

Preparation and characterization of ophthalmic polymers containing silicon nanoparticles

A-Young Sung*[†] and Tae-Hun Kim**

*Department of Ophthalmic Optics, Sehan University, Jeonnam 526-702, Korea
**Department of Visual Optics, Baekseok University, Chungnam 330-704, Korea
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Abstract—HEMA, MMA, NVP, EDGMA, and 3-vinylanisole were copolymerized with Si nanoparticles and silicon 2,3-naphthalocyanine bis (trihexylsilyloxi) for ophthalmic application. The physical, optical, and surface characteristics of the contact lens copolymers were investigated to examine the usefulness of the above nanomaterials as components for contact lenses. The water content and the refractive index were in the range of 26.03-37.61% and 1.435-1.479, respectively. Meanwhile, the tensile strength ranging from 0.156 to 0.802 kgf increased with increasing the addition ratio of 3-vinylanisole. Si nanoparticles reduce spectral transmittance in all wavelengths, whereas for silicon 2,3-naphthalocyanine bis (trihexylsilyloxi) the transmittance of visual light increased but the transmittance of UV and near infrared decreased. High contact angle was observed for contact lenses containing both Si nanopowder and silicon 2,3-naphthalocyanine bis (trihexylsilyloxi). The water content of contact lenses was not significantly affected by the addition of 3-vinylanisole. Nanomaterials such as Si nanoparticles and silicon 2,3-naphthalocyanine bis (trihexylsilyloxi) can be used for manufacturing hydrogel soft contact lenses with UV-blocking capabilities if the intensity and the wettability of the surface are properly controlled.

Key words: Silicon Nanoparticle, 3-Vinylanisole, Wettability, Contact Angle, Antimicrobial Property

INTRODUCTION

Nanotechnology is rapidly growing for everyday use. Due to size-related effects (i.e., quantum effects), nanostructured materials show unique electric, magnetic, and optical properties. Nanostructured materials in particular have anti-bacterial properties which make them very useful for medical purposes. Studies are actively being carried out on the application of nanomaterials for contact lenses because of their anti-bacterial properties [1-3]. The physiological characteristics of contact lens are very important because such ophthalmic materials come in direct contact with the cornea. The eye, easily exposed to bacteria due to its high humidity and proper temperature, is composed of many neurons and various types of fibers. Since ophthalmologic diseases occur acutely and frequently, the prevalence of ophthalmologic disorders caused by adverse contamination to contact lenses is increasing. Hart et al. [4] reported that 35% of soft contact lenses worn by people are contaminated with bacteria: *E. coli*, fungi, and *pseudomonas aeruginosa*. Among them, staphylococci are the most common bacterial pathogens related to the eye that can cause fungal corneal ulcer, *pseudomonas* corneal ulcer, acute catarrhal conjunctivitis, and chronic bacterial conjunctivitis [5-7]. Therefore, various studies are being carried out on metal nanoparticles such as gold, silver, and platinum with anti-bacterial properties that can be used in contact lenses that can minimize the risk of ophthalmologic complications [8-10].

Although studies are actively being conducted on contact lens materials based on nanotechnology with anti-bacterial properties, there is a lack of studies up to date on the changes in the physical and optical characteristics and surface characteristics that are unique

to nanomaterials.

Among the surface characteristics of contact lenses, wettability determines the wetting properties of the surface of contact lenses. It is the primary condition for the maintenance of the tear layer and the eye's adaptation of eye physiology and is the most important physiologic characteristic for a contact lens [11,12]. UV permeability, an optical characteristic of contact lenses, is a major factor related to ophthalmologic disorders and can cause damage to the cornea, retina, and lens [13,14]. Each type of nanostructured material can absorb light of certain wavelengths, which allows such materials to be used as UV-blocking materials for contact lenses. Since nanomaterials change the surface characteristics of the contact lens, the wettability of the contact lens material is subject to change, meaning that nanostructure materials can be used to improve the wettability of contact lenses.

Si nanoparticles are used in various fields such as solid state lighting, lasers, and microelectronics biological tags [15], and silicon 2,3-naphthalocyanine bis (trihexylsilyloxi) is recently gaining attention as a functional pigment that absorbs lights of certain wavelengths [16]. Here we report the copolymerization of 2-hydroxyethyl methacrylate, N-vinyl-2-pyrrolidone, methyl methacrylate, 3-vinyl anisol, and ethylene glycol dimethacrylate, which are commonly used materials to produce contact lenses, along with Si nanoparticles and silicon 2,3-naphthalocyanine.

The physical, optical, and surface characteristics of the contact lens copolymers were also analyzed to investigate the usefulness of the above nanomaterials as components for contact lenses.

