Soft Nanomaterials of POSS-based Copolymer for Arts Conservation

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1 Background of protective requirement and POSS-based materials

2 Fabrication of POSS-based materials for conservation of artworks

3 Evaluation of protective performance
1. Background

Silicate Cultural Heritage

Earth
Wall Painting
Pottery
Sandstone
Ceramic

......
* **support:** wood, stone, clay, fiber, brick……

* **pigments:** nature minerals and dye

* **binding medium:** nature organic materials or polymers

**What happened with time?**
The main problem of these precious heritages?

Lost the bindings and colors because of the water and salt.
Silicate Cultural heritage is a special patient:

✓ It holds values (cultural, historical, esthetical, material,…….)

✓ It ages in an *irreversible* way with time

✓ It is a *passive* patient (doesn’t speak and doesn’t complain!!)

The patient doesn’t go spontaneously to the doctor but need to be protected.
Who are the doctors???

Conservation scientist

Conservator-restorer

Art historian/archaeologist
Is it possible to perform surgery (restore) on a patient without knowing his case and history (anamnesis)?

(i.e.: materials over paintings, techniques, past restoration, the properties of protective materials)
The problems need to be solved

* Understand the real nature of original materials
* Develop useful and reliable materials for the protection
* Establish protective methods

The functional materials should be the idea candidate
The basic requirement for the materials???

Requirements of materials for conservation of artworks

- Security and harmless to relics
- Suitable respiratory function
- Conformable chemical and physical properties with substrate
- Influence on the follow-up retreatment

Challenge
- The design and realization of function materials
Periodic structures with special wettability in nature

(A, B) hydrophilic pearl (water CA=45°);
(C, D) hydrophilic longhorn beetles Tmesisternus isabellae (water CA =25°);
(E, F) superhydrophobic mosquito eye (water CA =149.8°);
(G, H) superhydrophobic peacock (water CA =150°).
Polyhedral Oligomeric Silsesquioxanes (POSS)

1-3nm molecular dimension

(a) Random structure
(b) Ladder structure
(c) T8
(d) T10
(e) T12
(f) Partial cage structure
Polyhedral Oligomeric Silsesquioxanes (POSS)

- excellent surface properties (silicon polymer)
- remarkable film-forming properties (polymers)
- high thermal stability and chemical resistance (POSS)
- microphase separation
- self-assembly behavior in the selected solution
- adhesive strength control
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2.1 PGMA-\textit{g}-P(MA-POSS)

\begin{align*}
\text{GMA} & \quad \xrightarrow{\text{AlBN,70°C, THF}} \quad \text{I-POSS} \\
\text{BIBA,50°C, THF, refluxing} & \quad \xrightarrow{} \quad \text{I-PGMA-Br} \\
\text{ATRP,100°C, MA-POSS} & \quad \xrightarrow{} \quad \text{PGMA-\textit{g}-P(MA-POSS)}
\end{align*}
The TEM pictures of uncured Sample 1-4 (a-d), cured Sample 1-4 (e-h) and the size distribution table of PGMA-g-P(MA-POSS) in THF solution (m).

<table>
<thead>
<tr>
<th>Samples</th>
<th>Uncured Samples</th>
<th>Cured Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TEM/nm</td>
<td>DLS/nm</td>
</tr>
<tr>
<td>Sample 1</td>
<td>115</td>
<td>2.4(14.8%)</td>
</tr>
<tr>
<td></td>
<td>128.1(85.2%)</td>
<td></td>
</tr>
<tr>
<td>Sample 2</td>
<td>136</td>
<td>2.1(5.9%)</td>
</tr>
<tr>
<td></td>
<td>121.4(94.1%)</td>
<td></td>
</tr>
<tr>
<td>Sample 3</td>
<td>400</td>
<td>2.5(13.6%)</td>
</tr>
<tr>
<td></td>
<td>414.8(86.4%)</td>
<td></td>
</tr>
<tr>
<td>Sample 4</td>
<td>800</td>
<td>2.8(7.5%)</td>
</tr>
<tr>
<td></td>
<td>761.4(92.5%)</td>
<td></td>
</tr>
</tbody>
</table>
Surface properties of PGMA-g-P(MA-POSS) film

<table>
<thead>
<tr>
<th>Sample</th>
<th>before</th>
<th>after</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ra/nm</td>
<td>Ra/nm</td>
<td></td>
</tr>
<tr>
<td>S1</td>
<td>0.19</td>
<td>0.14</td>
</tr>
<tr>
<td>S2</td>
<td>0.21</td>
<td>0.19</td>
</tr>
<tr>
<td>S3</td>
<td>0.33</td>
<td>0.63</td>
</tr>
<tr>
<td>S4</td>
<td>4.1</td>
<td>14.4</td>
</tr>
</tbody>
</table>
2.2 \textit{ap-POSS-PMMA}_m\text{-b-P(\text{MA-POSS})}_n
Sample 1: \( ap\text{-POSS-PMMA}_m \text{-b-} P(\text{MA-POSS})_n \) 
155nm shovel-shape

