Compatibility of POSS Composites with Silicone Monomers and Application to Contact Lenses Material

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(Received June 30, 2020; Accepted September 14, 2020)

ABSTRACT. This research was conducted to analyze the compatibility of used monomers and produce the high functional contact lens material containing silicone monomers. Silicone monomer (Sil-OH), Trimethylsilylmethacrylate (TSMA) were used as additives for the basic combination of Polyhedral Oligomeric Silsesquioxane (POSS), methyl methacrylate (MMA) and methyl acrylate (MA). And also, the materials were copolymerized with ethylene glycol dimethacrylate (EGDMA) as the cross-linking agent, AIBN (thermal polymerization initiator) as the initiator. It is judged that the fabricated lenses of all combinations are optically excellent and thus used monomers have good compatibility. Measurement of the optical and physical characteristics of the manufactured hydrophilic lens material were varied in each case. Especially TSMA with POSS increases the oxygen permeability and Sil-OH with POSS increases the wettability by the addition of Sil-OH. These materials were considered to have compatibility each other, so it can be used in functional contact lens material.

Key words: POSS, Silicone monomer, Compatibility, Contact lens material, Physical property

INTRODUCTION

As the polymer composite is produced by combining different types of material, phase separation is likely to occur due to the isomer components, such as the hydrophilicity or lipophilicity. In addition, even if a uniform mixture is formed, there may be a problem in the properties of the prepared composite. Therefore, to form a stable complex, it is very important to increase the affinity of the two phases so that they will not cause aggregation or separation. In an effort to overcome the problems, various research have been conducted to improve the compatibility by using additives like surfactants.1-3

Polyhedral oligomeric silsesquioxanes (POSS) was first discovered in the 1940s and may take various types of structure.4-8 Among the various structures, POSS, an organic-inorganic compound that has a cage structure, consists of silica on the inside and organic functional groups on the outside.9 The organic functional group on the outside has an affinity with various organic solvents and can easily introduce various functional groups through chemical reaction; as such, it has properties like polymer production through copolymerization, biology, and affinity with metals.10-13 Therefore, the existing compatibility issue can be resolved as such. In addition, POSS derivatives are introduced into the polymer to improve the polymer properties, such as the water resistance, heat resistance, corrosion resistance, gas permeability, surface hardness, and mechanical properties, as well as to lower the flammability and viscosity. Polymer composite materials using these POSS have excellent insulation and gas permeability, and have been applied to various fields, such as photoresist protective films, semiconductor low-dielectric thin films, optical fiber protective coatings, and gas separators.14,15

In the experiment in this study, POSS was intended to be grafted onto a highly oxygen-permeable hydrogel lens material by utilizing a material that has excellent gas permeability and improved mechanical properties. Based on POSS, silicone monomer (Sil-OH) and trimethylsilylmethacrylate (TSMA) were added as additives by ratio, and then polymerized through a thermal polymerization method. After measuring and evaluating the physical properties of the contact lens produced through the cast mold technique, the compatibility of POSS and the organic groups was evaluated to assess the usability of the lens material.

EXPERIMENTAL

Reagents and Materials

For the hydrogel lens material that was used in the experiment, POSS from Hybrid Plastics Co. and synthesized Sil-OH were used, while for TSMA and N,N-dimethyl...
acrylamide (DMA), TCI products were selected. For methyl methacrylate (MMA), methyl acrylate (MA), and azobisisobutyronitrile (AIBN), Junsei products were selected. For the crosslinking agent, ethylene glycol dimethacrylate (EGDMA), Sigma-Aldrich products were selected. The molecular weight of Sil-OH was 2165 Mw and the viscosity was measured as 40.4 cp. The structural formulas of the POSS, TSMA, and synthesized Sil-OH are shown in Fig. 1.

**Polymerization**

For the polymerization of a highly oxygen-permeable lens material, mixtures were prepared by adding POSS at a 1~10% ratio to the basic combination of DMA, MMA, MA, EGDMA, and AIBN, and the samples prepared as such were named P1, P3, P5, P7, and P10, respectively. To optimize the shape of the lens while maintaining its basic properties, the P10 sample, which had the best oxygen permeability, was selected, and Sil-OH and TSMA were added at a rate of 10, 30, 50, and 100%, respectively. The prepared samples were then named PS10, PS30, PS50, PS100, PT10, PT30, PT50, and PT100, respectively. The stirring solution was mixed for 60 minutes after mixing according to the mixing ratio, and for polymer polymerization, each sample was heat-treated in an oven at 135°C for 120 minutes. The prepared lens was hydrated in 0.9% physiological saline for 24 hours before its physical properties were measured. *Table 1* shows the mixing ratio of each sample.