EXPERIMENTAL SECTION

1. Reagents and Materials

HEMA (2-hydroxyethyl methacrylate) MMA (methyl methacry-

[†]To whom correspondence should be addressed.
E-mail: say@db.ac.kr

late) and AIBN (azobisisobutyronitrile) were purchased from JUNSEI while NVP (n-vinyl pyrrolidone), 3-VA (3-vinylanisole), EGDMA (ethylene glycol dimethacrylate), silicon nanoparticles (<100 nm particle size), and SiNc [silicon 2,3-naphthalocyanine bis (trihexylsilyloxiide)] were purchased from Sigma-Aldrich. They were used without further purification.

2. Copolymerization

HEMA, NVP, MMA, and the cross-linking agent EGDMA were determined to be used as the basic combination to copolymerize the materials used in this study to produce a soft hydrogel contact lens.

Each reagent was mixed and stirred for approximately 30 mins, and the reference sample was copolymerized with this combination. The concentration of 3-vinylanisole was diversified from 1% to 10%. Each concentration was mixed for approximately 30 mins to copolymerize the 3VA-1, 3VA-3, 3VA-5, 3VA-7 and 3VA-10 samples. 1% each of silicon nanoparticles and SiNc were added to this combination, and then the samples were dispersed for approximately 1 hr in an ultrasonic benchtop cleaner (Branson 2510) to copolymerize the 3VA_Si combination and 3VA_SN combination. The mixture ratios of each combination used in this study are summarized in Table 1.

The cast mould method for the thermal copolymerization was used to fabricate the contact lens. The monomers, stirred for the thermal copolymerization, were charged in a mould, and then the mixture was heated at 0-80 °C for 1 hr 30 mins and 100 °C for 40 mins to produce the contact lens. The copolymerized contact lens was then removed from the mould and stored in a 0.9% NaCl normal saline for 24 hrs.

3. Instruments and Analysis

All contact lenses that were used in this study were stored in a standard normal saline solution (0.9% NaCl solution) for at least 24 hrs before measurements were taken and were put in the experi-

ment temperature (room temperature) for at least 2 hrs to reach equilibrium. A total of five samples for each combination were produced, the samples were measured for their characteristics, and then the mean value was obtained.

To measure the water content of the produced contact lens, the gravimetric method was used, based on the ISO 18369-4:2006 standard. The weight of the water-containing lens was measured at room temperature after all the water was removed by using No. 1-whatman (Whatman International Ltd., England) filter papers. The refractive index was measured based on ISO 18369-4:2006 standard, and the ABBE refractometer (ATAGO NAR 1T, Japan) was used to measure the refractive index at room temperature. The refractive index of the sample hydrated through copolymerization was removed by using No. 1-whatman (Whatman International Ltd., England) filter papers, and then the sample was put under a prism and the refractive index was measured by reading the gradation of the measurement handle when the sample was positioned on the border line. Meanwhile, optical transmittance was obtained for UV-B, UV-A, and visible light using a spectral transmittance meter (TOPCON TM-2, Japan) and was recorded in percentage values. To measure the tensile strength, AIKOH Engineering's Model-RX series was used. To measure the maximum value the lens was destroyed when 0.00-2.00 kgf force was applied for 0-20 seconds.

The contact angle was measured with S.E.O's Phoenix-Mini to measure wettability. The sessile drop method in which pure distilled water is dropped on the contact lens at room temperature to obtain the angle between the water drop and the lens was used to measure the contact angle.

An atomic force microscope (XE-100, Parks System) was used to analyze the nanoparticles contained in the copolymer, and the surface of the polymer was investigated using FE-SEM (JSM-7500F+EDS, Oxford). The composition of the particles was analyzed with electron spectroscopy for the chemical analyzer (VG Multilab 2000).

Table 1. Percent compositions of samples

	HEMA	MMA	NVP	EGDMA	Si nano+	SiNc++	3-VA+++	Unit: %
Ref.	93.90	0.94	4.69	0.47	-	-	-	
Ref. (Si)	93.80	0.94	4.69	0.47	0.1	-	-	
Ref. (SN)	93.90	0.94	4.69	0.47	-	0.1	-	
3VA-1	93.02	0.93	4.65	0.47	-	-	0.93	
3VA-3	91.32	0.91	4.57	0.46	-	-	2.74	
3VA-5	89.69	0.90	4.48	0.45	-	-	4.48	
3VA-7	88.11	0.88	4.41	0.44	-	-	6.17	
3VA-10	85.84	0.86	4.29	0.43	-	-	8.58	
3VA_Si-1	92.92	0.93	4.65	0.47	0.1	-	0.93	
3VA_Si-3	91.22	0.91	4.57	0.46	0.1	-	2.74	
3VA_Si-5	89.59	0.90	4.48	0.45	0.1	-	4.48	
3VA_Si-7	88.01	0.88	4.41	0.44	0.1	-	6.17	
3VA_Si-10	85.74	0.86	4.29	0.43	0.1	-	8.58	
3VA_SN-1	92.92	0.93	4.65	0.47	-	0.1	0.93	
3VA_SN-3	91.22	0.91	4.57	0.46	-	0.1	2.74	
3VA_SN-5	89.59	0.90	4.48	0.45	-	0.1	4.48	
3VA_SN-7	88.01	0.88	4.41	0.44	-	0.1	6.17	
3VA_SN-10	85.74	0.86	4.29	0.43	-	0.1	8.58	