Sample 2: \( ap\text{-POSS-PMMA}_m \text{-b-} P(\text{MA-POSS})_{4.3} \) 
195nm core-shell

Sample 3: \( ap\text{-POSS-PMMA}_m \text{-b-} P(\text{MA-POSS})_{8.4} \) 
295nm core-shell

Sample 4: \( ap\text{-POSS-PMMA}_m \text{-b-} P(\text{MA-POSS})_{10.0} \) 
159nm core-shell-crown
2.2 $a_p$-POSS-$\text{PMMA}_m$-$b$-$\text{P(MA-POSS)}_n$

Sample 1
$Ra = 0.288 \text{ nm}$

Sample 2
$Ra = 0.816 \text{ nm}$

$\Delta m = 16520 \text{ ng/cm}^2$
$\Delta D/\Delta f = -0.02$

Sample 3
$Ra = 0.829 \text{ nm}$

Sample 4
$Ra = 1.690 \text{ nm}$

$\Delta m = 3540 \text{ ng/cm}^2$
$\Delta D/\Delta f = -0.18$
2.2 $ap$-$POSS$-$PMMA_m$-$b$-$P(MA$-$POSS)_n$
2.3 PDMS-b-PMMA_\textsubscript{m}-b-P(\text{MA-POSS})_n

\[
\text{PDMS-OH} \xrightarrow{\text{TEA, DMAP, 25°C}} \text{PDMS-Br}
\]

\[
\text{PDMS-Br} \xrightarrow{\text{CuCl / PMDETA, 80°C}} \text{PDMS-b-PMMA}_\text{m}-\text{Br}
\]

\[
\text{PDMS-b-PMMA}_\text{m}-\text{Br} \xrightarrow{\text{CuCl / PMDETA, 120°C}} \text{PDMS-b-PMMA}_\text{m}-\text{b-P(\text{MA-POSS})}_n
\]
2.3 PDMS-b-PMMA\textsubscript{m}-b-P(MA-POSS)\textsubscript{n}

- **S3**
  - $M\text{w}=53560$ g/mol
  - $M\text{n}=44090$ g/mol
  - PDI=1.215

- **S4**
  - $M\text{w}=58650$ g/mol
  - $M\text{n}=43040$ g/mol
  - PDI=1.363

- **S1**
  - $M\text{w}=45820$ g/mol
  - $M\text{n}=32930$ g/mol
  - PDI=1.391

- **S2**
  - $M\text{w}=50090$ g/mol
  - $M\text{n}=38420$ g/mol
  - PDI=1.304

- **S4**: 902MPa
- **S3**: 747MPa
- **S2**: 648MPa
- **S1**: 579MPa

**DSC Exotherm**
- **S1** (MA-POSS/\%w=0)
  - $T_g=95^\circ C$

- **S2** (MA-POSS/\%w=9.5)
  - $T_g=120^\circ C$

- **S3** (MA-POSS/\%w=17.3)
  - $T_g=129^\circ C$

- **S4** (MA-POSS/\%w=24)
  - $T_g=137^\circ C$

**Tan Delta vs. Temperature**

**Storage Modulus (MPa)**

**Heating Flow (mW/mg)**

**Temperature (°C)**
<table>
<thead>
<tr>
<th>Code</th>
<th>Solvents</th>
<th>$\Theta_{\text{H}_2\text{O}}$</th>
<th>$\Theta_{\text{Hex}}$</th>
<th>$\gamma$/mNm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>THF</td>
<td>108°</td>
<td>20°</td>
<td>26.10</td>
</tr>
<tr>
<td></td>
<td>CHCl$_3$</td>
<td>110°</td>
<td>22°</td>
<td>25.63</td>
</tr>
<tr>
<td>S3</td>
<td>THF</td>
<td>114°</td>
<td>26°</td>
<td>24.93</td>
</tr>
<tr>
<td></td>
<td>CHCl$_3$</td>
<td>120°</td>
<td>32°</td>
<td>23.96</td>
</tr>
</tbody>
</table>
(a) THF:
241.2 nm, 76.3%
11.8 nm, 23.7%

(b) CHCl₃:
283.0 nm, 90.3%
11.4 nm, 9.7%

CHCl₃ (Δf = -2300Hz)
(ΔD = 26 × 10⁻⁶)

THF (Δf = -1540Hz,
ΔD = 52 × 10⁻⁶)
2.4 POSS-(PMMA-b-PDFHM)$_{16}$ and ap-POSS-PMMA-b-PDFHM
$s$-POSS-($PMMA$-$b$-$PDFHM$)$_{16}$