**Experimental Method**

The optical transmittance, refractive index, water content, wettability, oxygen permeability, eluate, and differential scanning calorimetry (DSC) of the produced polymers were measured to analyze the optical, physical, and thermal properties. The relationships between the refractive index and the water content, the contact angle and the water content, and the oxygen permeability and the water content were compared. In the case of optical transmittance, a wavelength range of 280-780 nm, which is an ultraviolet and visible-ray region, and were measured five times per sample, respectively, and an average value was used. The refractive indices of the prepared hydrophilic hydrogel

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**Figure 1.** Chemical structures of monomer. (a) POSS, (b) Sil-OH (n=49.20), (c) TSMA.

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<table>
<thead>
<tr>
<th>Sample</th>
<th>POSS</th>
<th>DMA</th>
<th>MMA</th>
<th>MA</th>
<th>Sil-OH</th>
<th>TSMA</th>
<th>EGDMA</th>
<th>AIBN</th>
<th>Total</th>
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<td>1.90</td>
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<td>-</td>
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<td>2.80</td>
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<td>-</td>
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<td>1.80</td>
<td>0.90</td>
<td>-</td>
<td>-</td>
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<tr>
<td>P10</td>
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<td>1.75</td>
<td>0.87</td>
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<td>-</td>
<td>0.99</td>
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<td>PS10</td>
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<td>0.79</td>
<td>8.98</td>
<td>-</td>
<td>0.99</td>
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<td>0.67</td>
<td>22.80</td>
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<td>0.99</td>
<td>0.20</td>
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<td>PS50</td>
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<td>58.30</td>
<td>1.17</td>
<td>0.58</td>
<td>32.94</td>
<td>-</td>
<td>0.99</td>
<td>0.20</td>
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<tr>
<td>PS100</td>
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<td>43.72</td>
<td>0.87</td>
<td>0.44</td>
<td>49.41</td>
<td>-</td>
<td>0.99</td>
<td>0.20</td>
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<tr>
<td>PT10</td>
<td>7.95</td>
<td>79.50</td>
<td>1.59</td>
<td>0.79</td>
<td>-</td>
<td>8.98</td>
<td>0.99</td>
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<tr>
<td>PT30</td>
<td>6.73</td>
<td>67.27</td>
<td>1.35</td>
<td>0.67</td>
<td>-</td>
<td>22.80</td>
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<tr>
<td>PT50</td>
<td>5.83</td>
<td>58.30</td>
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<td>0.58</td>
<td>-</td>
<td>32.94</td>
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<tr>
<td>PT100</td>
<td>4.37</td>
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<td>0.87</td>
<td>0.44</td>
<td>-</td>
<td>49.41</td>
<td>0.99</td>
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2020, Vol. 64, No. 6
lenses were measured based on ISO 18396-4:2006 using an
ABBE refractometer (ATAGO DR-A1, Japan), and were
measured five times per sample, respectively, and an average
value was used. The water content was measured based on
ISO 1869-4:2006 using the gravimetric method, and were
measured five times per sample, respectively, and an aver-
age value was used. The weights of the dried and water-
containing samples were measured using an electronic
balance (XS205 DualRange, 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), and were mea-
sured five times per sample, respectively, and an average
value was used. The oxygen transmissibility was measured
using the polarographic method in ISO 18369-4:2006, Oph-
thalmic optics - Contact lenses - Part 4, and were measured
five times per sample, respectively, and an average value
was used. DSC analysis was conducted to obtain the ther-
mal properties of the polymer before measuring the pH
change and the presence of a potassium-permanganate-
reducing substance, to ensure safety.

RESULTS AND DISCUSSION

Addition of POSS

Optical transmittance. The result of the spectral trans-
mittance to determine the optical properties of the man-
ufactured lenses showed that the UV-B was 74.68-76.78%,
the UV-A was 89.51-90.57%, and the visible light trans-
mittance was 92.61% regardless of the POSS content in all
the groups. It is thus considered that the structure of POSS
does not have a significant influence in both the ultravi-
olet and visible regions. Table 2 shows the light trans-
mittance measurement results of each combination.

