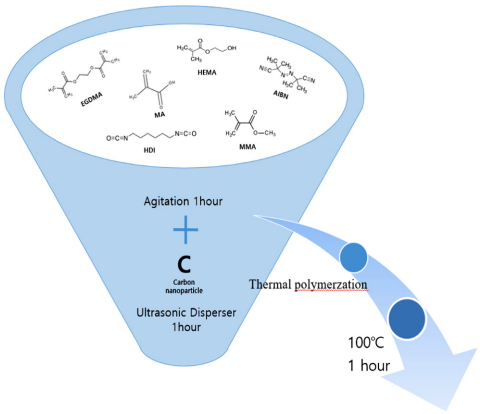


Fig 2. Schematic image of manufacturing method.

tion was done by adding carbon nanoparticles at 0.1 and 0.2% ratios to each of the HDI1, HDI3, and HDI5 combinations. The lenses were named H1C1, H1C2, H3C1, H3C2, H5C1, and H5C2, respectively. The mixing ratios of the samples are shown in Table 1.

2.2. Methods (Instruments and Analysis)

The refractive indices of the prepared hydrophilic hydrogel lenses were measured based on ISO 18396-4:2006 using an ABBE refractometer (ATAGO DR-A1, Japan). The water content was measured based on ISO 1869-4:2006 using the gravimetric method. The weights of the dried and water-containing samples were measured using an electronic balance (XS205 Dual-Range, METTLER TOLEDO) and were then calculated using the corresponding calculation formula. The wettability levels of the prepared lenses were evaluated by measuring the contact angles with a contact angle instrument (DSA30, Kruss GMBH). To determine the spectral transmittance, a spectral transmittance meter (Cary 60 UV-vis, Agilent) was used, and the transmittance was measured 5 times each for the UV-B, UV-A, and visible light areas, after which the percentage values were averaged. The tensile and breaking strengths were measured using a universal testing machine (UTM; AGS-X, Shimadzu), and the roughness of the lens surface was analyzed using an atomic force microscope (AFM; XE-100, Park Systems). The degrees of polymerization of the prepared lenses were evaluated using an absorbance meter (Rainbow Light, UVLS-1000).

3. Results and Discussion

3.1. Polymerization

To investigate the stability of polymerization of the prepared lenses, the absorbance of the immersion solution for each sample was measured by wavelength band. The results showed that the absorbance at 214 nm was in the -0.0666-0.0041 OD range, and there were no differences among all the samples. The absorbance was in the -0.0323-0.0411 OD range at 240 nm, and in the 0.0214-0.0698 OD range at 346 nm, but it was reduced according to the carbon nanoparticle content. Therefore, it is considered that the degree of polymerization was higher in H5C2 than in HDI5 and H5C1. The absorbance at 645 nm was in the 0.0029-0.0415 OD range and slightly increased according to the additive. As a result of this experiment, it is considered that the use of an additive will not greatly influence the hydrogel lens polymerization because the difference in the absorbance

Table 1. Percent composition of samples (Unit: wt%)

Sample	HEMA	MA	MMA	EGDMA	AIBN	HDI	Carbon	Total
Ref.	92.85	4.64	1.86	0.46	0.19	-	-	100.00
HDI1	91.93	4.60	1.84	0.46	0.19	0.99	-	100.00
HDI3	90.15	4.51	1.80	0.45	0.18	2.91	-	100.00
HDI5	88.43	4.42	1.77	0.44	0.18	4.76	-	100.00
H1C1	91.84	4.59	1.84	0.46	0.18	0.99	0.10	100.00
H3C1	90.06	4.50	1.80	0.45	0.18	2.91	0.10	100.00
H5C1	88.34	4.42	1.77	0.44	0.18	4.76	0.10	100.00
H1C2	91.75	4.59	1.83	0.46	0.18	0.99	0.20	100.00
H3C2	89.97	4.50	1.80	0.45	0.18	2.91	0.20	100.00
H5C2	88.25	4.41	1.77	0.44	0.18	4.75	0.20	100.00

Table 2. Absorbance of immersion solution for sample (Unit: OD)

