

Blending PLA(Poly-lactic acid) with layered silicates

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Master of Science

in Chemical and Biomolecular Engineering

by

Yoo Rang Heo

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Blending PLA(Poly-lactic acid) with layered silicates

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Abstract

Layered silicates are used for organic/inorganic hybrid fillers to reinforce the polymers. Dispersion of polymer and layered silicate is important because phase separation leads to weak interaction which makes poor property at polymer-layered silicate nanocomposites.

In this work, PLA(Poly-lactic acid) is synthesized from cyclic L-lactide with layered silicates through in-situ ring opening reaction with varying concentrations of layered silicate. PLA is an attractive biomaterial and is used for packaging due to high strength and high-modulus properties. Its shortcomings such as barrier property, brittleness can be enhanced by mixing it with organic modified layered silicate. The polymer-layered silicate nanocomposites are characterized by x-ray diffraction, thermal gravimetric analysis and optical microscopy. In this work, intercalated or exfoliated polymer layered silicate nanocomposites could be achieved. The analysis of samples shows that crystallinity is decreased with increasing inorganic concentration. In addition, thermal stability and morphology also depend on dispersibility and inorganic concentration.

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Chapter 1. Introduction

1.1. Background and motivation

Nowadays, environmental pollution has emerged as an important issue around the world. Accordingly, the development of biomaterials has garnered growing attention from the government and researchers.

In particular, PLA(Poly-lactide) is a promising semicrystalline biomaterial from renewable source such as corn [1-6]. The PLA industrial market is also increasing because of its high strength, high-modulus properties. As its physical properties are similar to petroleum-based polymers, it could also replace those polymers. It is primarily used in large scale industrial applications for packaging, medical devices and pharmaceutical products [2,6,7]. However, the relatively high cost, low thermal stability, brittleness, low moisture stability, medium gas barrier, low toughness cause limitations of PLA application [1,8]. To overcome these shortcomings, the polymer has to be mixed with various fillers such as talc, nanosiliate, carbon nanotube and calcium carbonate [4, 9-13]. In this experiment, PLA is blended with clay.

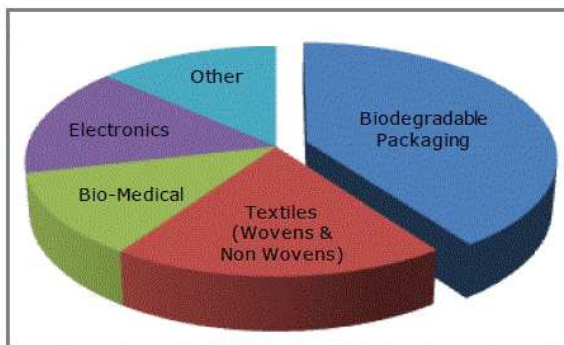


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1.2. Biodegradable PLA(poly-lactic acid)

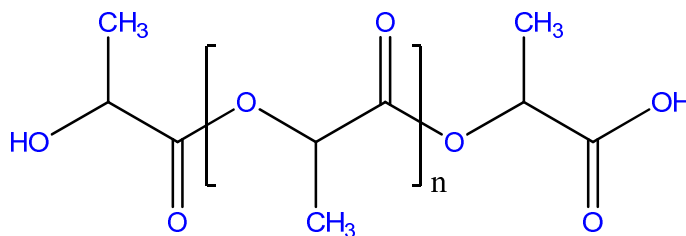


Figure 1-2. This picture represent general structure of poly-lactic acid. It has ester groups and its unit has two oxygen, three carbon and three hydrogen.

PLA is a biodegradable, thermoplastic, orthorhombic, semi-crystalline poly-ester polymer [5,14]. As mentioned above, its advantages have led to its wide use in various industries. Never the less, its poor thermal properties, and brittleness raises major concerns when used in the industry [15].

PLA is thermally degraded above 200° by hydrolysis and its glass temperature is around 55°C and the melting temperature is around 150 ~ 170° [16]. Although higher processing temperature up to 180°-190°C is necessary, their unzipping and chain scission phenomena induces degrading and molecular weight loss [1].

PLA is synthesized by direct condensation of lactic acid and ring-opening polymerization using cyclic Lactic acid [1]. When the direct condensation route is used, its molecular weight becomes low due to condensation. While direct condensation results in low molecular weight the ring-opening polymerization method leads to a higher molecular weight, which renders synthesizing PLA with cyclic Lactic acid the preferred method to direct condensation.

1.3. Layered silicate

Fiber and Talc are conventionally used for reinforcing polymer properties [17]. Among these, polymer layered silicate nanocomposites are regarded as attractive materials for over 50 years [18]. One of the reasons this is regarded efficient is due to the "nano-scale dispersion." This phenomena leads to high aspect ratio and high surface area [19]. In this experiment, nano-clay (layered silicates) is applied for reinforcing polymers. The reason for enhanced properties of the nanocomposites is its interfacial interaction between polymer and organosilicate. The thickness of layered silicates is 1nm and its aspect ratios are very high ranging from 10 to 1000 nm.

