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Synthesis and properties of polyimide/organo clay and polyimide/polyaniline-modified clay nanocomposites

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Abstract

Poly(amic acid) (PAA)/organo clay nanocomposites and PAA/polyaniline-modified clay nanocomposite were prepared by in situ polymerization processes. The progress of condensation polymerization was followed by measuring the shear viscosity for both neat and filled PAA polymerizing solutions. The shear viscosity of the polymerizing solution increases quickly during the initial stage of polymerization followed by a slight increase all the stage of polymerization. The presence of clay expedites the initial stage of polymerization reaction as shown by a much higher shear viscosity for PAA/PANi clay polymerizing solution during the initial 30 mins of reaction, but results in a lower solution viscosity after a long polymerization time. The optical property for the poly(amic acid) solution with and without clay was studied by using UV/Vis spectrophotometry. Both PAA/organo clay and PAA/PANi clay solutions showed well resolved absorption in the visible region, between 500 and 600nm. There was no noticeable UV/Vis absorption peak in the visible region for samples prepared by ex situ method.

Polyimide (PI)/clay coatings were cast from the PAA/organo clay and PAA/PANi nanoclay composite solutions onto steel and Al substrates, followed by thermal treatments at varying temperatures. The degree of imidization (DOI) of neat and filled PI resin was studied as a function of the curing temperatures by using the attenuated total reflectance infrared spectroscopy (IR-ATR). Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM) were used to determine the morphology of PI/clay nanocomposites. SEM images show much
larger clays for PI/organo clay nanocomposites than those for PI/PANi clay nanocomposites. TEM analysis shows that the clay platelets and tactoids are properly dispersed and oriented in the polyimide matrix. Wide-Angle X-ray Diffraction (WAXD) was utilized to analyze the structure of clays in the nanocomposites. The extent intercalation of clay improved with increasing imidization temperature and weight % of clay. The result suggests the existence of a hybrid clay structure in the nanocomposites cured at $T \geq 150^\circ$C: unintercalated or marginally intercalated, and highly intercalated or exfoliated clay platelets.

Corrosion inhibition properties for neat PAA, PAA/organo clay, and PAA/PANi clay nanocomposite coatings were tested by using DC Polarization (DCP). PI/organo clay coatings show superior corrosion inhibition properties. The corrosion rate decreases drastically as curing temperature and clay concentration increases for PAA/organo clay nanocomposites.
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Chapter 1 Introduction

1.1 Polymer matrix Nanocomposites

Nanocomposite material as a substitute to conventional material has been an interesting topic in both industry and academia for decades. Nanocomposites, typically organic/inorganic composites, are multiphase solid materials with one of the phases having one, two or three dimensions in nanometer-scale (1-100nm), or structures having nano-scale repeat distances between the different phases that make up the material [1-18]. The exceptionally high surface to volume ratio of the reinforcing phase and its exceptionally high aspect ratio enables nanocomposites to exhibit better properties when compared to the pristine polymers, such as higher modulus [2,3,7], enhanced thermal stability and conductivity [3, 30-32], improved solvent resistance [4], enhanced ionic conductivity [5], reduced gas permeability [3,6,33], and self-passivation [34].

Various kinds of host polymers have been studied as suitable matrix materials for nanofillers, including thermosets such as epoxy [6,9,10,20], thermoplastics such as poly(methyl methacrylate) [11,12,23], elastomers such as butadiene acrylonitrile copolymer [18], and conducting polymers such as polyaniline [17]. In the case of layered inorganic fillers, talc and mica had been traditionally attracted the most interest [24], while recent research has focused on montmotillonite (MMT)-based clays as reinforcing part of the polymer matrix [1-6, 19-23]. Significantly improved physical and chemical properties can be achieved by reinforcement with clays, provided that clays are well dispersed in the composites, and that the multiple phases
are well adhered [25,26].

1.2 Matrix: Polyimide (PI)

Polyimide (PI) is considered to be one of the most widely used high-performance polymers in microelectronic industries because of their outstanding tensile strength and elastic modulus, low coefficient of thermal expansion and dielectric constant, and good resistance to organic solvents [27,28]. The applications of PI include interlayer insulation films, buffer coating films, alpha-ray shielding films, and alignment films for liquid crystal displays [29].

The formation of PI can be divided into two steps: 1, Polymerization reaction to form the precursor, poly(amic acid) (PAA); and 2, Imidization (dehydration) reaction converting PAA to PI. The reaction scheme that shows the formation of PI is shown in Figure 1.1. Imidization is a cyclo dehydration process accomplished thermally by heating treatment of poly(amic acid) on the substrates or chemically. A high imidization temperature around 300°C is usually needed to provide a high degree of imidization of PI.

1.3 Filler: Clay

1.3.1 Organo MMT Clay

Montmorillonite (MMT) is currently under extensive study as fillers for polymer matrix composite materials [35-38]. MMT is mineral clay that possesses a crystal structure made up of stacked 2-dimensional hydrated aluminosilicate layers. Each layer has a width of 10Å, and is comprised of two silica tetrahedral sheets
sandwiching an alumina octahedral sheet by edge-sharing. The galleries between each two clay layers within a stack contain cations, which balance the charge deficiency resulting from the cation substitution of Si\(^{4+}\) by Al\(^{3+}\) in the clay layers.

Natural MMT has Na\(^+\) or Mg\(^{2+}\) interlayer cations. The organophobicity of natural MMT confines its application as fillers. To improve the compatibility of MMT with
polymer matrix, the interlayer cations are exchanged by organic ammonium cations (modifier). Different modifiers lead to diverse clay gallery spacing. The organically modified MMT clay used in this study is Cloisite 15A, whose modifier is quaternary ammonium cation with 2 methyl and 2 hydrogenated tallow branches as shown in Figure 1.2. The hydrogenated tallow (HT) contains 65% C18, 30% C16, and 5% C14 with chloride anion. The dry powder has particle sizes that range from 2μm to 13μm. Through the cation exchange, the gallery spacing is broadened from 10.4Å for sodium clay, to 31.5Å for organically modified clay Cloisite 15A. The interlayer modifiers anchor in the clay with their cationic head groups bonded to the clay layers, while the alkyl segments fills and expands the gallery [36-38].

![Figure 1.2](image)

*Figure 1.2 Structure of MMT clay and the organic modifier of MMT Cloisite 15A*

1.3.2 Polyaniline Modified Clay (PANi clay)

1.3.2.1 Intrinsically conducting polymer (ICP)
Intrinsically conducting polymers such as polypyrrole (PPy), polyaniline (PANi) and poly(p-phenylenes) are attracting increasing attention because of their unique high electrical conductivity and numerous potential applications including rechargeable batteries [40-41], electrochemical capacitors [41], electrochromic devices [42], electroluminescent devices [43], and corrosion inhibition [44-47]. ICPs are conductive due to the conjugated structure of polymer chain backbones. The doping of ICPs introduces extra electrons or positively-charged holes to carry electric current, and enables the delocalization of electrons along the π bonds. The conductivity of ICPs can be raised from $10^{-9} - 10^{-5}$ S/cm for a typical insulating material, to $10^5$ S/cm, which is in the same range of conductivity of metals [48, 49].

PANi is a conducting polymer which exists in a variety of oxidation states that differ in chemical and physical properties. The chemical formula of PANi is shown in Figure 1.3. The emeraldine base (EB), with $n$ and $m$ equal to 0.5, is regarded as the most useful form of PANi upon doping, due to its excellent electron conductivity and the high stability at room temperature. The conductivity of around $10^{-10}$ S/cm can be drastically increased by protonation (Figure 1.4) in aqueous acid (pH ~ 0) to around $10^5$ S/cm [50-55].

For corrosion inhibition, PANi can mediate the electrons from the metal substrate to the oxygen in the environment and passivate the metal through self-redox reactions. Combining PANi with different hosts produces hybrid materials that can render many superior properties. In some previous studies, polyaniline has been blended with other polymers, such as epoxy, polystyrene and polypyrrole, and also MMT clays, to deliver
highly conductive hybrids. [61-72]

1.3.2.2 PANi Clay

The weak mechanical properties of PANi stimulated the study of blending of PANi with various polymers as well as insulating fillers like clays. [61-72] PANi-modified clay is made from first-step intercalation process, which is an in situ polymerization and doping procedure of PANi in the presence of clay as shown in Figure 1.5. PANi chains are formed inside the inorganic clay galleries, broadening the gallery space. In
comparison with the corresponding organoclay, PANi clay has much larger gallery space, besides higher conductivity due to the addition of PANi. However, there could be a reduction in electrical conductivity of doped PANi, because the clay layers can interfere with the doping process and the chain-chain interactions of PANi, leading to lower electrical conductivity [56].

**Figure 1.5** First step intercalation

### 1.4 Polyimide/Clay Nanocomposites

Incorporating clays (both organo clay and PANi modified clay) in PI matrix can largely enhanced the mechanical and chemical properties. The performance of PI/clay
nanocomposites varies widely depending on the level of intercalation and exfoliation of clay, the size of the alkylated ammonium ions or the intercalated PANi chains, the silicates present in the clay, and the PI matrix [57-59]. Shown in Figure 1.6 are the prevalent dispersion types of clay including intercalation, exfoliation, and immiscible (phase separated) fashion [4]. Polymer chains intercalated in clay tactoids will expand the gallery space, producing intercalated clay stacks and exfoliated single clay layers. A microcomposite is obtained if polymer chains are not intercalated between the silicate sheets, and the clay is dispersed in the form of tactoids. Such poor dispersion of clay will lead to poor mechanical properties resulting from stress concentration, and the properties of the composites cannot be maximized.