Sample	Peak Wavelength (nm)			
	214	240	346	645
Ref.	-0.027	-0.0038	0.0698	0.0029
HDI5	-0.0666	0.0411	0.0383	0.0148
H5C1	0.0041	0.0359	0.0222	0.0398
H5C2	-0.0222	-0.0323	0.0214	0.0415

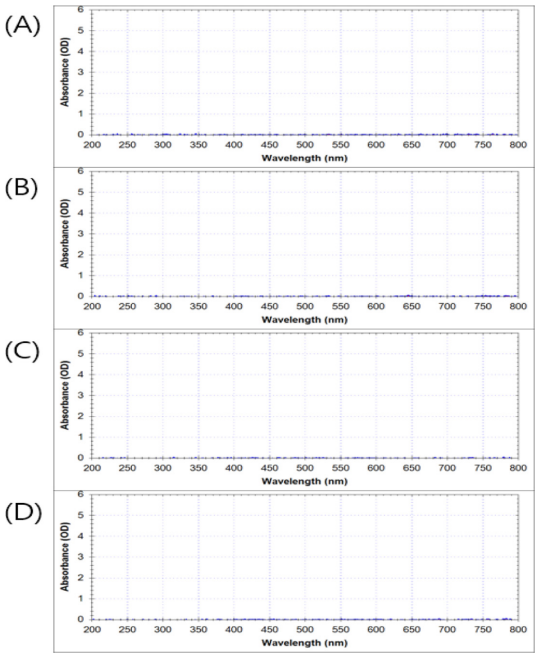


Fig. 3. Absorbance image of samples; [(A) Ref., (B) HDI5, (C) H5C1, (D)H5C2].

by wavelength band will be insignificant. The absorbance values of the immersion solutions for all the samples are shown in Table 2 and Fig. 3.

3.2. Physical Property

3.2.1. Refractive Index and Water Content

The refractive index of the Ref. without any additive was determined to be 1.4027. The average refractive indices of the samples prepared by adding HDI at 1-5% ratios to the Ref. were measured to be in the 1.4167-1.4473 range. Also, in the case of the samples prepared using 0.1% carbon nanoparticles as an additive for HDI1, HDI3, and HDI5, the refractive index ranged from 1.4178 to 1.4551. In the case of the samples prepared using 0.2% carbon nanoparticles as an additive, it ranged from 1.4186 to 1.4556. The water content measurement showed that the average water content of the Ref. was 44.01%, and that the average water content of the combinations prepared by adding HDI at a 1-5% ratio ranged from 40.06 to 27.81%. Also, in the case of the combinations prepared using 0.1% carbon nanoparticles as an additive for HDI1, HDI3, and HDI5, the average water content ranged from 39.78 to 25.76%. In the case of the combinations prepared using 0.2% carbon nanoparticles as an additive, the average water content ranged from 39.19 to 25.21%. These results showed that the refractive index increases and the water content decreases according to the amount of HDI and carbon nanoparticles added in all the combinations. It is considered that HDI improved the physical properties of the lens samples by working as a crosslinking agent, and that the hydrophobicity of the carbon nanoparticles reduced the water content of the prepared hydrogel ophthalmic lens. In addition, the decrease of the water content is considered to have led to the increase of the refractive index. The changes in the refractive index and water content of each combination are presented in Fig. 4-5.

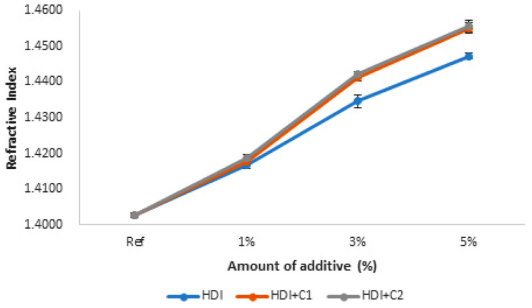


Fig. 4. Refractive index of samples.