Si nano+: silicon nanoparticle, SiNc++: silicon 2,3-naphthalocyanine bis (trihexylsilyloxiide)

RESULTS AND DISCUSSION

1. Copolymerization

A colorless transparent contact lens was produced from the copolymerization of the combination where Si nanoparticles and SiNc were not added. The contact lenses produced were hydrated in the standard normal saline solution for 24 hrs to generally exhibit the characteristics of flexibility and softness. The combination of copolymer in which Si nanoparticles were added produced a transparent contact lens with a light yellowish color. Similarly, the combina-

tion of copolymer in which SiNc was added produced a transparent contact lens with a greenish color. The colors did not differ significantly among the combinations in which 3-vinylisole and nanomaterials were added. Meanwhile, after the 24-hrs hydration process that was carried out in standard normal saline, all combinations exhibited softness and flexibility, but this flexibility differed according to the ratio of 3-vinylisole.

Analysis on the surface characteristics with nanomaterials by using an atomic force microscope (AFM) showed that the particle sizes were evenly distributed between 50-100 nm in Ref_Si sample (con-

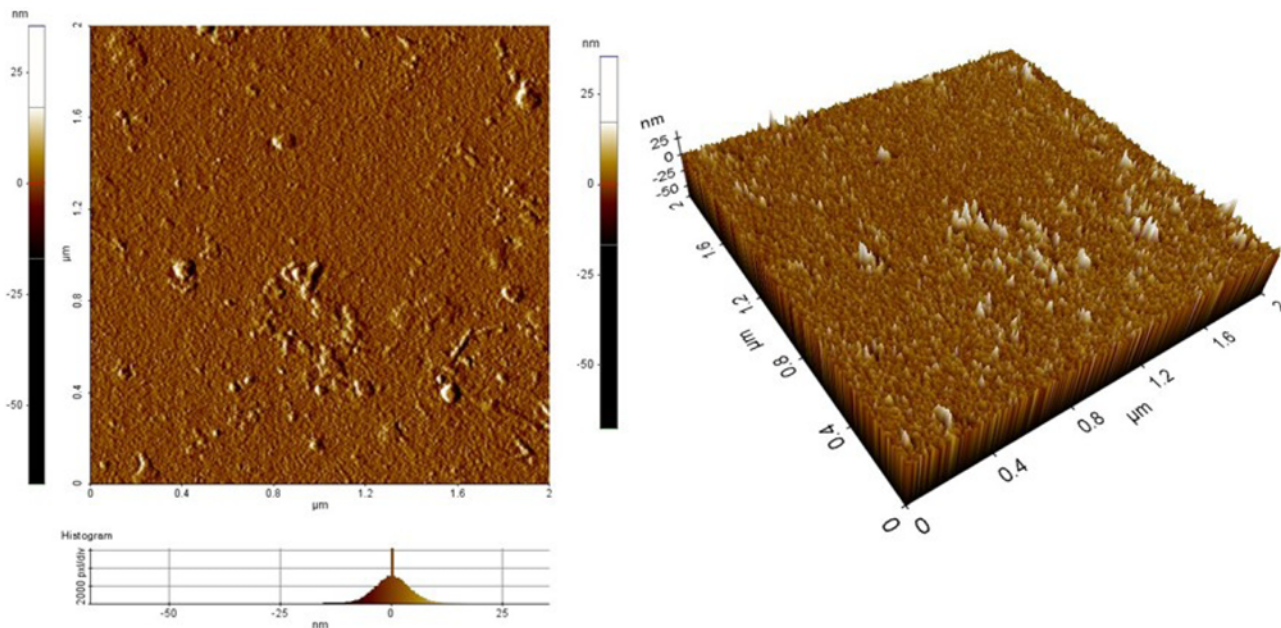


Fig. 1. Surface analysis of manufactured contact lens (Ref_Si) by AFM.