![Figure 1.6 Dispersion types of clays in polymer matrix](image)

(a) Intercalated  (b) Exfoliated  (c) Immiscible

Of particular interest are approaches that yield morphology with high extent of intercalation and exfoliation. According to Delozier et al. and Yeh et al., exfoliated and highly intercalated clay structure can be obtained by using in situ polymerization technique, which allows the polymer chains to form in the presence of clay [57,60,85,86]. Ex situ polymerization was observed to result in agglomeration that cannot be broken by using physical mixing coupled with high frequency sonication, and leads to poor dispersion of clay [57,60].
The fraction of exfoliated clay could be further improved by enlarging the size of the organic modifiers or by introducing additional polymer chains into the clay gallery through a second step of intercalation polymerization (double intercalation polymerization) technique. Besides rendering high extent of intercalation of clay, PI/PANi-modified clay (PI/PANi clay) nanocomposites have other advantages: 1st, polyimide as a host polymer has good mechanical properties and enhanced hydrophobicity; 2nd, polyaniline is a good conducting polymer, so that the hybrid may be semi-conductive, and may find wider applications; and 3rd, clay as fillers improves the physical and chemical properties of the nanocomposites. Several studies have reported novel techniques to produce PANi/clay nanocomposites, their characterization and the investigation of their electrical properties and mechanical properties [61-74]. However, little previous study was focused on PI/PANi clay nanocomposites made by using two-step intercalation (double intercalation) polymerization (DIP) technique. [79]

This study uses in situ intercalation condensation polymerization to produce PI/organo Clay nanocomposites and PI/PANi clay nanocomposites with enhanced extent of intercalation of layered-silicate clay in the polyimide matrix. As shown in Figure 1.7, the DIP technique comprises two steps: 1st, the synthesis of polyaniline-modified clay (PANi clay 15A) powder by mixing polyaniline, cloisite 15A powder, and dopant together; and 2nd, synthesis of PI/PANi 15A nanocomposites by using in situ intercalation condensation polymerization of PI and PANi 15A clay powder. The previous addition of PANi expands the d-spacing of clay stacks, produces a system with more exfoliated clays than the clays in PI/organo clay system.
Figure 1.7 Double Intercalation Polymerization producing PI/PANI 15A nanocomposites
In this study, the effect of intercalation polymerization of PAA reaction was evaluated on the structure and orientation of organo clay and PANi clay composites in a PI matrix. The rheological behavior of neat PAA and PAA/clay solutions was determined, and the structure and the morphology of clay in PI were studied.

Delozier et al. showed that both the structure of clay in the PI matrix are affected by the processing temperature \cite{57,60}. In this study, the imidization temperature and weight percent of clay were varied in order to understand their effects on the structure and orientation of clay. The degree of imidization (DOI) was calculated. The clay d-spacing and the number of layers of clay sheets per stack were shown to vary with varying imidization temperature and weight % of clay. The imidization temperature was varied from 70°C to 250°C, while the weight percent of clay was varied from 2 to 20%. The results show that the structure of clay in PI/clay nanocomposites can be controlled by the preparation methods. Unlike the results from previous studies, this study provides evidence that high imidization temperature has the ability to improve both the structure and orientation of the clay structure. PAA and PAA/clay nanocomposites heat treated at high temperatures (\(\geq 150^\circ C\)) resulted in more polydispersed clays, containing both exfoliated, and moderately intercalated but oriented clays. Such coexistence is rarely observed in previous studies. The improved extent of intercalation of clay can be proved by the reported significant decrease in viscosity of the nanocomposite solution over the neat PAA solution. Furthermore, the addition of PANi improves the systems by additional broadening of the clay galleries.

Also studied was the optical behavior of PAA/organo clay and PAA/PANi clay
solutions. It was shown that both PAA/organo clay and PAA/PANi clay solutions show interesting optical activity in the visible region between wavelength of 500 nm and 600 nm. The doped PANi improves the optical activity for PAA/PANi clay nanocomposites, and the intensity of the UV/Vis peak increases with the PANi Clay content. Like PAA/PANi clay composites, organo clay is able to form a complex with PAA, and thereby increases the optical activity, which is indicative of electro activity, of PAA/organo clay nanocomposites. The conversion between benzenoid and quinoid structure may be responsible of the increased electron activity in the PAA/organo clay nanocomposites.

1.5 Corrosion resistant properties for PI/clay nanocomposite coatings

Another topic is the corrosion resistant properties of the PI/clay nanocomposite coatings. The AA 2024 used in this study is an Al alloy (90.9% Al / 4.9%Cu / 0.1% Cr / 0.5% Fe / 0.9% Mn / 1.8% Mg / 0.5% Si) [73] with wide applications in the aerospace industry. The electrochemical reactions governing the corrosion of aluminum in neutral atmosphere are as follows:

\[ Al \rightarrow Al^{3+} + 3e^- \] .........................Anodic Reaction

\[ O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \] ..........................Cathodic Reaction

Corrosion protection can be achieved by two methods:

1. Cathodic protection:

The use of a sacrificial material as an anode or an external power supply can decrease the potential of the metal, slow its rate of oxidation.
2. Anodic protection:

Produce a protective, usually passive, layer on the metal surface, and/or reduce the rate of the reduction process.

Al alloy 2024 has two phases including aluminum and the Cu-rich intermetallic phase. These heterogeneously distributed phases throughout the alloy generate local galvanic cells on the alloy surface, resulting in increased probability for localized corrosion attack. The Cu phase plays the role of a cathode, and its contact with water and oxygen enables the oxidation reaction of the Al as anode. Since the alloy has both the anodic and cathodic sites in constant electrical contact, the only way to inhibit corrosion is to eliminate the contact with electrolyte and the cathodic reactant. The main method to prevent such corrosion is by a passivating coating on the surface of the metal to suppress the cathodic reaction by limiting the diffusion of the electrolyte, oxygen and water to the substrate. It also limits the transport of electrons to the metal interface.

A typical coating utilizes organic or inorganic barrier to inhibit corrosion. Polyimide is known for its hydrophobicity. The addition of organo clay to PI assists increased the tortuosity of the diffusion of water and oxygen. The conjugated structure (alternating single and double bonds along the backbone) of polyaniline allows delocalization of electrons when doped. Therefore through redox reactions, PANi mediates the electrons between the metal substrate and the oxygen in the environment, passivating the metal. In terms of corrosion inhibition, the new hybrid of polyimide/polyaniline-modified clay nanocomposite can take the advantage of polyimide
as a host polymer with good mechanical properties and hydrophobicity, polyaniline as a good conducting polymer, and clay as barriers of permission of moisture and oxygen.

DC polarization (DCP) used in this study is a potential dynamic corrosion testing technique. A polarized electrode generates currents in the electrolyte via electrochemical reactions that occur at the electrode surface. The circuit is made up of the cathodic reaction, the anodic reaction, and the current flowing via both the wires outside and the electrolyte. The open circuit potential is the potential at which the cathodic and anodic currents are equal. Tafel plots are generated by measuring the current density on a logarithmic scale as a function of applied potential.

The corrosion potential (Ecorr) and the corrosion current (Icorr) are obtained from the Tafel plots. The corrosion rate and the corrosion resistance are calculated accordingly.
Tangents are drawn to the anodic and cathodic curves of the Tafel plot, and the intersection is projected on the X and Y axes to give the Icorr and the Ecorr values. The over-potential $\eta$ is calculated using the following equation:

$$\eta = \pm \beta \log \frac{i}{i_0}$$

Where $\beta_a$ & $\beta_c$ are the Tafel proportionality constants for the anodic and the cathodic reactions, respectively, and $i$ and $i_0$ are the current density and the exchange current density, respectively. The polarization resistance is calculated using the Stern-Geary equation:

$$R_p = \frac{B}{I_{corr}}, \quad B = \frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c)}$$

The corrosion rate is calculated accordingly using the following equation:

$$CorrosionRate = C\left(\frac{EW \cdot I_{corr}}{d \cdot A}\right)$$

Where $C$ is the conversion constant of $3.268 \times 10^3$, $EW$ is the equivalent weight of the sample in gm/equivalent, $A$ is the sample area in cm$^2$, and $d$ is the density of the sample in g/mm$^3$.

1.6 Objectives of this thesis -- summary

The objective for this project is to develop corrosion resistant and environmentally benign coatings on metals. According to previous studies, polyimide/organo clay nanocomposite coatings exhibit promising properties in corrosion inhibition. [80-84]
However, the coatings were not optimized, and intensive efforts have been made to improve the compatibility of clay fillers to the polyimide host, and the structure of clay in the matrix. [75-77, 87-100] Therefore one aim of this study is to study and optimize the structure of clay by varying several parameters during the synthesis and preparation of the coatings.

Also, introducing polyaniline as a conductive polymer by using double intercalation polymerization technique to further improve the structure of clay, the imidization of PI, and the conducting properties of the coatings, thereby enhance the corrosion resistant properties of the nanocomposite coatings.
Chapter 2 Experimental

2.1 Materials and synthesis process

Cloisite 15A used in this experiment is a natural montmorillonite clay modified with dimethyl dehydrogenated tallow quaternary ammonium, and was purchased from Southern Clay Products Inc. The monomers used in the synthesis of PAA are 4,4’-Oxydianiline (ODA) (97%), and pyromelittic dianhydride (PMDA). 1-Methyl-2-Pyrroldinone (NMP) was used as solvent. The flowchart of the synthesis process is shown in Figure 2.1.