110 nm CS micelles

ap-POSS-$PMMA$-$b$-$PDFHM$ 200 nm CS micelles
Self-assembled micelles

POSS-(PMMA-b-PDFHM)$_{16}$  POSS-(PMMA)$_{16}$
ap-POSS-PMMA-b-PDFHM  ap-POSS-PMMA
CHCl$_3$                     (THF)                          (TFT)                    (CHCl$_3$-TFT)

1µm and 2µm round-flat convex

homogeneous film

3µm and 8µm round-flat convex

1µm round-flat aggregates

500 nm                  1.3 nm                         42 nm                         1.5 nm

homogeneous film
### Surface chemical composition

<table>
<thead>
<tr>
<th>Copolymers</th>
<th>Samples</th>
<th>Surface roughness</th>
<th>Chemical composition/wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ra/nm</td>
<td>RMSR/nm</td>
</tr>
<tr>
<td>s-POSS-(PMMA-b-PDFHM)$_{16}$</td>
<td>Powder</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Film/THF</td>
<td>4.9</td>
<td>50.4</td>
</tr>
<tr>
<td></td>
<td>Film/CHCl$_3$</td>
<td>6.1</td>
<td>82.8</td>
</tr>
<tr>
<td></td>
<td>Film/DMC</td>
<td>3.6</td>
<td>36.3</td>
</tr>
<tr>
<td>ap-POSS-PMMA-b-PDFHM</td>
<td>Powder</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Film/THF</td>
<td>18.5</td>
<td>100.6</td>
</tr>
<tr>
<td></td>
<td>Film/CHCl$_3$</td>
<td>23.6</td>
<td>143.0</td>
</tr>
<tr>
<td></td>
<td>Film/DMC</td>
<td>4.0</td>
<td>68.8</td>
</tr>
</tbody>
</table>
$\Delta f = -290 \text{ Hz}$;
$\Delta D/\Delta f = -0.27 \times 10^{-6} \text{ Hz}^{-1}$

$\Delta f = -1300 \text{ Hz}$;
$\Delta D/\Delta f = -0.077 \times 10^{-6} \text{ Hz}^{-1}$
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3.1 P1 and P2

**P1**
ap-POSS-PMMA$_{152}$-b-P(MA-POSS)$_{8.4}$

**P2**
PDMS-b-PMMA$_{408}$-b-P(MA-POSS)$_{8.2}$
<table>
<thead>
<tr>
<th>Materials</th>
<th>CA/g·cm$^{-2}$·s$^{-1/2}$</th>
<th>Water absorption/wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>R(D1)</td>
<td>$1.53 \times 10^{-3}$</td>
<td>6.89</td>
</tr>
<tr>
<td>P1-D1</td>
<td>$7.89 \times 10^{-5}$</td>
<td>2.46</td>
</tr>
<tr>
<td><strong>P2-D1</strong></td>
<td><strong>$6.58 \times 10^{-5}$</strong></td>
<td><strong>2.22</strong></td>
</tr>
<tr>
<td>R(D2)</td>
<td>$2.50 \times 10^{-3}$</td>
<td>11.15</td>
</tr>
<tr>
<td>P1-D2</td>
<td>$1.98 \times 10^{-3}$</td>
<td>8.42</td>
</tr>
<tr>
<td><strong>P2-D2</strong></td>
<td><strong>$1.47 \times 10^{-4}$</strong></td>
<td><strong>5.95</strong></td>
</tr>
</tbody>
</table>
$ap$-POSS-$\text{PMMA}_{152}$-$b$-$\text{P(MA-POSS)}_{8.4}$

$\text{PDMS}$-$b$-$\text{PMMA}_{408}$-$b$-$\text{P(MA-POSS)}_{8.2}$

$SCA = 128.6 \pm 3.6$

$SCA = 138.9 \pm 2.4$
$a_{p}$-POSS-PMMA$_{152}$-b-P(MA-POSS)$_{8.4}$

PDMS-b-PMMA$_{408}$-b-P(MA-POSS)$_{8.2}$

$SCA = 122.9 \pm 2.1$

$SCA = 128.7 \pm 1.6$
D1-

R(D1) 60.94% wt
P1-D1 3.43% wt
P2-D1 0.07% wt

D2-

R(D2) 24.66% wt
P1-D2 20.23% wt
P2-D2 23.88% wt

9 cycles for salt-crystallization

60 cycles for freeze-throwing
3.2 Hydrophobic application

Untreated  THF  CHCl₃  DMC

ap-POSS-PMMA-b-PDFHM
The contact angle (CA) of the stones after treated by the acid (pH=1) and alkali (pH=14)
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