The layered silicates consist of thin layers which are bindings of tetrahedral sheets and octahedral sheets. Silicon is surrounded by four oxygen atoms at the tetrahedral sheets and the metal such as aluminum is surrounded by eight oxygen atoms at the octahedral sheets [19]. The general scheme of layer silicate is as follows. In this structure, the ratio of octahedral and tetrahedral sheets is 1:2 which is known as phyllosilicates [19].

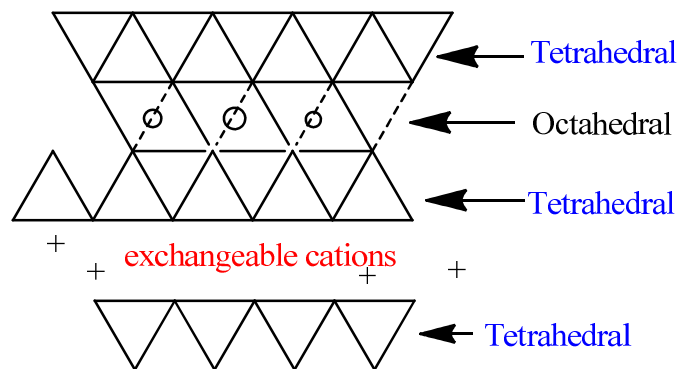


Figure 1-3. Structure of general layered silicate. One layered silicate consists of two tetrahedral sheets surrounded by 4 oxygen atoms and one octahedral sheet surrounded by 8 oxygen atoms. Between the layered silicates, there are exchangeable cations such as sodium.

Especially in the case of mica, the silicon of the tetrahedral sheet is changed to Al. When this substitution happens, negative surface charges arise which has balance due to interlayer potassium cations. If the Al-cation of the octahedral layer in mica partially changes to a Mg-cation, this is called montmorillonite or smectite clays [20].

These materials could reinforce polymers because of a high aspect ratio and its dispersing characteristic [21]. The thickness of an individual clay sheet is 1nm, which is much smaller than that of the carbon nanotube for showing the highest elastic modulus. The small clay sheet shows atomic and molecular levels, which lead to becoming a perfect crystalline structure and its effect is larger even with a smaller concentration. However, its large internal surface tends to agglomerate instead of dispersing homogeneously because silicate layers are likely to make stacks due to van der Waals gap [19].

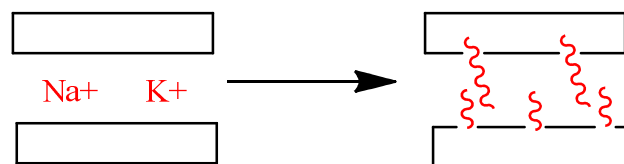


Figure 1-4. The exchangeable cations are changing to organophilic chains through an ion exchange reaction. These ion exchange reactions help the layered silicate mix with polymers. In addition, it broadened the spacing between the layers with a long organic chain.

These layered silicates could blend with only hydrophilic polymers and these should be modified as OMLS (organic modified layered silicate). In order to mix with hydrophobic polymers, alkali counter-ions should be substituted by cationic-organic

surfactant. This can be achieved through ion-exchange reactions [19]. The alkali cations, called exchangeable cations, are especially known for this since it can be substituted by other positively charged atoms or molecule [22]. Long organic chains with positively charged ends produce increases of interlayer spacing by attaching negative charged silicate layers. Not only that, but it makes hydrophilic materials change organophilic materials [21]. The excess negative charge from exchange ion can be evaluated by cation-exchange capacity (CEC) and unit is mequiv./g [21].

For preparing nanocomposites, there are several methods such as in-situ polymerization, melt intercalation, and solution blending [21]. In-situ polymerization means that the monomer solution is dissolved with modified layered silicate between layered silicate and then polymerization is conducted. In this case, polymerization happens between layered silicate with the initiator or catalyst attached during the cationic exchange between layered silicate. Polymerization reaction may also lead to broaden clay galleries. At the solution blending, layered silicate is dispersed in the adequate solution and then the polymer is added to this solution. Finally, solvent could be removed through vacuum filtration and precipitation. In the case of melt blending, layered silicate and polymer blending occurs in the molten stage. Melt blending and in-situ polymerization are considered as two attractive methods. Through layered silicate nanocomposites reinforcement, mechanical properties such as modulus and strength, barrier property, thermal stability, and flame retardence could be improved.