![Figure 2.1 Flowchart of the synthesis of PAA/clay nanocomposites](image)
Both organo clay (Cloisite 15A) and polyaniline-modified clay 15A were used in the preparation of PI/clay nanocomposites. The polyaniline-modified clay (PANi clay) powders were prepared previously by Stephen Hall [74]. According to Stephen Hall, aniline was mixed with 0.2 mol/L dopant (CSA) in distilled water and the mixture was magnetically stirred at 20°C till a homogeneous dispersion was obtained. 0.5g Cloisite 15A clay was added into the mixture, followed by the drop wise addition of a 0.6 mol/L ammonium persultate (APS) water solution. The prepared mixture was stirred overnight at 5°C for full polymerization, and was thereafter filtered. The preparation parameters were listed in Table 4. The precipitate was dried at 100°C in a vacuum oven for 3 hours to obtain PANi 15A powder.

0.025 mol of ODA was dissolved in 100 ml of NMP and placed in a three-neck flask maintained at 10°C with stirring for 30min. Clay, either organo clay 15A or PANi clay 15A, was then mixed with the diamine solution and stirred for 6h at 10°C before polymerization. PMDA was thereafter added into the mixture, which was then kept under stirring for 15h at 10°C. The concentration of clay was varied from 2 to 20 wt%.

The polymer and nanocomposite solutions were ultra-sonicated for five minutes, and then cast onto glass, steel (Fe3C), and Al substrates, respectively, before curing at 70°C for 5h. The substrates were cleaned in advance using Alkaline cleaner purchased from Chemetall Corp to remove the grease on the surface of the substrates and the oxide layer of Al. The cure temperature was subsequently raised to 150°C for 2.5h.

2.2 Characterization
The progress of condensation polymerization was followed by a time based viscosity measurements on aliquots drawn from the polymerizing solutions. The viscosity of the polymerizing solution was measured as a function of polymerization time by using the Brookfield Viscometer (DV I). The Viscometer spindle speed was varied from 1 to 100 RPM. Viscosity measurement was carried out at ambient temperature. The optical properties for both PAA/organo clay solution samples and PI/PANI clay solutions were determined by using Cary 50/Bio UV/Vis absorbance spectrophotometer. The wavelength range between 190 nm and 800 nm was used.

Attenuated Total Reflectance Infrared Spectroscopy (IR) was used to determine both the chemical structure of PAA and the extent of imidization of PI. IR spectra of the coatings and free-standing films were collected at a resolution of 4 cm\(^{-1}\) after 32 scans per sample between 4000 and 400 cm\(^{-1}\). A background spectrum of a bare-polished steel substrate was subtracted from the acquired spectrum for the coating cast on steel.

Wide Angle X-ray Diffraction (WAXD) was carried out by using the Philips X-Ray Diffractometer located at the University of Cincinnati. The X-Ray Diffractometer for WAXD is equipped with a Cu-K radiation source. WAXD tests were carried out at a wavelength of 1.54Å between \(\theta\) angle of 0.5° and 10° at a scan rate of 0.005°/sec.

Differential scanning calorimetry (DSC) was done with a Polymer Laboratories instrument. About 5 mg of each sample initially cured at 70°C for 5 hours was scanned from 25°C upto 300°C at a heating rate of 10°C/min under a nitrogen atmosphere. The thermograms were used to measure the heat of polycondensation and
imidization reactions and determine the peak temperatures for the polymerization and curing.

The structure of the free standing films was observed by using an FEI XL30 environmental scanning electron microscope (ESEM) and a JEOL JEM-1230 Transmission Electron Microscope (TEM). The SEM samples were coated with silver to enhance conductivity and microscopy was performed under the environmental mode. Secondary electrons were collected at an accelerating voltage of 20 kV. The ESEM pictures of the cross-section of the films were examined at a magnification of up to 100k to gain an insight into the structure and orientation of clay in the matrix. An accelerating voltage of 80kV was used for TEM observation.

DC polarization (DCP) test was used to analyze the corrosion resistant properties of the PI/clay nanocomposite layers coated on Al substrates. 10% NaCl solution was prepared in advance as the corrosive environment. Data was collected using an EG&G potentiostat model 273A equipped with a 352 softcorr III corrosion software.
Chapter 3 Results and Discussion

3.1 Degree of imidization (DOI)

The imidization reaction of PAA is a cyclization reaction that produces a cyclic imide functional group as shown in Figure 1.1. Of particular interest is the effect of curing temperatures and clay concentration on the imidization process. Previous studies have shown that clay can significantly enhance the imidization of PI [9]. The additional increase in the degree of imidization of PI in the nanocomposites is believed to be due to the increase in the surface area and available active sites [11] for dehydration and the cyclization reactions. The dispersion of clay platelets is therefore influential in that the clay dispersed in nano-scale provides better conditions that favor imidization. Improved physical and mechanical properties of PI/clay nanocomposites can be obtained at relatively low curing temperatures through the addition of well dispersed clay to the PI matrix.

Imidization of neat PAA, PAA/organo clay, and PAA/PANi clay nanocomposites was performed at varying curing temperatures. DOI was calculated as a function of curing temperature, clay type and weight percent of clay. A fully cured PI sample was obtained by heating PAA and PAA/clay nanocomposite films at 300°C for 10 hours under a vacuum atmosphere. The IR absorption peaks and the corresponding characteristic functional groups for PAA and PI are tabulated in table 1 [7]. Characteristic PI absorption peak at 1778 cm\(^{-1}\) due to the cyclic imide ring was used to calculate the degree of imidization in this study. Another characteristic PI absorption peak, due to the C-N-C tertiary amine functional group, is observed at
1378 cm\(^{-1}\). It should be noted that the wavenumber for IR absorption of C-N-C functional group covers the same IR region where the solvent, NMP, absorbs, and may affect the precision in the measurement of the degree of imidization. The phenyl group absorption intensity at 1495 cm\(^{-1}\) does not vary during curing, and was used to normalize the imide group absorption intensity.

### 3.1.1 PAA/organo clay nanocomposites

#### 3.1.1.1 Calculation using IR data

The IR absorption spectra for PI/organo clay nanocomposites containing 2wt% clay cured at varying temperatures are shown in Figure 3.1. A drastic decrease in the intensity of the peak at 1655 cm\(^{-1}\) with increasing curing temperature is observed, corresponding to the decrease in PAA functional group and the increase in the PI functional units, due to increased imidization. Also, the characteristic IR absorption peaks for organo clay 15A at 2925 cm\(^{-1}\) and 2860 cm\(^{-1}\) show decreasing intensity, indicating either decomposition, or replacement with PI chains. Characteristic polyimide peaks due to the cyclic imide ring are observed at 1778 cm\(^{-1}\).

The degree of imidization is calculated by using equation (1) [10,78], where “H” refers to the peak height, and “100%” refers to the extent of imidization of the fully imidized polyimide.

\[
\alpha = \frac{H_{1778}}{H_{1495}} \div \frac{H_{1778\_100\%}}{H_{1495\_100\%}}
\]

(1)

Deviations are introduced due to base line correction. Averages and deviations were
calculated and plotted. As shown in Figure 3.1, the intensity of the IR absorption peaks at 1778\,cm\(^{-1}\) increased with increasing imidization temperature. As shown in Figure 3.2, the DOI of PI containing clay varied around 10\% when the sample was cured at 70\,^\circ\text{C}, and remains low when cured at slightly higher temperature of 110\,^\circ\text{C}, followed by a subsequent sharp increase to 65\% ~ 85\% when the curing temperature was increased to 150\,^\circ\text{C}. A further increase in the curing temperature from 200\,^\circ\text{C} to 250\,^\circ\text{C} resulted in a moderate increase in the extent of imidization to 91\% ~ 99\%. In the presence of clay nanofillers, the PI/organo clay nanocomposite samples are nearly fully imidized at 200\,^\circ\text{C}.

Also shown in Figure 3.2 is the effect of weight percent of clay on the degree of imidization. The corresponding IR spectra for PI/organo clay nanocomposite coatings are shown in Figures 3.3. For PI/organo clay nanocomposites cured at 150\,^\circ\text{C}, as the clay content increased from 2\,wt\% to 20\,wt\%, the DOI increases by 20\%. The DOI increases sharply with clay concentration in the region between 110\,^\circ\text{C} and 200\,^\circ\text{C}. For PI/organo clay nanocomposites containing only 2\,wt\% clay 15A, the DOI is about 65\% at 150\,^\circ\text{C}, but increased sharply to 88\% when the wt\% of clay is increased to 20\,wt\%.

Within the range of my study, the addition of Cloisite 15A clay to the PAA resin significantly enhanced the imidization of PI in agreement with the literature [9]. The extent of curing of PI can be increased up to 88\% by adding about 20wt\% organo clay at a relatively low curing temperature of 150\,^\circ\text{C}.

3.1.1.2 Calculation using DSC data (Thermal properties)

Differential scanning calorimetry (DSC) is done on the free standing films of neat PI
and PI/organo clay nanocomposites containing varying clay concentrations. As shown in Figure 3.4, the heat flow curves show similar trend for all the samples indicating that they follow the same curing reaction process. After the first-stage stabilization process, the samples experienced an endothermic process, corresponding to imidization with negative peaks around 150°C. This imidization energy peak located between 140°C and 165°C, and is associated to the highest activity of dehydration reaction in agreement with the trend in the DOI obtained from IR data. The peak area of the heat flow curve calculated as a function of time gives the energy absorbed for the imidization reaction. As shown in Figure 3.5, the peak area increases with increasing clay concentration, indicating a higher extent of imidization in agreement with the DOI calculated using IR data.

