Effect of Photoelectron on the Condensed Film of Poly(oxypropylene)amine Intercalated Silicates

Rong-Jer Lee', Wen-Tung Cheng',*, Jiang-Jen Lin'

1Department of Chemical Engineering, National Chung-Hsing University
250 Kuo Kuang Rd. Taichung 402, Taiwan, R.O.C.
2Institute of Polymer Science and Engineering, National Taiwan University,
Taipei 10617, Taiwan, R.O.C.

In this paper, photoelectron effect is applied to describe the reaction mechanism of macroscopic orderly stacking new crystalline from the poly(oxypropylene)amine modified clays. With X-ray fluorescent irradiates the condensed film of poly(oxypropylene)amine intercalated smectite silicates, a special inhomogeneous Si photoelectron (102.1 electron volts) concentration pattern was revealed. Silicone with shifted electron binding energy on the surface of the organo-silicates causes the photoelectron energy differentiated. Analysis of the FTIR vibration spectrums show no new chemical bonding assigned to the organo-silicate condensation. It is proposed the radius of ionic outer shell of silicone was altered as the poly(oxypropylene)amine intercalated montmorillonite proceeding a organo-mineral polymerization by self assembly process. Optical polarized microscope and X-ray diffraction pattern also confirmed the transformation of random particulate to a special nematic texture of organo-clay hybrid polymer.

keywords : photoelectron, organo-silicate, poly(oxypropylene)amine

1. Introduction

X-ray photoelectron (XPS) is usually used for surface chemical quantitative analysis and typically examines the top surface structure of a solid material. Survey scans was obtained to determine the elements present at or near the surface of the powder fillers. XPS wide scan spectra of both untreated and treated clay fillers are shown [1]. The reaction of organoammonium to clay minerals has been studied extensively because both organoamine and clays are common components in nature [2-4]. Montmorillonite layered silicate clay can be modified by an ultraviolet irradiated photoacid reaction with cationic iodonium salt [5], and also positive charged alkylammoniums [6-9]. The bulk properties [10-14] of the interlayer reaction of organoammonium and clay were well established by vibration spectrum and X-ray diffraction analysis.

To study inter-particulate polymerization of organo-silicate monomer, a secondary polymerized condense film of organo-silicate is synthesized and irradiated by monochromatic X-ray (hv), an electron of silicone composition is expelled out of element’s atomic shell. The kinetic energy (Ekin) of the expelled electron is measured by an electron spectrometer. For element with specific surrounding, the binding energy (Ebind) of the electron is then simply given by the relationship [15].

\[
E_{\text{bind}} = h\nu - E_{\text{kin}} \tag{1}
\]

The element’s chemical surrounding of material surface is determined by analyze the binding energy. Since the molecular bonds are generally not purely covalent but at least partly ionic. In reality the charge is mainly transferred to the surrounding ions, and assuming that these can be represented by a uniformly charged spherical shell of radius R as
illustrated in Fig. 1a,

Fig. 1. The photoelectron model of effective charge effect for silicone center atom and an approaching ammonium outer spherical shell (a) proposed larger outer shell radius R for POP/MMT monomer with 58Å d-spacing and (b) shorter R for polymerized POP/MMT with 42Å d-spacing.

The effective energy shift (ΔE bind) would be estimated by

$$\Delta E \text{bind} \sim \left( \frac{Q}{4\pi\varepsilon_0} \right) \times \left( \frac{1}{r} - \frac{1}{R} \right)$$  \hspace{1cm} (2)

where Q is the charge of the central ion, assumed to be distributed uniformly on a sphere of radius r, is removed to infinity, the potential inside that shell would be changed by $Q/(4\pi\varepsilon_0)$. This simple model gives a qualitative explanation of the shift in the binding energy.

The X-ray photoelectron scan is applied to analyze ionic surrounding perturbation of silicone as organo-clay self-assembly to hybrid polymer. The vibration band of organic-inorganic polymer and phase transformation of the polymerized hybrid material was also identified.

2. Experimental

The preparation for the organo-silicates was reported previously [12]. Typically, Na⁺-montmorillonite with (Na⁺-MMT, 10g, cationic exchange capacity CEC=1.15 mequiv/g) was vigorously dispersed in 1 liter of de-ionized water at 80 °C. The slurry was added with amine salts prepared from the poly(oxypropylene)amine Mw 2000 (POP) with 33 units of propylene oxide (23 g, 11.5 mmol) and equivalents of hydrochloric acid in water. After being vigorously stirred at 80 °C for 5 hrs, the precipitation was collected at room temperature, washed thoroughly with warm water/ethanol, and dried in vacuum. The intercalated MMTs were analyzed by X-ray diffraction, to have a d-spacings of 58.0 Å, and assigned as POP/MMT intercalated crystalline. The mass losses had been measured to determine weight fraction of POP/MMT by Thermogravimetric analysis, the highest calcination temperature of the poly(oxypropylene)amine is 800°C. The properties of POP, MMT and the intercalation POP/MMT was shown in Table 1.