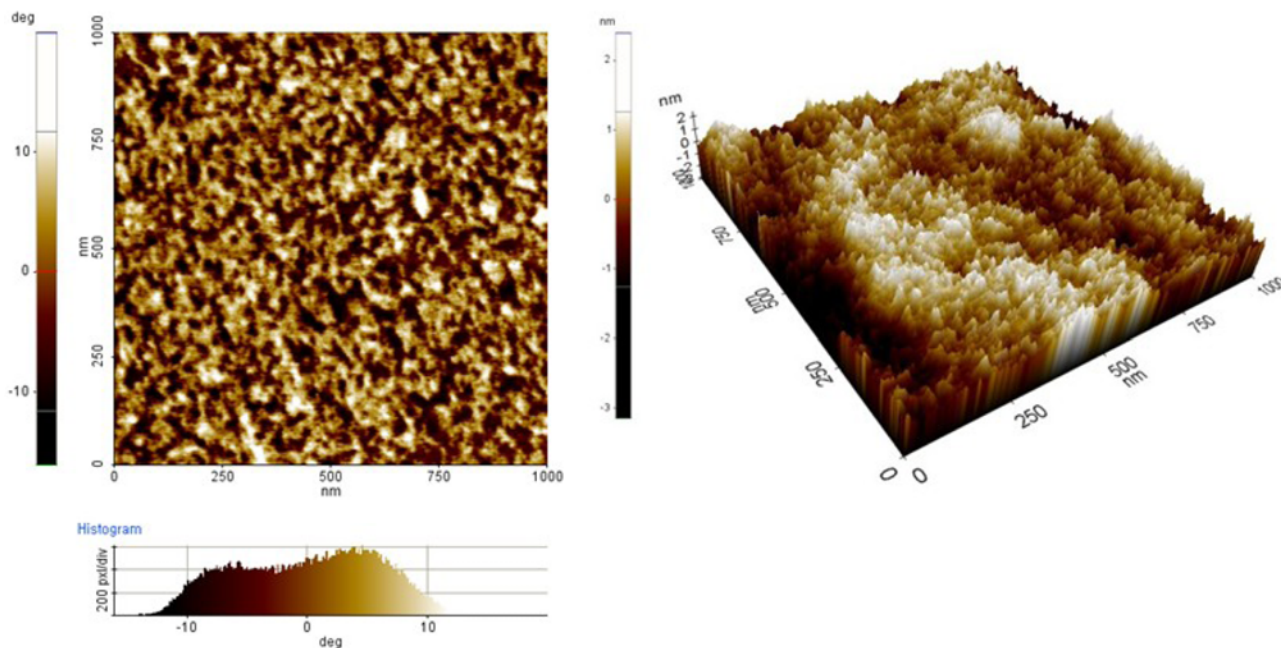


Fig. 2. Surface analysis of manufactured contact lens (Ref_SN) by AFM.

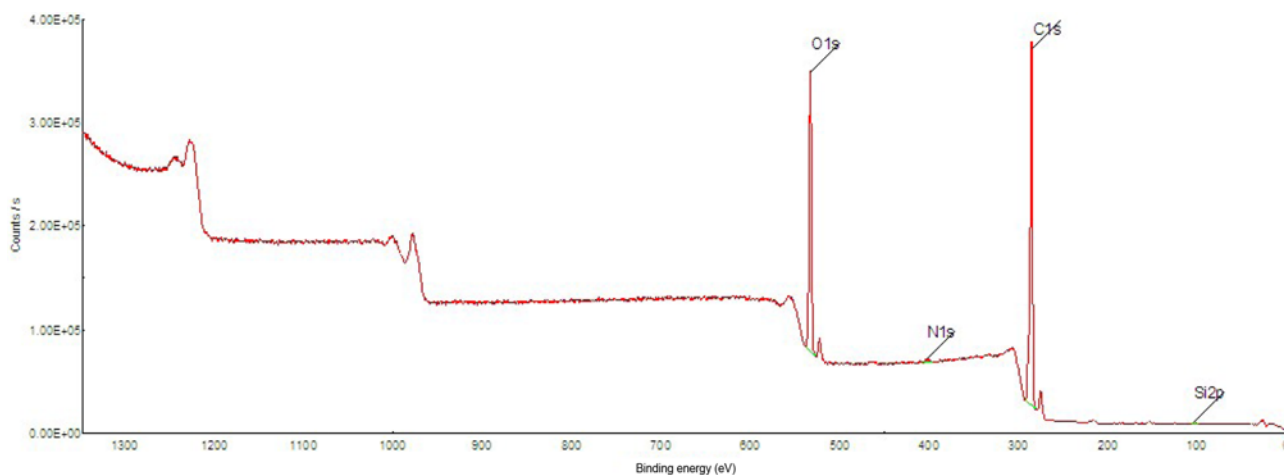


Fig. 3. XPS spectrum of manufactured contact lens (Ref_Si).

taining silicon nanoparticles only). The Ref_SN sample (containing silicon 2,3-naphthalocyanine bis(trihexylsilyloxi) only) particles were observed to be evenly distributed between the size 20-50 nm. The results of the atomic force microscope observation and ESCA analysis of the produced contact lens are shown in Figs. 1-3.