3.1.2 PAA/PANi clay nanocomposites

Figure 3.6 shows the IR curves for PAA/PANi clay 15A nanocomposites resemble those for PAA/organo clay nanocomposites cast at the same temperatures. The characteristic peaks of PANi are shown at 3450 cm⁻¹, 1310 cm⁻¹, 1577 cm⁻¹ and 1495 cm⁻¹, and are attributable to N-H stretching, C-N stretching of a secondary aromatic amine, quinoid structure of PANi, and benzenoid structure of PANi, respectively. The peaks at 3450 cm⁻¹ and 1310 cm⁻¹ can also be found in PAA IR spectrum. The peak absorption corresponding to the quinoid structure in PANi is overlapped with the absorption peaks and the absorption background for PAA and PI.

DOI was analyzed as a function of curing temperature and clay concentration. Although the intensity of the peak at 1495 cm⁻¹ varies with varying PANi clay
concentration, it can be used to normalize the imide peak absorption for the
PAA/PANi clay nanocomposites containing the same amount of clay.

As shown in Figure 3.7, the DOI curve as a function of curing temperature for
PI/PANi clay nanocomposites resembles that for PAA/organo clay nanocomposites.
The DOI is 20% when the sample is cured at 70°C, while increases to 40%
subsequently when increasing the curing temperature to 110°C. The DOI thereafter
increases sharply to 97% after curing at 150°C, and remains nearly 100% at higher
curing temperatures. Like PI/organo clay, PI/PANi clay nanocomposites have the DOI
curve showing an increase in Sigmoidal shape with increasing curing temperature.

Also, by comparing DOI of both nanocomposites, the DOI is largely improved for the
PAA/PANi clay nanocomposites cured at the identical curing temperatures. At 150°C,
DOI for PAA/PANi clay nanocomposites is around 90%, which is higher than the DOI
below 85% for PAA/organo clay samples. The improvement is due to the enhanced
dispersion of clay (higher extent of exfoliation) as the dehydration sites favoring the
imidization reaction. [39]

Shonw in Figure 3.8 is the comparison of DOIs for both nanocomposites as a function
of clay concentration. It can be observed that the DOIs for both PI/organo clay and
PI/PANi clay nanocomposites increase with increasing clay concentration. By
changing the fillers from organo clay to PANi clay, the DOI is also significantly
improved.

3.2 Structure of clay – WAXD
3.2.1 PI/organo clay nanocomposites

3.2.1.1 Impact of curing temperature and solvent (NMP) on the d-spacing of clay

In order to gain some insight into the effects of processing conditions on the structure of clay 15A, the clay structure were examined by using the nanocomposite samples processed at different curing temperatures and weight percent of clay. Both dry clay powders and swollen clay were individually heated at predetermined temperatures and studied by using WAXD.

The comparison between the WAXD curves for untreated and heated clay powder 15A shown in Figure 3.9 indicates that a heating the samples at 250°C gives wider clay gallery spacing. The pristine powdered clay shows three diffraction peaks at 2θ angles of 2.8°, 4.5°, and 7.2°, corresponding to the d_{001}, d_{002}, and d_{003} reflections, respectively. The positions of the clay diffraction peaks are not coincident with those of a perfect lattice due to the mixed-layering of clay [4, 12]. After being baked at 250°C, the clay powder has a d_{001} peak shifting from 2θ angle of 2.8° to 2.5°, corresponding to an increase of d-spacing from 31.5Å to 35.3Å. The disappearance of the d_{002} peak indicates an increasing disorder of clay powder. A new WAXD peak appeared at 2θ angle of 6.3°, corresponding to clay stacks with narrower gallery spacing of 14.0Å. The narrowing of the clay gallery was reported to result from the partial thermal decomposition of the organic modifier, the aliphatic quaternary ammonium compound, contained in the clay gallery [6], as the decreased clay gallery spacing is still larger than that of 10.4Å for sodium clay.

The solvated organo clay powders were expected to swell in the solvent. Figure 3.10
shows the WAXD spectra for dry clay powder and the clay dispersed in NMP and cast onto a steel substrate and then heated at (i) 70°C and (ii) 250°C, respectively. The WAXD pattern for organo clay 15A dispersed in NMP and cast onto steel substrate followed by heating at 70°C for 5 h showed a single broadened primary peak with weak intensity at 2θ angle of 2.7°, suggesting an increase in the average d-spacing when compared with powder. The drastic broadening effect and the decrease in the intensity of this peak suggests a highly disordered and exfoliated clay structure similar to that observed in swollen mineral clay. For the NMP swollen organo clay cured at 250°C for 2.5 h, two distinctive diffraction peaks are shown at 2θ angles of 2.3° and 6.3°, respectively. The low 2θ peak is broadened and shifted from 2θ angle of 2.8° (for powder clay) to 2.4°, corresponding to a change in the gallery distance d₀₀₁ from 31.5Å to 36.8Å. This result shows that the clay suspension cast on steel and heated at 250°C has larger d-spacing than both the neat clay powder and the NMP swollen clay cured at 70°C. The d-spacing for the swollen clay powder after heat treatment at 250°C is only slightly larger than the unswollen sample (36.8Å > 35.3Å) cast at the same temperature, indicating that the main reason for the broadening is the heating of the samples at 250°C. This slight increase was hardly reported in previous studies [57,60], and may be due to the expulsion process of the solvent. The co-existence of both high angle and low angle peaks confirms that the swollen clay heated at 250°C has a disordered and polydispersed structure. The effects of heating on the samples include (i) the expulsion of most of the NMP solvent and the resulting expanded clay gallery; (ii) possible degradation of alkylated quartenenary ammonium ions [5] and the corresponding clay stacks with narrower gallery spacing; and (iii) enhancement of
the orientation of clay as shown by the prevalence of fewer, sharper and better resolved WAXD peaks.

3.2.1.2 PI/organo clay nanocomposites

The WAXD spectra for PI/organo clay nanocomposites are shown in Figure 3.11. The WAXD curve for clay dispersed in PAA matrix shows that the low $d_{001}$ peak has shifted to a lower angle than those for the pristine clay powders, the heated powders, and the NMP swollen clay samples. The low $d_{001}$ peak was shifted from 20 angle of 2.8°, for the pristine clay powder, to 20 angle of 2.6°, for PAA/organo clay nanocomposite coatings cured at 70°C, and to 2.2° and 2.1° for PI/organo clay nanocomposite coatings cured at 150°C and 250°C, respectively. The corresponding $d_{001}$ for the clays are 31.5Å, 34.0Å, 40.1Å, and 42.2Å, respectively. In comparison with clay powder that was swollen in NMP and heat treated afterwards at 70°C, 150°C and 250°C, the d-spacing for the clay in the nanocomposites cured at the same temperatures were significantly larger (42.2Å compared to 36.8Å for the samples cured at 250°C), suggesting that PI is intercalated into clay thereby causing greater separation of the gallery.

The broadening effect and the significant decrease in intensity of the low angle $d_{001}$ peak that occurred with increasing curing temperature shows an opposite trend from what reported in previous studies. [8,57,60] It is believed that at a low temperature (70°C), the structure of the clay stacks are disordered as indicated by the broadened $d_{001}$ peak, and the galleries of clays are expanded by the insertion of NMP-solvated PAA into the galleries.
As shown in Figure 3.11, when the samples are heated above 150°C, two types of clay structures are created constituted of: (i) exfoliated or highly intercalated clays, characterized by the diffraction peaks at low 2θ angles; and (ii) clay stacks with narrower d-spacing characterized by the high angle diffraction peak located between 6.4° and 6.6°, with d-spacing between those for pristine Cloisite 15A (d_{001} = 31.8Å) and mineral clay (d_{001} = 10.4Å). The presence of the intermediate d-spacing is also in accordance with the conclusion from the IR spectra (Figure 3.1): the IR peaks corresponding to clay have decreasing intensity, yet do not disappear during the heating process.

As cited before, the occurrence of the clays with narrower d-spacing has been previously reported for PI/organo clay hybrid and other clay/polymer nanocomposites [8]. The high 2θ angle peak is also present in both the baked clay powder and the NMP swollen clay sample cured at 250°C. However, a co-existence of 2 clay structures was rarely observed. Also, the narrowing of the clay gallery could result from other reasons than the partial thermal decomposition of the interlayer organic modifier [6], for the decomposition should also happen in the “intercalated” clay stacks, as shown by the low 2θ angle peak, whose position shifts to a lower angle rather than a larger one. It indicates increasing d-spacing with increasing temperatures rather than the decreasing d-spacing due to decomposition.