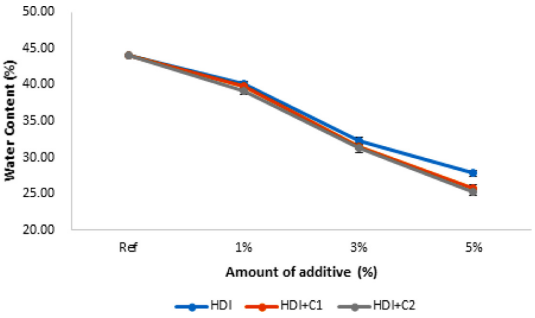
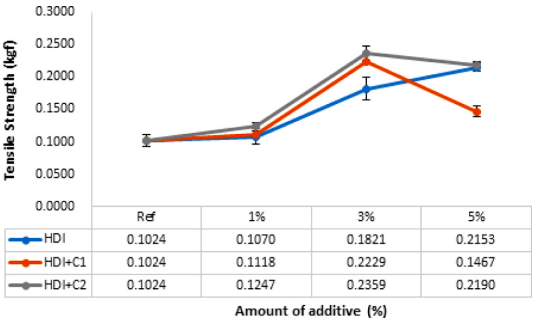


Fig. 5. Water content of samples.

3.2.2. Tensile and Breaking Strengths

The average tensile strength of the Ref. without any additive was 0.1024 kgf, and those of the combinations prepared by adding HDI at a 1-5% ratio to the Ref. ranged from 0.1070 to 0.2153 kgf. The average tensile strength of the combinations prepared by adding carbon nanoparticles at a 0.1-0.2% ratio to the HDI combinations was in the 0.1118-0.2359 kgf. The average breaking strength of the Ref. without any additive was 0.0872 kgf, and those of the combinations prepared by adding HDI at a 1-5% ratio to the Ref. ranged from 0.1142 to 0.2498 kgf. Also, the average breaking strength of the combinations prepared by adding carbon nanoparticles at a 0.1-0.2% ratio to the HDI combinations were found in the 0.1350-0.2825 kgf range. As the addition ratio of HDI increased, both the tensile and breaking strengths increased. In particular, when HDI and carbon nanoparticles were simultaneously added, the strength of the lens greatly increased due to the synergistic effect. In the case where both additives were used simultaneously, the tensile strength was highest at 3% HDI and decreased as the amount of HDI added increased, suggesting that the excessive HDI did not polymerize uniformly with the carbon nanoparticles. The results showed that the lens can have the optimal strength when HDI and carbon nanoparticles are polymerized at an appropriate ratio. The tensile and breaking strengths of all the sample combinations are shown in Fig. 6-9.



	Ref	1%	3%	5%
HDI	0.1024	0.1070	0.1821	0.2153
HDI+C1	0.1024	0.1118	0.2229	0.1467
HDI+C2	0.1024	0.1247	0.2359	0.2190

Fig. 6. Tensile strength distributions of samples.

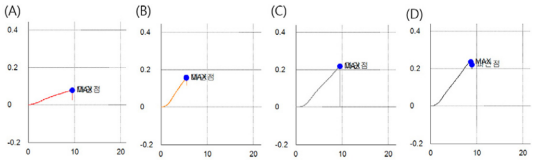
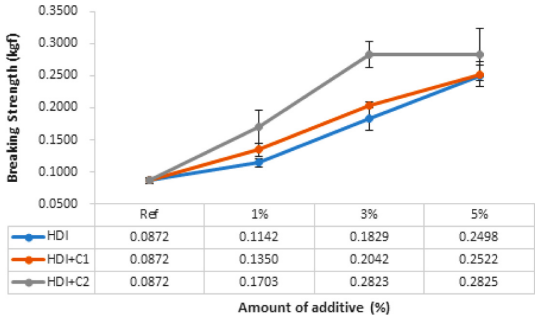


Fig. 7. Tensile strength image of samples; [(A) Ref., (B) HDI3, (C) H3C1, (D) H3C2].



	Ref	1%	3%	5%
HDI	0.0872	0.1142	0.1829	0.2498
HDI+C1	0.0872	0.1350	0.2042	0.2522
HDI+C2	0.0872	0.1703	0.2823	0.2825

Fig. 8. Breaking strength distribution of samples.