2. Physical Characteristics

The measurement of the water content of the produced contact lens showed that the mean water content of the Ref to which Si nanoparticles, SiNc and 3-vinylisole were not added was 37.61%, which is similar to the water content of commonly used hydrogel contact lenses. The mean water content of Ref_Si, in which Si nanoparticles were added to Ref was 37.56%. The mean water content of Ref_SN, in which 1% SiNc was added to Ref was 36.07%, showing a similar value to that of Ref. Overall, the addition of a nanomaterial did not significantly affect the water content.

The average water content of the 3VA combination to which 3-vinylisole was added at each ratio was 35.93% for 3VA-1, 32.54% for 3VA-3, 30.76% for 3VA-5, 29.21% for 3VA-7, and 26.65% for 3VA-10, respectively. Generally, the water content decreased as the ratio of 3-vinylisole increased. The mean water content of 3VA_Si (Si nanoparticles were added to 3VA) was in the range of 26.68-35.23%, and the water content was found to decrease as the ratio of 3-vinylisole increased. The mean water content of 3VA_SN (SiNc was added to 3VA) was in the range of 26.03-35.71%, and the water content decreased as the ratio of 3-vinylisole increased. The change in the water content of 3VA_Si and 3VA_SN showed a similar trend to that of 3VA, suggesting that nanomaterials do not have a significant impact on the water content.

Measurement of the refractive index of the produced contact lens showed that the mean refractive index is 1.4357 for Ref (Si nanoparticles, SiNc, and 3-VA were not added). The average refractive index of Ref_Si (1% Si nanoparticles were added to Ref) was 1.4350, and that of Ref_SN (1% SiNc was added to Ref) was 1.4380: the three combinations do not differ significantly in refractive index, indicating that the addition of nanomaterials does have a significant effect in the refractive index. Meanwhile, the measurements of the refractive index of each combination to which 3-vinylisole was added to Ref showed that the water content is in inverse proportion to all combinations, and the refractive index increased as the ratio

of 3-vinylisole increased. The average refractive index for 3VA was in the range of 1.4390-1.4780, for 3VA_Si was 1.4393-1.4790, and for 3VA_SN was 1.4400-1.4785, respectively.

The average tensile strength of the produced contact lens was 0.156 kgf for Ref, showing a similar tensile strength as that of a general hydrogel contact lens. The average tensile strength of Ref_Si, in which 1% Si nanoparticles were added to Ref, was 0.187 kgf. The average tensile strength of Ref_SN (1% SiNc was added to Ref) was 0.178 kgf, showing that the combination to which nanomaterial had been added had a higher tensile strength compared to Ref. This indicates that nanoparticles containing silicon affect tensile strength. The average tensile strength of 3VA, in which 3-vinylisole was added for each ratio to Ref was in the range of 0.315-0.767 kgf, showing that the tensile strength increases significantly as the ratio of 3-vinylisole increases. The average tensile strength of 3VA_Si was 0.324-0.802 kgf, and the tensile strength increased significantly as the ratio of 3-vinylisole increased.

The average tensile strength of 3VA_SN was in the range of 0.322-0.776 kgf. Like the previous cases, the tensile strength was observed to increase as the ratio of 3-vinylisole increased. Although the tensile strength was significantly affected by 3-vinylisole in all combinations, the tensile strength measured was slightly high in combinations containing nanomaterials when compared to combinations that did not contain nanoparticles. This indicates that silicon nanoparticles as well as 3-vinylisole have a significant effect on tensile strength. The changes, however, were not significant between the two types of nanomaterials. The measurements of the physical characteristics of each combination are summarized in Table 2.

3. Optical Characteristics

According to the measurements of spectral transmittance obtained to investigate the optical characteristics of each combination, the average transmittance for visual light of Ref (Si nanoparticles and SiNc were not added), was a high value of 90.30%. The transmittance was found to be 85.30% for UV-B, and 87.70% for UV-A, showing that these materials cannot sufficiently block UV and were observed to have similar optical properties as those of a general hydrogel contact lens.

Meanwhile, the average transmittance for Ref_Si (Si nanoparticles were added to Ref) was 79.50% for visual light, 73.00% for UV-

Table 2. Physical properties of the copolymers

Sample	*m _{dry} (g)	**m _{hydrated} (g)	***w _{H₂O} (%)	****RI	Tensile strength (kgf)
Ref.	0.0460	0.0737	37.61	1.4357	0.156
Ref_Si	0.0465	0.0745	37.56	1.4350	0.187
Ref_SN	0.0456	0.0713	36.07	1.4380	0.178
3VA-1	0.0455	0.0711	35.93	1.4390	0.315
3VA-3	0.0436	0.0646	32.54	1.4523	0.591
3VA-5	0.0418	0.0603	30.76	1.4640	0.604
3VA-7	0.0428	0.0605	29.21	1.4683	0.727
3VA-10	0.0410	0.0558	26.65	1.4780	0.767
3VA_Si-1	0.0467	0.0721	35.23	1.4393	0.324
3VA_Si-3	0.0405	0.0598	32.27	1.4520	0.574
3VA_Si-5	0.0435	0.0624	30.29	1.4647	0.635
3VA_Si-7	0.0429	0.0598	28.26	1.4685	0.764
3VA_Si-10	0.0426	0.0581	26.68	1.4790	0.802
3VA_SN-1	0.0468	0.0728	35.71	1.4400	0.322
3VA_SN-3	0.0426	0.0641	33.54	1.4520	0.611
3VA_SN-5	0.0456	0.0654	30.28	1.4643	0.612
3VA_SN-7	0.0459	0.0648	29.17	1.4690	0.734
3VA_SN-10	0.0432	0.0584	26.03	1.4785	0.776