The reasons for narrowing of clay galleries can be uncovered by the following questions: (a) Are the clay stacks intercalated by PAA chains before the clay is heated above 150°C, and (b) What is the effect of imidization on the intercalation of clay.
The PI/clay nanocomposites cured at low temperature have \(d_{001}\) peak at 2\(^\circ\)-2.2\(^\circ\). As the curing temperature was increased to 250\(^\circ\)C, the conversion of PAA into PI is shown to be nearly completed, resulting in predominately PI, which is stiffer and more rigid than PAA. The intercalated PI chains stabilize and expand the clay gallery, producing exfoliated and highly intercalated clay platelets. The WAXD peak shown at high 2\(^\theta\) angle between 6\(^\circ\) and 6.7\(^\circ\) for the PI/organo clay samples cured at 150\(^\circ\)C and 250\(^\circ\)C represent the clays that are only marginally intercalated. The partial decomposition of the intercalating aliphatic quaternary ammonium ions may be responsible for the shrinkage of the d-spacing by about 0.6\(\text{Å}\) with increasing curing temperature between 150\(^\circ\)C and 250\(^\circ\)C, corresponding to the 2\(^\theta\) angle increasing from 6.4\(^\circ\) to 6.7\(^\circ\). However, the reasons for the decreased gallery spacing may also be due to the compression force of clay by the surrounding stiff PI chains encapsulating the clay stacks. The WAXD peak at 6.7\(^\circ\) for PI/organo clay nanocomposites is slightly higher than the value of 6.3\(^\circ\) obtained for both the baked clay powders and the swollen clay powders subsequently heated to 250\(^\circ\)C, confirming that the clays experience more severe clay gallery shrinkage at the presence of surrounding PI chains. On the contrary, the clay stacks intercalated by PI show significant expansion of the gallery.

Also, a comparison of the WAXD spectrum of the swollen organo clay 15A (Figure 3.11, (c)) with those for the nanocomposites coatings cured at the same temperature (Figure 3.10 curve (d)) shows that the PI/clay composite has higher ratio of the height of the high 2\(^\theta\) angle peak to the low 2\(^\theta\) angle peak. This phenomenon is believed to be due to the increased extent of exfoliation with the addition of PI. The clay particles
that are intercalated by PI chains have larger d-spacing, which leads to better extent of intercalation of clay.

The WAXD data for PI/organo clay coatings with varying weight percent of clay is shown in Figure 3.12. It is suggested that if cured at the same temperature, the PI/organo clay nanocomposites containing higher concentrated clay have increased extent of the clay stacks with narrower d-spacing, indicated by the high 2θ (between 6° and 7°) peak, in agreement with literature [5]. Therefore extent of intercalation of clay can be improved by decreasing the clay content, which renders more fully exfoliated or highly intercalated clays.

The nature of clay structure in a PI matrix is quantified by calculation using equation (2) and (3) [13]. The average thickness of the clay crystal aggregates perpendicular to the (0 0 1) plane, Lc, was calculated using the Scherrer equation (equation 2), where k = 1, and β_{001} is the width, in radians, at half maximum intensity of the (0 0 1) peak.

\[
L_c = \frac{k \lambda}{\beta_{001} \times \cos \theta}
\]  
(2)

The average number of layers in each aggregate, Nc, was then calculated by using equation 3:

\[
N_c = \frac{L_c}{d_{001}} + 1
\]  
(3)

Table 3 shows the influence of curing temperature on the extent of intercalation of clay in polyimide based on the low 2θ WAXD peak. It can be concluded that: (1) the
clay/polyimide coatings containing 20 wt% clay cured at 70°C contains clay tactoids that have about 4-5 clay layers, which is slightly higher than that obtained for the neat clay powder. This indicates that clay dispersed in PAA is agglomerated and swollen; (2) the number of layers per stack decreases from 4.2 through 2.8 to 2.4 as the curing temperature increases, indicating a higher extent of intercalation, and thus better extent of intercalation of clay with increasing curing temperature. The change of clay gallery spacing due to the curing temperature has the same trend as concluded from the WAXD data.

3.2.2 PI/PANi clay nanocomposites

PANi 15A clay powder is prepared from a 2-step intercalation polymerization process, resulted in a more drastic expansion of the clay galleries. Different parameters of synthesis were used to produce PANi 15A clay. Among these powders, 3B shows a peak at small 2θ angle below 1°, corresponding to a d-spacing about 126Å. The WAXD experiment was repeated for 2 times to confirm the gallery spacing. Considering the cost of maintaining low temperatures in the process of preparation, 3B powder was selected as the PANi clay 15A used in this study.

The effect of the 1st intercalation of the double intercalation procedure can be shown by Figure 3.14. The powdered organo clay 15A shows three diffraction peaks at 2θ angles of 2.8°, 4.5°, and 7.2°, corresponding to the d_{001} of 31.5Å (d-spacing), d_{002}, and d_{003} reflections, respectively. In comparison, the spectrum of PANi clay 15A powder shows d_{001} peak at a much smaller 2θ angle of 0.7° as compared to that for organo clay 15A powder. After the in situ intercalation polymerization procedure of PANi (1st
intercalation process), the d-spacing of clay powder was broadened from 31.5Å to 126.0Å, which was an increase of 300%. The insertion of PANi broadens the d-spacing of Cloisite 15A, and the extent of intercalation was drastically increased by the 1st step intercalation.

Figure 3.15 shows the spectra of PAA/PANi clay 15A nanocomposites cured at different temperatures. The WAXD curves for PAA/PANi clay 15A nanocomposites exhibit few peak at low 2θ angle (below 3°). The sample heated to 70°C shows a peak at 2θ angle of 0.52°, corresponding to a d-spacing of 169.7Å. In comparison with that of PAA/organo clay 15A sample containing the same amount of clay and cured at the same temperature, the gallery spacing is much larger (169.7Å ≈ 5 × 42.0Å) for PAA/PANi clay 15A samples. There is no peak between 6° and 7°, showing monodispersity of highly-intercalated clay stacks. As the curing temperature increases, the disappearance of the peaks between 2° and 3° represents the conversion from highly intercalated clay stacks to fully exfoliated clay platelets. For the spectra of PAA/PANi clay 15A samples cured at 110°C, 150°C, 200°C, and 250°C, the peaks between 6° and 6.5° have much lower heights compared to those for PAA/organo clay 15A samples, indicating a much smaller amount of the clay tactoids with narrower d-spacing for PAA/PANi clay 15A nanocomposites. The peaks between 6° and 7° result from the partial exfoliation of the organic modifier and the compressing effect of the surrounding PI as described for the PAA/organo clay 15A samples. This peak shifts to higher angle with increasing curing temperature, showing that a decreasing d-spacing resulted from more severe degradation of the organic modifier and the increasing compression force by the surrounding PI.
In comparison with PAA/organo clay 15A nanocomposites, PAA/PANi clay 15A nanocomposites prepared by double intercalation polymerization technique have much higher extent of exfoliated clays, and much smaller amount of clay stacks with small gallery-spacing, both of which leads to better structure of clay. The comparison of d-spacing is listed in Table 5.

3.3 Morphology of clay – SEM and TEM

3.3.1 PI/organo clay nanocomposites

3.3.1.1 Scanning Electron Microscopy -- SEM

Shown in Figure 3.16 (a), (c), and (e) are the SEM pictures of the cross sections of the PAA/organo clay (Cloisite 15A) nanocomposite free standing films with varying clay loadings cured at 250°C. The thickness of each stack encapsulated by PI, and also sandwiching PI inside, is around 20nm, while the lateral size of the tactoids is about 200nm – 1µm. Also shown in the figures is the evidence of increasing clay concentration and volume fraction with the theoretical values (initial weight % of clay).

EDX-mapping of Si was used to analyze the distribution of clay as shown in Figure 3.16 (b), (d), and (f) was used to analyze the distribution of clay, since the Silicon was only identified in clay in this study. It was observed that clay is uniformly dispersed in the composites and the concentration of clay increases apparently with increasing clay content.

In comparison, shown in Figure 3.17, the SEM images for the cross sections of neat
PAA exhibit plain PAA/PI surfaces without the stack-like structure shown in the images for PAA/organo clay. The presence of clay platelets affects the morphology of the PAA (or PI)/clay nanocomposites in large scale.

3.3.1.2 Transmission Electron Microscopy -- TEM

The TEM images of the free standing films prepared from PAA/organo clay (Cloisite 15A) nanocomposites cured at 70°C and 250°C are shown in Figure 3.18. The sample cured at 70°C is indicative with PAA and intercalated structure. The clay stacks are aligned and dispersed in the matrix, while the clay stacking appear to be more compacted for the samples cured at 250°C, in which both clays with narrowed d-spacing and exfoliated layers can be observed.

3.3.2 PI/PANi clay nanocomposites

Shown in Figure 3.19 are the top-surface SEM images of the free standing films for PAA/organo clay and PAA/PANi clay nanocomposites cured at 250°C. Comparing to PAA/organo clay Cloisite 15A nanocomposites cured at 250°C, PAA/PANi 15A nanocomposites have much better distribution of clays with much smaller size in the matrix. The lateral size for the organo clay nanocomposites is larger than 1μm, while the dimension of the PANi clay particles dispersed in PI is smaller than 50nm. The organo clay nanocomposite membranes have micro cracks on the surface, while the PANi clay nanocomposites exhibit nano-sized holes distributed on the surface.

In Figure 3.20 of the cross sections of the PAA/PANi clay nanocomposites containing
different amount of clay, the increasing packing of clays is apparent with increasing concentration of clay. However the clay particles representing the small amount of clay tactoids maintain their size around 50nm in radius. The matrix has highly-rough and nearly fibrous-shaped cross section surfaces, which are unique for PI/PANi clay nanocomposites if compared to those for neat PAA or PAA/organo clay samples.