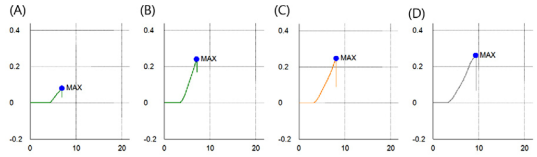


Fig. 9. Breaking strength image of samples; [(A) Ref., (B) HDI5, (C) H5C1, (D) H5C2].

3.3. Optical Property

The transmittance values of the Ref. for the UV-B, UV-A, and visible light was 51.26, 77.76, and 85.57%, respectively. The light transmittance measurement results according to the added amount of HDI were 60.61-60.94% for the UV-B area, 85.57-87.76% for the UV-A area, and 91.16-92.09% for the visible light area. For the combinations prepared using 0.1% carbon nanoparticles as an additive, the transmittance was in the 35.21-39.70% range for the UV-B area, 49.21-58.21% for the UV-A area, and 60.13-63.49% for the visible light area. For the combinations prepared using 0.2% carbon nanoparticles as an additive, the transmittance was in the 33.09-34.86% range for the UV-B area, 46.29-47.02% for the UV-A area, and 53.03-54.21% for the visible light area. The addition of HDI was found to improve the overall light transmittance, and the transmittance increased according to the amount added. Therefore, it is considered that HDI can be used as an additive to make ophthalmic lens materials optically excellent, thereby enhancing the contrast sensitivity. Moreover, the carbon nanoparticles showed the effect of coloring the prepared lens gray; thus, they can be applied to colored lenses. The light transmittance values

Table 3. Optical transmittance of samples

(Unit: %)

Sample	UV-B	UV-A	Vis.
Ref.	51.26	77.76	85.57
HDI1	60.61	85.57	91.16
HDI3	60.68	85.90	91.50
HDI5	60.94	87.76	92.09
H1C1	35.21	49.21	60.13
H3C1	38.38	56.33	62.61
H5C1	39.70	58.21	63.49
H1C2	33.09	46.29	53.03
H3C2	33.79	46.98	53.40
H5C2	34.86	47.02	54.21

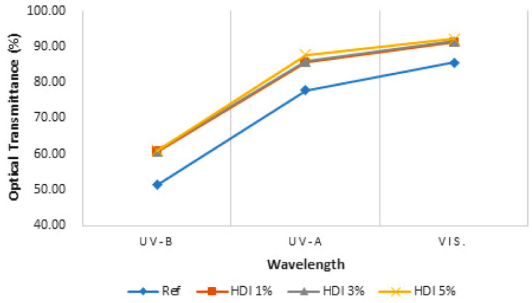


Fig. 10. Optical transmittance distribution of samples.

of all the combinations are shown in Table 3 and Fig. 10.

3.4. Surface Analysis

The contact angles were measured using the sessile drop method to evaluate the wettability of the prepared lenses. As a result, the contact angle of the Ref. was 63.05°, and the average contact angle of the combinations prepared by adding HDI at a 1-5% ratio ranged from 69.45 to 72.58°. For the combinations prepared using 0.1% carbon nanoparticles as an additive (HDI1, HDI3, and HDI5), it was measured in the 69.38-72.94° range. For the combinations prepared using 0.2% carbon nanoparticles as an additive (HDI1, HDI3, and HDI5), it was measured in the 54.18-61.51° range. In addition, the results of the AFM measurement for the analysis of the lens surface showed that the particle size of the Ref. without any additive ranged from 8.817 to 21.072 nm, and the average roughness was 1.501 nm. In the case of HDI5, the particle size was distributed in the 32.218-57.158 nm range, and the average roughness

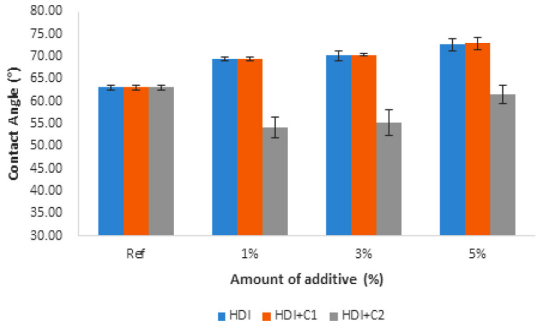


Fig. 11. Contact angle distribution of samples.