*m_{dry} is the mass of the dry test specimens

**m_{hydrated} is the mass of the hydrated test specimens

***w_{H₂O} is the water content

****RI is the refractive index

B, and 79.50% for UV-A. In general, the transmittance was lower compared to that of Ref. The average transmittance of Ref_SN (SiNc was added to Ref) was 88.70% for visual light, 62.00% for UV-B, and 59.30% for UV-A. In the case of Ref_SN, the transmittance for visual light was high while that for UV was low. This shows that SiNc is capable of absorbing UV. The spectral transmittance of Ref. (s) was observed to drop at over 600 nm and measured to be low at near infrared region, showing that SiNc is capable of absorbing near infrared. The spectral transmittance of the Ref, Ref_Si, and Ref_SN samples is shown in Figs. 4 and 5. According to the measurements of the spectral transmittance of each combination to which 3-vinylanisole is added to Ref, the transmittance was in the range of 87.00-89.7% for visual light, 75.40-84.30% for UV-B, and 81.00-86.50% for UV-A. In general, the transmittance was low for

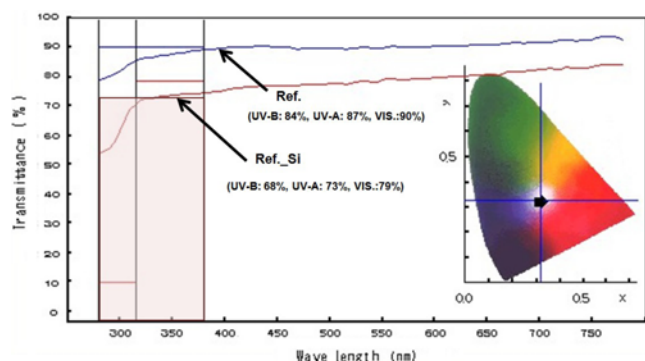


Fig. 4. Spectral transmittances of samples (Ref. and Ref_Si).

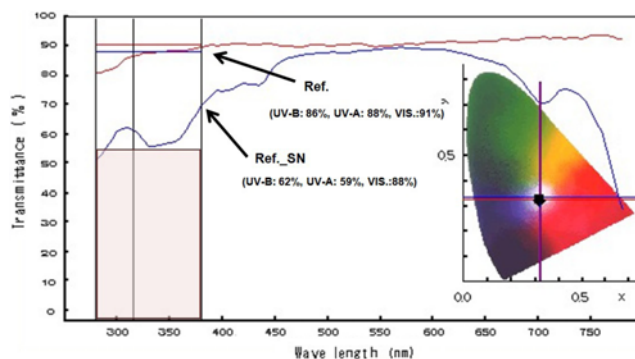


Fig. 5. Spectral transmittances of samples (Ref. and Ref_SN).

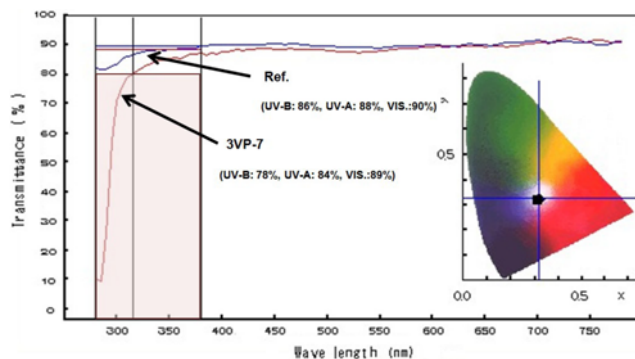


Fig. 6. Spectral transmittances of samples (Ref. and 3VP-7).

all wavelengths as the ratio of 3-vinylanisole increased, but the reduction rate was especially high for UV-B and the transmittance was significantly low in wavelengths shorter than 310 nm. The spectral transmittance for samples Ref and 3VP-7 is shown in Fig. 6.