<table>
<thead>
<tr>
<th>monomers</th>
<th>Formula</th>
<th>Basal spacing (Å)</th>
<th>Primary dimension (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Montmorillonite</td>
<td>Na₀.5A₀.₅M₀.₂5Si₂O₅(OH)₀.₅</td>
<td>14</td>
<td>100</td>
</tr>
<tr>
<td>(MMT)</td>
<td>nh₂O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poly(oxypropylene)</td>
<td>H₃NC(CH₂)₃NH₂</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>amine (POP)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>POP/MMT intercalation</td>
<td>POP(6)/MMT(27)¹</td>
<td>58</td>
<td>100</td>
</tr>
</tbody>
</table>

¹Weight fraction: organic composition/silicate is measured by TGA.

POP/MMT powder is prepared to be as monomer of a hybrid polymerization in self-assembly process.

The self-assembly polymerization in the water/toluene interface was performed by dispersing POP/MMT powder in toluene, carefully pouring to the surface of distilled water. The same solution was allowed to evaporate the upper toluene phase completely at room temperature to obtain thin dry film, evaporation of toluene takes at least 14 days to dry. The film was further dried at 80 °C for 5 hrs before the examination by polarized optical microscope, Scanning Electron Microscope (SEM, Topcon, ABT 150S).

The Photoelectron mapping of silicone is scanned by Electron Spectroscopy for Chemical Analysis (ESCA), a function of Topcon ABT 150 with AlKα light source. The tested sample is prepared as experimental process of hybrid polymerization and the photoelectron 102.1 eV is assigned to Si element of organo-silicates.

3. Results and Discussion

For the polymerization of organo-silicate to get orderly alignment nematic phase from smectite clay, special treatment, such as spin-coat concentrated suspension to an radial aligned film on quartz [16,17], is necessary.

In this work, the hydrophobic acidified poly (oxypropylene) amine intercalated montmorillonite (POP/MMT) powder was well dispersed into clear toluene solution, and allowed to condense in toluene/water interface to form a thin film structure through solvent evaporation. The liquid/liquid interface was functioning to align the organo-clay
monomer to the specific director direction of interface. Gravitational force and electrostatic attraction cause the monomer to orderly sedimentation. Comparing with the reported techniques such as spin coating or concentrated suspension to get crystalline meso-phase, this self-alignment polymerization in liquid-liquid interface has advantages to provide nano-metric control of organo-inorganic hybrid materials, as shown in Fig. 2.

Fig. 2. Condensed polymerization of intercalated POP/MMT on toluene/water interface.

To analyze the element surrounding of this polymerized hybrid organo-silicate, element silicon is mapping by Electron Spectroscopy for Chemical Analysis with AlKα 15KV. The condensed polymerization film of poly(oxypropylene)amine intercalated montmorillonite shows islanded inhomogeneously image. The bright dotted area is assigned to be rich of target silicone (102.1 eV), in contrast with dark shade of depleted target silicone, the two dimension image is recoded as shown in Fig. 3.

Fig. 3. Element silicon mapping the condensed polymerization film of poly(oxypropylene)amine intercalated montmorillonite, T. scanned by Electron Spectroscopy for Chemical Analysis with AlKα 15KV.

The inhomogeneous Si photoelectron concentration pattern was revealed with two distinct areas. A chemical shift of silicone should be involved in the condensed polymerization process of poly(oxypropylene)amine intercalated smectite silicates. The chemical surrounding of silicone was changed as ammonium of POP approaching the anionic silicone of MMT.

The hybrid polymerization is a chemical or electrostatic interaction between the –NH₂⁺ of acidified poly (oxypropylene) amine and Si-OH of montmorillonite. To confirm the reaction mechanism, the condensed film was examined with vibration adsorption of FTIR (Fig. 4).

Fig. 4. Fourier Transfer Infrared spectra of (a) MMT (b)POP/MMT condensed polymerization film.

The polymerization of intercalated organo-silicate showed changes in intensities of adsorption bands and an occurrence of new ones at 2930 - 2859 cm⁻¹ due to asymmetric and symmetric C-H stretching bands of propylene oxide, respectively. The band presents near 1600 and 1450 cm⁻¹ corresponding to symmetric deformation vibration of the NH₂⁺ suggested that amino groups should be protonated, resulting from the acidified interaction of polyoxypropylene amine with OH of silicate. The band 1630 cm⁻¹ assigned to δ(OH) show water is present in MMT and intercalated MMT. The infrared spectra at 3447 cm⁻¹ attributed to O-H stretching of hydroxyl groups of water associated to the hydration and the silanol groups bonded to the native matrix and the stretching vibrations corresponding to Si-O-Si and Si-O-Al bonds that appeared at 997 cm⁻¹.

The specific adsorption of NH₂⁺ or Si-O-H hydration in new infrared band assignment for organo-silicate hybrid polymer was proposed to be major reaction. The hybrid reaction is assumed to be an electrostatic aggregation growth by self-assembly on liquid/liquid interface.