3.4 Optical properties – UV/VIS

3.4.1 PI/organo clay nanocomposites

Shown in Figure 3.21 are the UV/VIS spectra of pure PAA/organo clay dissolved in NMP, and PAA/organo clay nanocomposites. They all show UV absorption between 250nm and 400nm, corresponding to the $\sigma$ to $\sigma^*$ or $\pi$ to $\pi^*$ transition of isolated alkenes. However, the UV/Vis spectra of PAA/organo clay nanocomposites show a broad absorption peak between 450nm and 600nm. Although the intensity for this peak is low, this peak located in the visible region is due to the $\pi$ to $\pi^*$ transition of conjugated double bonds.

The PAA/organo clay synthesized by ex situ polymerization method, in which clay is dispersed in fully polymerized PAA, does not show any UV/Vis absorption peak above 400nm. The origin of the absorption peak between 500nm and 600nm may be due to the interaction between the PAA chains and the quaternary alkylated ammonium ions during the polymerization reaction. Figure 3.23 shows a scheme representation of the interaction between PAA and $(\text{N}^+\text{R}_4)$. The organic modifier present in clay is a positively charged amino group with hydrogenated tallow branches.
The interaction between PAA and clay can lead to a charge transfer complex and delocalized electrons.

### 3.4.2 PI/PANi clay nanocomposites

Figure 3.24 shows the UV/Vis spectrum for PAA/PANi clay composite dispersed in NMP. It shows a prominent peak at 390nm similar to that produced by neat PAA/NMP solution. It also shows a broad peak between wavelength of 400nm and 700nm. Comparing to the weak UV/Vis absorption in the visible region for the spectra of PAA/organo clay 15A, the absorption for PAA/PANi clay is much larger, indicative of much higher optical/electric activity. The intensity of this peak increases with increasing concentration of PANi clay in direct proportion. Therefore, this absorption is due to the \( \pi-\pi^* \) transition of a conjugated structure, presumably the quinoid structure in the molecules of polyaniline. After being doped, the charge can be delocalized and transferred between single and double bonds in the big \( \pi \) bond.

This study provides the evidence of both PI/organo clay and PI/PANi clay nanocomposites as semi-conductive materials to show conductive features. Using the double intercalation polymerization technique, the electro/optical properties can be dramatically enhanced, comparing to that of PAA/organo clay 15A nanocomposites. It brings about new possibilities to utilize these nanocomposites as corrosion protectors.

### 3.5 Rheological properties – the procedure of polymerization (Shear Viscosity Measurement)

#### 3.5.1 PI/organo clay nanocomposites
The formation of PAA by polycondensation reaction in the presence of clay is marked by a drastic increase in the viscosity of the polymerizing solution. Rheological measurements done at a spindle speed of 2 rpm shows that the initial stages of polymerization is characterized by a sharp increase in viscosity from 320 cP to 960 cP as the reaction time was varied from 30 to 90 minutes, respectively (Figure 3.25). The viscosity of the polymerizing solution also increased with increased shear rate (spindle speed). Increasing the spindle speed from 1 rpm to 100 rpm resulted in a significant increase in the viscosity of the solution from 320 cP to 1110 cP after 30 minutes of polycondensation reaction (Figure 3.25).

The polymerization of neat PAA shows similar trend, however, the polymerizing solution shows significantly higher viscosity for reactions carried between 90 and 1140 minutes of reaction, irrespective of the spindle speed (shear rate). The presence of clay during polymerization results in a higher initial polymerizing solution viscosity, however, the long time effect of clay seems to be to decrease the final solution viscosity of the solution (Figure 3.26). It appears that the presence of clay may lead to a significant decrease in the molecular weight of PAA.

Both systems of neat PAA and PAA/organoclay 15A nanocomposite solutions show increasing viscosity with increasing reaction time. Between 30 and 90 minutes of reaction the viscosity of the solution increased rapidly due to increasing molecular weight of PAA, and remained constant at 1000 cP. Only a slight increase in the viscosity of the solution occurred after 90 minutes of polymerization (Figures 3.25 and 3.26). It is concluded that polymerization reaction almost completed after about
90 minutes of polycondensation. The polymerizing solution shows a rheological
dilatability, increasing viscosity with increasing shear rate due to increasing molecular
weight of PAA.

3.5.2 PI/PANi nanocomposites

Figure 3.26 also shows the dependence of viscosity of the polymerizing solution of
ODA/PMDA, ODA/neat 15A/PMDA, and ODA/PANi 15A/ PMDA, respectively, on
the polymerization time. The viscosity of the polymerizing solution increases with
increasing polymerization time and approaches an asymptote at about 90 minutes of
polymerization for the formation of both neat PAA and PAA/organo clay 15A, while
the duration for for PAA/PANi clay 15A liquid is 30 mins, which is much shorter than
the other two groups.

Other than the effect of expediting the polymerization reaction, the presence of PANi
clay was observed to suppress the polymerization of PAA. The final viscosity for the
PAA/PANi clay 15A sample is much lower than that for both neat PAA solution, and
PAA/organo clay 15A nanocomposites. Figure 3.28 supplements the conclusion,
showing that the shear viscosity decreases drastically with increasing clay
concentration at low clay weight percent (below 2 wt%), followed by a constant
viscosity up to 20 wt% of clay. This phenomenon is due to the fact that the better
dispersion of clay in PAA/2 wt% PANi clay solution. Clays dispersed in the
ODA/PMDA mixtures play a role of barrier, suppressing the polymerization of
ODA/PMDA by hindering intimate contacts between the monomers. As PANi clay
was proved to be better dispersed in the PAA matrix, lower shear viscosity was
obtained for it. On the other hand, the lower ultimate shear viscosity additionally affirms the more exfoliated and more uniform dispersion of clay particles for PAA/PANi clay system.

Figure 3.27 exhibits that the shear viscosity of PAA solution increases with shear rate. The PAA/PANi clay nanocomposite solution shows non-Newtonian behavior at low shear rate (below 6), and nearly Newtonian behavior at higher shear rates.

### 3.6 Corrosion resistant properties – DC polarization (DCP)

DCP tests were taken on PI/clay nanocomposite coatings on Al substrates for 3 times each. Averages and deviations were calculated and plotted in Figures 3.30, 3.32, and 3.33. The thickness of the PI/clay nanocomposite coatings ranges from 40µm to 80µm. All potentials were taken compared to SCE coordinate. Deviations are due to sampling, homogeneousness of the coatings, and systematic error.

#### 3.6.1 PI/organo clay nanocomposites

Tafel plots for PAA (or PI)/organo clay nanocomposite coatings cast on Al 2024 panels are shown in Figure 3.29. The plots for the samples cured at 70°C and 110°C show activation controlled corrosion curves with negative Ecorr. The anodic and cathodic reactions are reaction (1) and (2), respectively.

\[
\text{Al} = \text{Al}^{3+} + 3e^- \quad \text{(1)}
\]

\[
\text{O}_2 + 2\text{H}_2\text{O} + 4e^- = 4\text{OH}^- \quad \text{(2)}
\]

For the samples cured at 150°C, 200°C and 250°C, the Tafel plots have positive
corrosion voltages, indicating that the corrosion of metal can hardly occur if not attached to an external potential stat. The cathodic curve representing the reduction reaction of oxygen is diffusion controlled. The anodic curve for the Tafel plot of the samples cured at 150°C may be due to the oxidation reaction of water (3), which is the reverse reaction of (2), since the positive Ecorr cannot result from the oxidation of metal.

\[2H_2O = 4H^+ + 4e^- + O_2\] \hspace{1cm}(3) [101]

As shown in Figure 3.30 (a), (c), and (e), Ecorr of the PAA/organo clay coatings shifts positively with increasing curing temperature. Both the cathodic and the anodic curves shift to the left of the Tafel curve to lower current values, and the corrosion current and the corrosion rate decrease drastically accordingly. It is indicative of decreasing diffusion rates of water, oxygen, and electrons.

Figure 3.30 (b), (d), and (f) show effect of DOI on Ecorr, Icorr, and corrosion rate as a function of DOI. Improved corrosion resistant properties are found as curing temperature increase due to a higher concentration of PI. With its hydrophobicity and dense texture, PI greatly assists to lower that diffusion of water and oxygen to the surface of metal, lowering the corrosion rate.

Figure 3.33 compares the corrosion inhibition properties of the coatings as a function of clay concentration. As the wt% of organo clay increases from 2 wt% to 20 wt%, both corrosion rate and corrosion current experienced a drastic decrease. Within the range of clay concentration studied, corrosion rate decreases with increasing organo
clay concentration. The reason for this decrease in corrosion rate with increasing clay concentration may be due to the increasing tortuosity of diffusion path. The addition of organo clay assists the imidization of PAA to PI. Increasing DOI reduces porosity and increases diffusion path.

3.6.2 PI/PANi clay nanocomposites

The DCP plots for PAA/PANi 15A series are shown in Figure 3.31. For the samples with lower clay loadings (from 0.2 wt% to 2 wt%), the DCP curves resemble those for PAA/organo clay coatings. The samples cured at lower temperatures (70°C and 110°C) exhibit activation controlled anodic curves representing the reduction reaction of oxygen. When only a small amount of PAA is imidized, oxygen and water are easily diffused through the coatings. While the samples cured at higher temperatures showed diffusion controlled anodic curve, indicating a lower diffusion rate of oxygen and water.

As shown in Figure 3.31, as the curing temperature increases, both the anodic and the cathodic curves shift left, indicating that the corrosion rate and the corrosion current decrease drastically. The corrosion voltage increases, and the positive $E_{corr}$ may represent the open circuit potential of the oxidation reaction of water.