According to the measurements of the spectral transmittance for

Table 3. Optical transmittances of samples Unit: %

Sample	UV-B	UV-A	Vis.
Ref.	85.3	87.7	90.3
Ref_Si	68.5	73.0	79.5
Ref_SN	62.0	59.3	88.7
3VA-1	84.3	86.5	89.7
3VA-3	82.0	85.0	88.7
3VA-5	80.5	84.4	88.0
3VA-7	77.7	83.3	88.3
3VA-10	75.4	81.0	87.0
3VA_Si-1	65.0	80.0	79.8
3VA_Si-3	62.5	79.5	78.2
3VA_Si-5	59.0	79.0	78.0
3VA_Si-7	59.5	78.2	78.0
3VA_Si-10	57.4	77.0	78.5
3VA_SN-1	65.7	64.0	92.3
3VA_SN-3	63.0	62.7	93.5
3VA_SN-5	63.5	63.0	92.0
3VA_SN-7	62.0	62.5	90.0
3VA_SN-10	61.3	59.0	89.7

the 3VA_Si sample (Si nanoparticles were added to 3VA), the transmittance was in the range of 78.00-79.80% for visual light, 57.40-65.00% for UV-B, and 77.00-80.00% for UV-A. Overall, the transmittance was lower in all wavelengths when compared to other combinations because of the Si nanoparticles, and the transmittance for UV-B was also low due to the addition of 3-vinylanisole. According to measurements of the spectral transmittance for the 3VA_SN (SiNc was added to 3VA), the transmittance was 89.70-92.30% for visual light, 61.30-65.70% for UV-B, and 59.00-64.00% for UV-A. For the 3VA_SN combination, the transmittance for visual light was measured to be high and that for UV was measured low, showing that the combination lacks sufficient UV-blocking capability. The transmittance for UV-A was the lowest of all the combinations. The transmittances for all combinations are shown in Table 3, and the spectral transmittance for 3VP-7 and 3VP-SN-7 is shown in Fig. 7.

4. Surface Characteristics

According to the measurements of the wettability obtained by

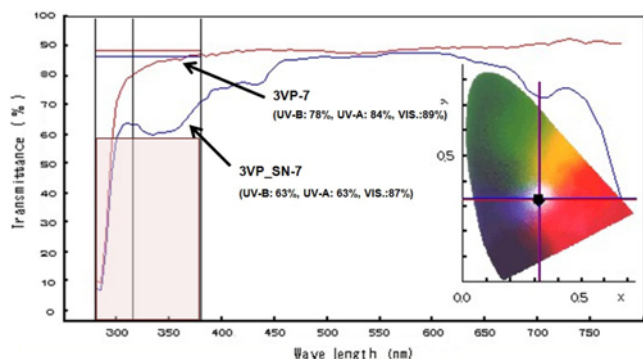


Fig. 7. Spectral transmittances of samples (3VP-SN-7 and 3VP-7).

measuring contact angle to investigate the surface characteristics of each combination, the average contact angle for Ref (Si nanoparticles and SiNc were not added) was 27.58°. The average contact angle was 46.84° for Ref_Si (Si nanopowder was added to Ref), and the average contact angle for Ref_SN (SiNc was added to Ref) was 40.52°. The contact angle for the two combinations in which nanomaterials were added showed a large increase, which indicates that the silicon nanomaterial affects the hydrophobic characteristic of the lens surface. The measurements of the contact angle of Ref., Ref_Si and Ref_SN are shown in Fig. 8.

The contact angles for 3VA-1, 3VA-3, 3VA-5, 3VA-7, and 3VA-10 (where 3-vinylanisole was added in each ratio) were measured to be 30.54°, 35.49°, 40.84°, 49.21°, and 54.35°, respectively. Generally, the contact angle increased as the mixture ratio of 3-vinylanisole increased, thus leading to a reduction in wettability. The average contact angles for 3VA_Si, 3VA_Si-1, 3VA_Si-3, 3VA_Si-5, 3VA_Si-7, and 3VA_Si-10 (where Si nanoparticles were added) are 47.21°, 43.45°, 45.66°, 46.94° and 46.98°, respectively. For 3VA-Si, the contact angle did not increase with the increase of the mixture rate of 3-vinylanisole. It is estimated that the existence of the nanomaterials in the lens surface has a greater effect compared to that of the changes in wettability caused by 3-vinylanisole.

Meanwhile, the contact angle for 3VA_SN (where SiNc was added to 3VA) was observed to be 41.65° for 3VA_SN-1, 43.64° for 3VA_SN-3, 42.65° for 3VA_SN-5, 45.65° for 3VA_SN-7, and 47.94° for 3VA_SN-10. For the 3VA_SN combination, the amount of change was not significant and remained relatively constant even though there were changes in the contact angle based on the mixture ratio of 3-vinylanisole. This result is due to the effects of the nanomaterial. The measurements of the contact angles for 3VA-7, 3VA_Si-7, and 3VA_SN-7 are shown in Fig. 9, and the changes in the contact