Refractive index and water content. The measurement
of the refractive indices of the manufactured lenses showed
that the refractive index increased from P1 1.369 to P10
1.390 according to the POSS addition ratio, and that the
water content decreased from P1 75.24% to P10 60.79%.
It is thus judged that the water content decreases as the
amount of POSS increases, and the refractive index increases
due to the increase in the crosslink density between the
molecules. The refractive index and water content showed
an inverse relationship with each other, which in turn showed
the same trend as in the previous studies: that the refrac-
tive index was inversely proportional to the changes in the
water content due to the nature of the material. The rela-
tionship between the refractive index and the water con-
tent of each combination is shown in Fig. 2.

Contact angle and water content. The measurement
of the contact angles of the manufactured hydrogel lenses
showed that the contact angle increased from P1 20.14° to
P10 35.77° according to the POSS addition ratio, indicating
that it is inversely proportional to the water content. In the
case of a general hydrogel lens, when the water content is
high, the wettability also tends to increase. Based on the
results of this study, it is judged that the wettability also
increases according to the water content, thus affecting the
hydrophilicity. Table 3 shows the relationship between the
contact angle and the water content of each combination.

Oxygen permeability and water content. The mea-
surement of the oxygen permeability of the prepared lenses
showed that the oxygen permeability increased from P1
22.01×10^{-11} cm²/sec (mLO₂/ml×mmHg) to P10 36.84×10^{-11}
cm²/sec (mLO₂/ml×mmHg) according to the POSS addi-
tion ratio, indicating that it is inversely proportional to the
water content. In general, an increase in water content makes
the oxygen molecules dissolve in water, which makes it

| Table 2. Optical transmittance distribution of samples |
|-------------|-------------|-------------|
|            | UV-B (%)    | UV-A (%)    | Visible (%) |
| P1         | 76.75       | 90.24       | 92.72       |
| P3         | 76.78       | 90.57       | 92.61       |
| P5         | 76.24       | 90.34       | 93.12       |
| P7         | 74.68       | 89.51       | 93.33       |
| P10        | 76.71       | 89.83       | 93.26       |

| Table 3. Contact angle & water content of samples |
|-------------|-------------|-------------|
| Contact Angle (degree) | Water Content (%) |
| P1          | 20.14       | 75.24       |
| P3          | 20.48       | 73.83       |
| P5          | 25.38       | 71.56       |
| P7          | 29.40       | 62.32       |
| P10         | 35.77       | 60.79       |
easier to transfer the oxygen, thereby increasing the oxygen permeability. In the experiment, however, the oxygen permeability increased despite the decrease in water content, prompting the conclusion that the gas permeability of the material increased due to the structure of POSS. The relationship between the oxygen permeability and the water content of each combination is shown in Fig. 3.

Addition of Sil-OH and TSMA

Thermal analysis via DSC. Sil-OH and TSMA were added to the P10 sample showing the optimum shape and physical properties. And PS50 and PT50, which show the best physical properties, were selected and compared. In the DSC measurement, the PS50 sample was found to have a glass transition temperature (Tg) of 114.5°C in the first heating, and a crystalline temperature (Tc) of 66.7°C in the cooling process. As for the PT50 sample, the Tg was 117.6°C in the first heating, and the Tc was 110.9°C in the cooling process. As the Tg of PS50 is lower, it is considered that the elongation is excellent. When the temperature is raised at a constant rate, the temperature at which the peak that generates heat at a specific temperature is the maximum is the Tc. If the polymers do not mix with each other and all their properties appear, multiple peaks can occur. In this experiment, it was judged that polymerization of the polymer was well performed because one peak was formed in the PT50 sample. Fig. 4 shows the thermal properties of each combination of DSCs.

Optical transmittance. The measurement of the spectral transmittance to determine the optical properties of the manufactured lenses showed that the PS group had 66.51-29.45% UV-B transmittance, 88.89-80.07% UV-A transmittance, and 92.57-89.75% visible light transmittance. Although there was no significant difference in percentage, the transmittance was slightly lower in the UV-B

Figure 3. Comparison of the relation between DK and water content of samples.