It can be concluded that with increasing curing temperature, the corrosion resistant behavior for PAA/PANi clay coatings is improved (corrosion rate decreases, corrosion resistance increases). Increasing the clay loading contained in the PAA/PANi clay nanocomposite coatings (to 5 wt%, 10 wt%, and 20 wt%) largely increases the corrosion
rate. The presence of polyaniline affects the corrosion resistant behavior severely (Figure 3.32).

Also, comparison of the corrosion resistant properties as a function of clay loading (Figure 3.33) shows that the properties are enhanced with decreasing clay concentration, which corresponds to decreasing PANi loading. The samples show best properties are PAA/PANi clay nanocomposite coatings containing 0.2 wt%, 0.5 wt%, and 1 wt% PANi clay 15A.

A possible explanation of the decrease in the corrosion resistant properties in the presence of high concentration of PANi/clay (>2 wt%) in the coatings is that:

(1) According to Hall [74], DSC for PANi clay shows a melting peak staring from 220°C. The PI/PANi clay samples heated above the melting temperature of PANi have different Coefficients of Thermal Expansion (CTE) during the cooling process. Such difference produces cracks or microcracks, which provide the channels introducing the oxygen and moisture to the Al surfaces.

(2) PANi results in a unique porous morphology of the PI matrix, and clays with much smaller lateral sizes, both of which enhance the diffusion of water and oxygen.

Comparisons shown in Figure 3.34 and 3.35 reveal that the corrosion resistant properties of PI/0.2 wt% (and 0.5 wt%) PANi clay are better than those of PI/2 wt% (and 5 wt%) organo clay. It has been reported that PANi is able to enhance the corrosion inhibition ability of the nanocomposite coatings by mediating currents between the Al substrates and the surrounding oxygen and water, and thus passivating
This study proves that the addition of PANi drastically improves the corrosion resistant properties of the PI/clay nanocomposite coatings at lower clay loadings. Therefore, besides the barrier mechanism of corrosion protection, PANi introduced electronic mechanism. This mechanism assists to obtain improved corrosion protection at the presence of PANi by adding lower loadings of clay.
Chapter 4 Conclusions and future work suggestions

PI/organo clay nanocomposites were prepared by varying curing temperature and the weight percentage of clay. Curing temperature as high as 250°C gave fully imidized PI in the nanocomposites. A fraction of the fully cured PI is believed to be inserted into the galleries of a portion of clay stacks resulting in exfoliation and extensive intercalation of clay as shown by the broadening of the lamella gallery of clay represented by the shifting of low angle \( d_{001} \) peak to 2°. As the curing temperature increases, the degree of imidization increases, and the clays show higher extent of exfoliation.

Another portion of clay in the nanocomposites is only marginally intercalated. The nanocomposite coating cured at 70°C contains large amount of NMP soluble PAA and high boiling point NMP which can dissolve and extract the intercalating compounds during evaporation at higher temperatures. The nanocomposite coatings cured at both 150°C and 250°C contain hybrid clays composed of both exfoliated or highly intercalated clays, and marginally intercalated clays. According to the results from WAXD, SEM, and TEM studies, the occurrence of the latter type is believed to be due to the partial decomposition of the aliphatic ammonium cations, the expulsion of solvent from the swollen fractions, and the compressing force by the surrounding stiffer PI chains. Indicated by the UV/VIS data, a PAA–\( N^+R_4 \) complex is formed by the interaction between the PAA chains and the organic modifiers of the organo clay 15A.

PAA (PI)/PANi clay nanocomposites were synthesized using double intercalation
polymerization technique. Compared to the nanocomposites synthesized by using organo clay, the structure of clay was improved significantly: larger extent of exfoliated clays and smaller amount of clay stacks with narrower gallery spacing were obtained. The viscosity data further confirmed the enhancement in clay structure. Comparison of the viscosity of neat PAA solution and PAA/organo clay suspensions shows that PAA in PAA/PANi clay system is fully polymerized within 30mins of polymerization. The ultimate viscosity of PAA/PANi clay solution is much lower than that for PAA/organo clay solution, confirming better clay dispersion.

Due to the presence of PANi, PAA/PANi clay nanocomposites show detectable absorption in the visible range of UV/Vis spectrum similar to that observed for neat PANi solution.

PI/PANi clay nanocomposites have unique morphology as shown by the SEM images: the matrix, which comprises PI and PANi, exhibits fibrous morphology. Such behavior is indicative of improved orientation and higher porosity of the materials.

The corrosion resistant properties of the PAA/organo clay nanocomposite coatings are improved with increasing curing temperature and clay loading. PAA/20 wt% organo clay nanocomposite has the best corrosion inhibition properties in this study. However, the corrosion protection properties decrease with increasing clay loading for PAA/PANi clay nanocomposites. The PI/PANi clay coatings containing 0.2 wt%, 0.5 wt%, and 1 wt% PANi clay show promising corrosion inhibition properties. However, increasing the concentration of PANi clay to above 2 wt% resulted in a drastic decrease in the corrosion resistant properties. This trend may be due to the shrinkage
of the coatings during the cooling process as a result of the variation in the CTEs for the PI/PANi clay nanocomposites coatings; and/or the porous morphology and much smaller clay particle lateral sizes of the PI/PANi clay nanocomposites.

Conductivity measurements may be one of the focuses for future work to uncover the effects of PANi and/or the PAA—N+R4 complex, and how the conductivity could be enhanced. The mechanisms how PI/PANi clay nanocomposite coatings protect the aluminum from corrosion is yet to be analyzed. Thermal stability of the nanocomposite coatings should be improved to minimize the degradation of the coatings. Also, effort should be taken to further improve the extent of intercalation of clay in the polymer matrix.
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Figure 3.1 IR spectra of PAA/2 wt% organo clay 15A solution cured at (a) 70°C, (b) 110°C, (c) 150°C, (d) 200°C, (e) 250°C.
Figure 3.2 Effect of temperature on the degree of imidization of PI calculated using the peak at 1778 cm$^{-1}$. 
Figure 3.3 IR spectra of (a) Neat PAA cured at 150°C, (b) PAA/2 wt% organo clay 15A cured at 150°C, (c) PAA/10 wt% organo clay 15A cured 150°C, (d) PAA/20 wt% organo clay 15A cured at 150°C.
Figure 3.4 DSC of Neat PAA, PAA/2 wt% organo clay 15A, PAA/5 wt% organo clay 15A, PAA/10 wt% organo clay 15A, and PAA/20 wt% organo clay 15A free standing films cured at 70°C.
Figure 3.5 (a) Imidization peak area as a function of clay concentration; (b) corresponding DOI change at curing temperature of 150°C depending on clay concentration calculated using IR data.)
Figure 3.6 IR spectra of PAA/2 wt% PANi clay 15A solution cured at (a) 70°C, (b) 110°C, (c) 150°C, (d) 200°C, (e) 250°C.
Figure 3.7 Comparison on the degree of imidization as a function of curing temperature for PAA/5 wt% organo clay 15A and PAA/5 wt% PANi clay 15A nanocomposites calculated using the peak at 1778 cm\(^{-1}\).

Figure 3.8 Comparison on the degree of imidization as a function of clay concentration for PAA/organo clay 15A and PAA/PANi clay 15A nanocomposites cured at 150°C calculated by using the peak at 1778 cm\(^{-1}\).
Figure 3.9 WAXD patterns for (a) organo clay 15A powders at room temperature, and (b) organo clay 15A powders heated in vacuum atmosphere at 250°C.

Figure 3.10 WAXD patterns for (a) organo clay 15A powders, (b) cast sample of organo clay 15A powders dispersed in NMP at 70°C, (c) cast sample of organo clay 15A powders dispersed in NMP at 250°C.
Figure 3.11 WAXD patterns for (a) organo clay 15A powders, and PAA/20 wt% organo clay cast at (b) 70°C, (c) 150°C, (d) 250°C.

Figure 3.12 WAXD patterns for (a) organo clay 15A powders, (b) PAA/2 wt% clay cast at 250°C, (c) PAA/10 wt% clay cast at 250°C, (d) PAA/20 wt% clay cast at 250°C.
**Figure 3.13** WAXD patterns for PANi clay powders of 3B.