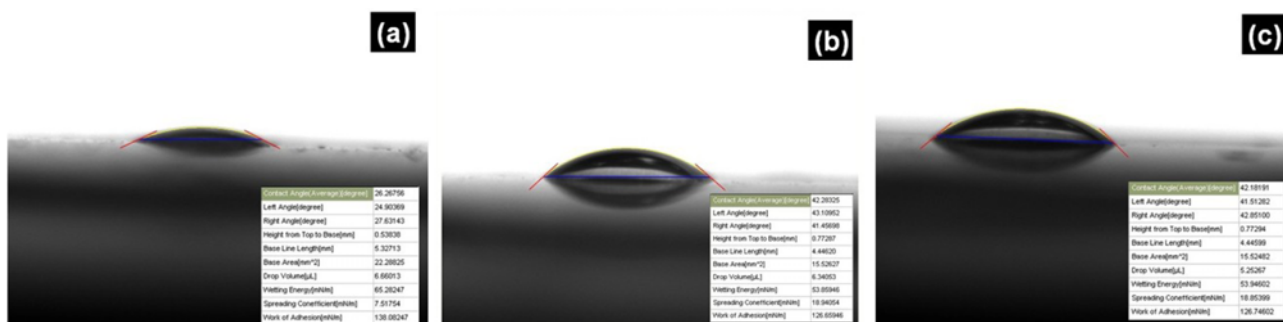


Fig. 8. Contact angles of the copolymers (a) Ref., (b) Ref_Si, (c) Ref_SN.

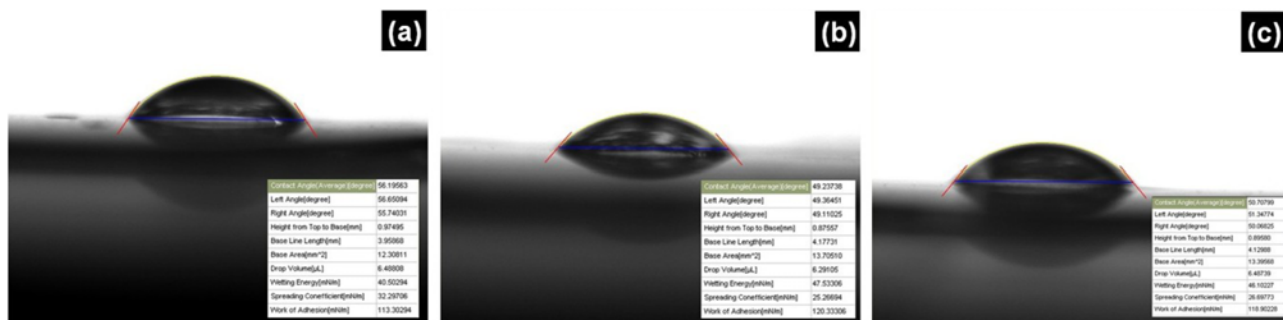


Fig. 9. Contact angles of the copolymers (a) 3VA-7, (b) 3VA_Si-7, (c) 3VA_SN-7.

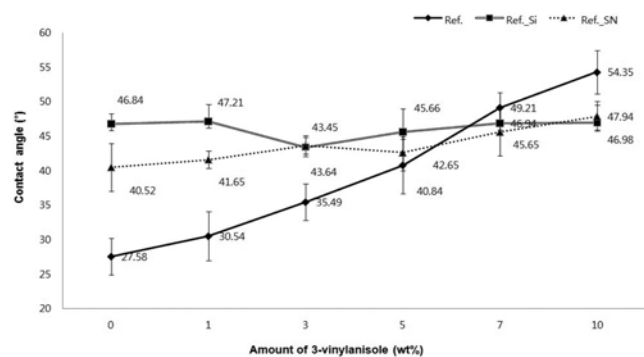


Fig. 10. Effect of 3-vinylanisole on contact angle.

angles of all combinations are shown in Fig. 10.

CONCLUSION

Si nanoparticles and silicon 2,3-naphthalocyanine bis (trihexylsilyloxy) were copolymerized with 2-hydroxyethyl methacrylate, N-vinyl-2-pyrrolidone, methyl methacrylate, 3-vinylanisole, and ethylene glycol dimethacrylate, which are commonly used as materials for contact lenses. The physical, optical, and surface characteristics of the copolymerized contact lens were investigated to examine the functionality of the above nanomaterials as components for contact lenses. Although the added nanomaterials did not significantly affect both the water content and refractive index, the tensile strength slightly increased.

The measurements of the optical characteristics showed that Si nanoparticles reduced spectral transmittance in all wavelengths, while the transmittance of visual light increased, but the transmittance of UV and near infrared decreased. High contact angles for the copolymers containing Si nanoparticles and SiNc were observed. The water

content, however, was not significantly affected by the addition of 3-vinylanisole.

Thus, nanomaterials such as Si nanoparticles and SiNc can be used for hydrogel soft contact lenses with UV-blocking capabilities if controls on the intensity and the wettability of the surface can be properly made.

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