Figure 4. Typical DSC thermogram analysis of sample. (a) PS50 heating state, (b) PS50 cooling state, (c) PT50 heating state, (d) PT50 cooling state.
significant change in both the ultraviolet and visible regions. Table 4 shows the measurement results of the light transmittance of each combination.

**Refractive index and water content.** The measurement of the refractive indices of the prepared lenses showed that the refractive index increased from PS10 1.397 to PS100 1.433 according to the Sil-OH addition ratio, and that the water content decreased from PS10 60.66% to PS100 42.35%. Conversely, the addition of TSMA decreased the refractive index of PT10 from 1.386 to 1.368, and increased the moisture content from PT10 64.48% to PT100 70.63%. The refractive index and water content are inversely proportional to each other, showing the same tendency as in the previous study. The relationship between the refractive index and water content of each combination is shown in Fig. 5.

**Contact angle.** The measurement of the contact angles of the prepared lenses showed that the contact angle decreased from PS10 102.74° to PS100 89.30° according to the Sil-OH addition ratio, and increased from PT10 75.46° to PT100 80.01° according to the TSMA addition ratio. In contrast to the results of the previous studies, where the wettability also tended to increase when the water content was high, the results of this study are judged to indicate a change in wettability regardless of the water content depending on the surface properties of the silicone material. The contact angle results of each combination are shown in Fig. 6-7.

**Oxygen permeability and water content.** The oxygen permeability of the prepared lenses increased from PS10 36.04×10^{-11} cm^2/sec (mlO_2/ml×mmHg) to PS50 37.61×10^{-11} cm^2/sec (mlO_2/ml×mmHg) according to the Sil-OH addition ratio, and increased from PT10 39.03×10^{-11} cm^2/sec (mlO_2/ml×mmHg) to PT50 41.09×10^{-11} cm^2/sec (mlO_2/ml×mmHg) according to the TSMA addition ratio. Based on the experiment results of this study, it is thought that the gas permeability increased due to the characteristics of the silicone material, owing to the increased oxygen permeability regardless of the change in water content. The relationship between the oxygen permeability and the water content of each combination is shown in Fig. 8.

### Table 4. Optical transmittance distribution of samples

<table>
<thead>
<tr>
<th></th>
<th>UV-B (%)</th>
<th>UV-A (%)</th>
<th>Visible (%)</th>
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<tr>
<td>PS10</td>
<td>66.51</td>
<td>88.89</td>
<td>92.53</td>
</tr>
<tr>
<td>PS30</td>
<td>56.47</td>
<td>88.25</td>
<td>92.37</td>
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<td>PS50</td>
<td>41.74</td>
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<td>93.64</td>
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<tr>
<td>PS100</td>
<td>29.45</td>
<td>80.07</td>
<td>89.75</td>
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<tr>
<td>PT10</td>
<td>53.54</td>
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<td>88.80</td>
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<td>PT30</td>
<td>44.36</td>
<td>71.15</td>
<td>84.62</td>
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<td>PT100</td>
<td>41.87</td>
<td>80.23</td>
<td>88.68</td>
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</table>

**Figure 5.** Comparison of the relation between refractive index and water content of samples.

**Figure 6.** Contact angle of samples.

**Figure 7.** Contact angle image of samples. (a) PS50, (b) PT50.

**Figure 8.** Comparison of the relation between DK and water content of samples.
CONCLUSION

The results of this study showed that polyhedral oligomeric silsesquioxanes does not affect the optical transparency of the lens, and increases the refractive index and lowers the water content. In addition, the cage-type structure makes it possible to make highly oxygen-permeable materials by increasing the gas permeability in the molecular structure. The results of the thermal analysis of the polymer prepared in this study showed that silicone monomer lowered the glass transition temperature to increase the elasticity of the lens, and trimethylsilylmethacrylate showed a single peak, confirming that the polymerization was more stable. The additive that was used in this study showed good compatibility with the existing POSS, and was shown to maintain optical transparency. In addition, the wettability was maintained irrespective of the water content, and the oxygen permeability was also maintained or slightly increased. It is thus considered that POSS can be applied to acrylate and silicone materials to maintain compatibility, as well as to lens materials with high oxygen permeability.

Acknowledgments. This research was financially supported by the Ministry of Small and Medium-sized Enterprises (SMES) and Startups (MSS), Korea, under the “Regional Enterprise Open-Innovative Voucher Program (R&D, P0010722)” supervised by the Korea Institute for Advancement of Technology (KIAT).

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