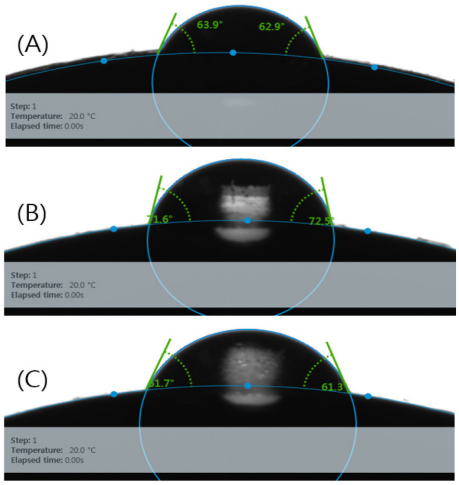


Fig. 12. Contact angle image of samples.; [(A) Ref., (B) HDI5, (C) H5C2].

was 8.068 nm. In the case of H5C2 prepared by adding 0.2% carbon nanoparticles to HDI5, the particle size was distributed in the 6.552-11.768 nm range, and the average roughness was 2.923 nm. As the ratio of HDI increased, the wettability decreased, and the addition of 0.1% carbon nanoparticles did not have a great effect on the wettability. When the amount added was increased to 0.2%, however, the wettability was greatly improved. It is considered that the wettability is increased when a certain amount (or more) of carbon nanoparticles is added. It is known that the contact angle may change depending on the various factors affecting the wettability of the lens, such as the hydrophobicity of the material, the surface energy, and the surface roughness. The AFM analysis result for the average surface roughness showed that when HDI is added, the surface of the lens becomes rougher, resulting in a higher roughness value.

Table 4. Surface roughness of samples by AFM analysis (Unit: nm)

	Sample		
	Ref.	HDI5	H5C2
Roughness	1.501	8.068	2.923

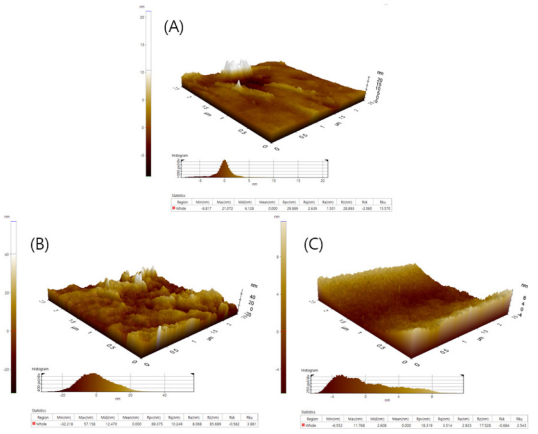


Fig. 13. AFM image of samples; [(A) Ref., (B) HDI5, (C) H5C2].

When carbon nanoparticles are added, however, homogeneous polymerization is achieved, and the wettability is increased due to the reduction of the surface roughness value. The contact angle changes and AFM measurement results for each group are presented in Table 4 and Fig. 11-13.

4. Conclusion

This study aimed to manufacture a high-wettability and high-strength ophthalmic lens by adding HDI and carbon nanoparticles at various ratios into the basic-combination Ref. prepared using HEMA, a base polymer used as a material for hydrophilic ophthalmic lenses; EGDMA, a crosslinking agent; and AIBN, an initiator. To increase the strength and wettability of the lens, HDI and carbon nanoparticles were added at various ratios, and the physical properties (i.e., refractive index, water content, contact angle, light transmittance, tensile strength, breaking strength, and absorbance) were measured. When HDI and carbon nanoparticles were added, the water content decreased but the tensile and breaking strengths increased, along with the wettability, according to the carbon nanoparticle addition ratio. In particular, when two additives were used together, the strength increased due to the interaction between the HDI and carbon nanoparticles. Therefore, carbon nanoparticles with no cytotoxicity and excellent impact resistance can be used as a high-performance ophthalmic lens material when an additive such as HDI with a crosslinking property and thus with the capacity to improve the mechanical properties is added to hydrogel lens materials.

Acknowledgments

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