**Figure 3.14** WAXD for (a) Organo clay 15A clay powder and (b) PANi clay 15A powder.
Figure 3.15 WAXD spectra of PAA/PANi clay 15A nanocomposites cured at: (a) 70°C, (b) 110°C, (c) 150°C, (d) 200°C, and (e) 250°C. Inserted: Blow-up plot at the range of 2θ from 0 to 2°.
Figure 3.16 SEM and EDX picture images of (a) and (b) PAA/2 wt% organo clay 15A.
Figure 3.16 (Continued) SEM and EDX picture images of (c) and (d) PAA/10 wt% organo clay 15A.
Figure 3.16 (Continued) SEM and EDX picture images of (e) and (f) PAA/20 wt% organo clay 15A.
Figure 3.17 SEM images for cross sections of neat PAA samples cured at (a) 70°C, and (b) 250°C.
Figure 3.18 TEM images of PAA/20 wt% organo clay 15A cured at (a) 70°C, and (b) 250°C.
Figure 3.19 SEM images for the surfaces of the free standing films of (a) PAA/2 wt% organo clay 15A, and (b) PAA/2 wt% PANi clay 15A.
Figure 3.19 (Continued) SEM images for the surfaces of the free standing films of (c) PAA/20 wt% organo clay 15A, and (d) PAA/20 wt% PANi clay 15A cured at 250°C.
Figure 3.20 SEM images of cross sections of (a) PAA/2 wt% PANi clay 15A cured at 250°C, and (b) PAA/10 wt% PANi clay 15A cured at 250°C.
Figure 3.20 (Continued) SEM images of cross sections of (c) PAA/20 wt% PANi clay 15A cured at 250°C.
Figure 3.21 UV/VIS Spectra of neat PAA, PAA/organo clay 15A composites, and dissolved organo clay 15A in solvent NMP.
Figure 3.22 UV/VIS Spectra of PAA/2 wt% organo clay 15A and PAA/10 wt% organo clay 15A nanocomposites synthesized through in situ and ex situ polymerization.
Figure 3.23 Formation of the conjugated structure.
Figure 3.24 UV/Vis spectra of (a) neat PAA, (b) PANi clay 15A dissolved in solvent NMP, and PAA/PANi clay 15A nanocomposites containing clay of various concentration: (c) 2 wt%, (d) 5 wt%, (e) 10 wt%, and (f) 20 wt%. Inserted: Blow-up plot in the range of wavelength from 450nm to 700nm.
Figure 3.25 Change of viscosity as a function of polymerization time and spindle speed for PAA/2 wt% organo clay 15A nanocomposite solution during the polymerization of PAA at the spindle speeds of (a) 1 RPM, (b) 2 RPM, (c) 5 RPM, (d) 20 RPM and (e) 100 RPM.
Figure 3.26 (I) Viscosity as a function of polymerization time for (a) and (b) neat PAA liquid, (c) and (d) PAA/2 wt% organo clay 15A liquid, and (e) and (f) PAA/2 wt% PANi clay 15A liquid measured at the spindle speed of 2 RPM and 100 RPM, respectively. (II) Blow-up plot for the viscosity measured within the first 30 mins of polymerization.
Figure 3.27 Shear viscosity as a function of shear rate for PAA/20wt% PANi clay 15A liquid measured at different polymerization time.

Figure 3.28 Shear viscosity as a function of clay loading for PAA/PANi clay 15A nanocomposite liquid measured at different spindle speeds.
Figure 3.29 DCP plots for PAA/organo clay 15A nanocomposite coatings cured on Al panels at varying temperatures containing clay of various concentrations: (a) 2 wt%, (b) 5 wt%.
Figure 3.29 (Continued) DCP plots for PAA/organo clay 15A nanocomposite coatings cured on Al panels at varying temperatures containing clay of various concentrations: (c) 10 wt%, and (d) 20 wt%.
Figure 3.30 Comparison of corrosion rate as functions of (a) curing temperature, and (b) degree of imidization for PAA/organo clay 15A nanocomposite coatings cured at different temperatures.
Figure 3.30 (Continued) Comparison of corrosion resistance as functions of (c) curing temperature, and (d) degree of imidization for PAA/organo clay 15A nanocomposite coatings cured at different temperatures.
Figure 3.30 (Continued) Comparison of $E_{corr}$ as functions of (e) curing temperature, and (f) degree of imidization for PAA/organo clay 15A nanocomposite coatings cured at different temperatures.
Figure 3.30 (Continued) Comparison of Icorr as functions of (g) curing temperature, and (h) degree of imidization for PAA/organo clay 15A nanocomposite coatings cured at different temperatures.
Figure 3.31 DCP plots for PAA/PANI clay nanocomposite coatings cured at different temperatures containing PANi clay of various concentrations: (a) 0.2 wt%, (b) 0.5 wt%.
Figure 3.31 (Continued) DCP plots for PAA/PANi clay nanocomposite coatings cured at different temperatures containing PANi clay of various concentrations: (c) 1 wt%, (d) 2 wt%.
Figure 3.31 (Continued) DCP plots for PAA/PANi clay nanocomposite coatings containing 5 wt% PANi clay cured at (e) 70°C, 110°C, and 150°C; and (f) 200°C and 250°C.
Figure 3.31 (Continued) DCP plots for PAA/PANi clay nanocomposite coatings containing 10 wt% PANi clay cured at (g) 70°C, 110°C, and 150°C; and (h) 200°C and 250°C.
Figure 3.31 (Continued) DCP plots for PAA/PANI clay nanocomposite coatings containing 20 wt% PANi clay cured at (i) 70°C, 110°C, and 150°C; and (j) 200°C and 250°C
Figure 3.32 Comparison of corrosion rate as functions curing temperature for PAA/PANi clay 15A nanocomposite coatings containing clay of varying concentrations of (a) 0.2 wt%, 0.5 wt%, and 1 wt%; (b) 2 wt%, 5 wt%, 10 wt%, and 20 wt%.
Figure 3.32 (Continued) Comparison of corrosion resistance as functions curing temperature for PAA/PANI clay 15A nanocomposite coatings containing clay of varying concentrations of (c) 0.2 wt%, 0.5 wt%, and 1 wt%; (d) 2 wt%, 5 wt%, 10 wt%, and 20 wt%.
Figure 3.32 (Continued) Comparison of $E_{corr}$ as functions curing temperature for PAA/PANI clay 15A nanocomposite coatings containing clay of varying concentrations of (e) 0.2 wt%, 0.5 wt%, and 1 wt%; (f) 2 wt%, 5 wt%, 10 wt%, and 20 wt%.
Figure 3.32 (Continued) Comparison of Icorr as functions curing temperature for PAA/PANi clay 15A nanocomposite coatings containing clay of varying concentrations of (g) 0.2 wt%, 0.5 wt%, and 1 wt%; (h) 2 wt%, 5 wt%, 10 wt%, and 20 wt%.
Figure 3.33 Comparison of (a) corrosion rate and (b) Rp as functions of clay concentration for PAA/PANi clay 15A nanocomposite coatings cured at 150°C.
Figure 3.33 (Continued) Comparison of (c) Ecorr, and (d) Icorr as functions of clay concentration for PAA/PANi clay 15A nanocomposite coatings cured at 150°C.
Figure 3.34 Comparison of DCP curves of (a) PAA/2 wt% organo clay and PAA/0.2 wt% PANi clay cured at 70°C and 110°C; and (b) PAA/5 wt% organo clay and PAA/0.5 wt% PANi clay cured at 70°C and 110°C.
(a) Cure temperature dependence of resistivity for neat PAA, PAA/2 wt% organo clay, and PAA/0.2 wt% PANi clay.

(b) Cure temperature dependence of resistivity for neat PAA, PAA/5 wt% organo clay, and PAA/0.5 wt% PANi clay.
Figure 3.35 Comparison of $R_p$ of (a) neat PAA, PAA/2 wt% organo clay and PAA/0.2 wt% PANi clay; (b) PAA/5 wt% organo clay and PAA/0.5 wt% PANi clay; and PAA/5 wt% organo clay and PAA/2 wt% PANi clay.
<table>
<thead>
<tr>
<th>Frequency (cm⁻¹)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1495</td>
<td>Stretch (C=C-C) of aromatic ring</td>
</tr>
<tr>
<td>1778</td>
<td>Vibration (C=O) of imide</td>
</tr>
<tr>
<td>721</td>
<td>Stretch (C=O) of imide</td>
</tr>
<tr>
<td>1378</td>
<td>Vibration (C-N-C) of imide</td>
</tr>
<tr>
<td>588</td>
<td>Asymmetric Stretch (C-N-C) of imide</td>
</tr>
<tr>
<td>1655</td>
<td>C=O of amide</td>
</tr>
</tbody>
</table>

**Table 1.** IR Peak assignment for polyimide

<table>
<thead>
<tr>
<th>Clay concentration</th>
<th>Peak Area</th>
<th>Peak Imidization Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>14.14</td>
<td>167.12</td>
</tr>
<tr>
<td>2%</td>
<td>20.78</td>
<td>162.64</td>
</tr>
<tr>
<td>5%</td>
<td>22.88</td>
<td>141.90</td>
</tr>
<tr>
<td>10%</td>
<td>23.22</td>
<td>148.47</td>
</tr>
<tr>
<td>20%</td>
<td>26.51</td>
<td>148.29</td>
</tr>
</tbody>
</table>

**Table 2.** Effect of wt% clay on imidization energy
### Table 3. Effect of temperature on clay dispersion in PAA/PI.

<table>
<thead>
<tr>
<th>Clay Type</th>
<th>Organo clay Cloisite 15A</th>
<th>PANi 15A</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Processing</strong></td>
<td>Powder</td>
<td>Baked at 250°C</td>
</tr>
<tr>
<td>d-spacing (Small)</td>
<td>31.5</td>
<td>35.3</td>
</tr>
<tr>
<td>d-spacing (Large)</td>
<td>14.0</td>
<td></td>
</tr>
</tbody>
</table>

### Table 4. Gallery spacing for organo clay, PANi clay and PAA/clay, PAA/PANi clay composites after various process procedures (All the units are Å).

<table>
<thead>
<tr>
<th>Clay Type</th>
<th>PAA/Organo clay Cloisite 15A</th>
<th>PAA/PANi 15A</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Processing</strong></td>
<td>Cured at 70°C</td>
<td>Cured at 110°C</td>
</tr>
<tr>
<td>d-spacing (Small)</td>
<td>34.0</td>
<td>40.1</td>
</tr>
<tr>
<td>d-spacing (Large)</td>
<td>13.8</td>
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</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Clay Type</th>
<th>PAA/PANi 15A</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Processing</strong></td>
<td>Cured at 70°C</td>
</tr>
<tr>
<td>d-spacing (Small)</td>
<td>169.7</td>
</tr>
<tr>
<td>d-spacing (Large)</td>
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</tr>
</tbody>
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