The interaction between polyions and anionic silicone of clay nano-plates imposed anchoring force on particulate monomer to form hybrid
polymer. The condensed polymerization reaction of POP/MMT would also compress the spacing between the polymeric ammonium NH$_2^+$ and anionic silicone as shown in Fig. 1a and 1b. The radius R of ionic outer shell may be altered by polymerized compaction, and the effective energy $\Delta E_{bind}$ is then shifted with $(1/ \ r \ -1/\ R)$ factor of equation (1). The condensation reaction of hybrid organo-silicates transferred NH$_2^+$ to the surrounding of hydrated Si-O-H, and assuming that these can be represented by a uniformly photoelectron chemical shift of dark shade formation, as shown in Fig. 3.

Polymerization of self-assembly organo-silicates shown compactness effect to ion charge distribution and may also compressed d-spacing of layered. A well-aligned d-spacing deduced from the Bragg equation (3) displays in X-ray scattering pattern of dried POP/MMT monomer power, as shown in Fig. 5a and 5b.

![X-ray Diffracting Powder Pattern](image)

**Fig. 5.** X-ray diffracting powder pattern of (a) POP/MMT powder (b) POP/MMT self-assembly polymerized on toluene/water interface.

$$d = \frac{n \lambda}{2 \sin \Theta}, \quad (3)$$

here $\lambda$ is CuK$\alpha$ light wavelength; and $\Theta$ is the diffraction angle of XRD.

The intercalated POP/MMT show an orderly structure of [001] Bragg peaks and basal spacing of 58 Å. The hybrid polymer of the same material after the self-assembling in the toluene/water interface, show n= 3 to 5, and the basal spacing is 42 Å, which is smaller than the original intercalated MMT powder pattern. It seems the polymerization stacking of smectite POP/MMT in bipolar interface affects a higher polarity stress on [001] layer silicate and the face-to-face packing, so the basal spacing is smaller than the primary smectite particle. The polarity stress applied on [001] layer silicate can also applied on the ionic layer distance of silica, as comparable to the ion pair distance of Fig. 3.

The self-assembly of poly(oxypropylene)amine intercalated MMT shows a new Bragg peak in Fig. 5b, and a secondary crystallization phase [010] is assuming to support the macroscopic order texture formation of hybrid organo-silicate polymer. Under the examination of optical polarized microscope and electron microscopy, islanded crystalline with dimension around 100 um was observed spreading on the condensed film, as presented in Fig. 6.

![Optical Polarized Microscope Image](image)

**Fig. 6.** A condensed polymerization film of poly(oxypropylene)amine intercalated montmorillonite show (a) crystalline structure by SEM, (b) scattered nematic texture by optical polarized micoscope.

Comparing the conformation of islanded crystalline with the dark shade of photoelectron mapping, it is found the self-assembly polymerization of organo-silicate is in specific crystallization form. Through the organo-silicate template on liquid/liquid interface, a high orderly epitaxial structure of POP/MMT polymerization is created. It shows scattered bright islands under cross polarizer optical microscope and has found a specific nematic texture of birefringence.

The nematic texture of poly(oxypropylene)amine intercalated MMT was proposed that the hybrid condensation should be surface anchoring on liquid/liquid interface, which is assuming the face platelets of layered silicate template on toluene/water interface as crystalline seeds. The adhering force of ionic bridges between the polymeric ammonium NH$_2^+$ and hydrated Si-OH of clay plate surface, supporting the dispersed organo-silicates self-assembly to a face-to-face fashion stacking.

The face-to-face stacking of POP/MMT would decrease the X-ray exposure area on [001] phase. And alternatively, the side face of new hybrid polymer structure is accumulating on surface as self-assembly reaction proceeds (Fig. 7).
Fig. 7. X-ray irradiates on (010) phase of self-assembly nematic polymerization of POP/MMT

The side face is layered structure of poly(oxypropylene)amine and silicate, and most of the anionic silicone site would be surrounding by cationic organoammonium. The new conformation of organo-silicate shows enhancing depletion of photoelectron Si(102.1 eV) for target silicone atom.

**Conclusion**

Through the photoelectron model of effective charge effect for silicone center atom and an approaching ammonium outer spherical shell, this study has identified the self-assembly polymerization of organoammonium-silicate in toluene/water interface to obtain some significant results as summarized as below:

1. ammonium NH$_2^+$ and hydrated Si-OH is an electrostatic reaction.
2. the d-spacing of [001] phase for self-assembly stacking poly(oxypropylene)amine intercalated montmorillonite on liquid/liquid interface may be compressed from 58Å to 42Å.
3. the binding energy differentiation may be correlated to the radius of cationic outer shell which surrounding the silicone atom is assumed to be altered by interlayer compaction.
4. as the hybrid polymerization proceeds, the conformation of hybrid polymer is found to be changed.
5. the face-to-face packing of smectite monomer decreased the exposure area on [001] phase when irradiated by X-ray fluorescent.
6. the organic and inorganic stacking in [010] phase displayed lower possibility of Si photoelectron effect with the higher ammonium content beside the silicone atom.

**References**