1.4. Dispersion of Polymer-layered silicate nanocomposites

As mentioned above chapter, an aspect ratio up to 1000 could be achieved if the dispersion occurs [18]. However, when polymer blends with silicate layers, phases separation happens because of the poor physical attraction between organic and inorganic components. The consequent attraction leads to poor mechanical properties and reduce strength [23].

Generally, there are three types of nanocomposite structures for polymer-filler composites. The first case is the unmixed type which leads to phase separation. In this case, it is difficult to achieve improved properties. With the intercalated, exfoliated structures, we could get the enhanced properties. Ultimately, exfoliation structure is superior to the intercalated structure although complete exfoliated polymer-nanocomposite is almost impossible. Intercalated structure consists of well ordered multilayer structure, in that polymer and nanosilicate layers alternate each other. The usual separation length is from 20Å to 30Å [24]. The other structure is exfoliated or delaminated structures which implies that clay layers are dispersed well individually. In general, its separation length is from 80 Å to 100Å. Between two structures, the exfoliated option is more attractive since it has large surface area which could engender improved mechanical properties.

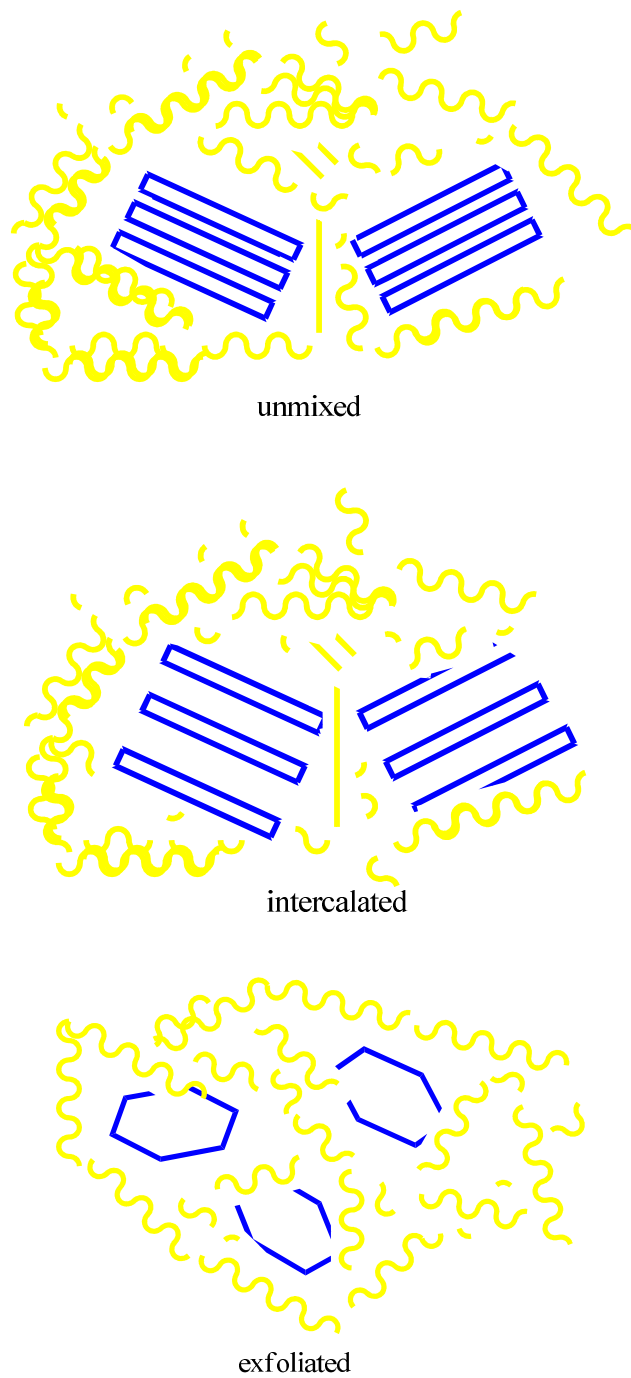


Figure 1-5. When the polymer is mixed with layered silicates, there are three types (a) Unmixed dispersion state leads to phase separation which results in poor property (b) Intercalated dispersion with ordered structure (c) Exfoliated polymer layered silicate nanocomposites. This is the ideal polymer layered silicate nanocomposites we want to obtain because it is well dispersed into polymer.

In order to get high molecular weight materials, the masterbatch method is usually used. When the polymer is synthesized with clay, its molecular weight is likely to decrease. However, when high concentration is mixed with high molecular weight commercial PLA, its molecular weight could be increased and its mechanical property could be enhanced. In previous research, some scientists have shown that the masterbatch method helps improve mechanical properties by increasing the molecular weight [25]. In addition, masterbatch is also efficient for mass-production. To apply to masterbatch, high concentration exfoliated PLA layered silicate nanocomposites should be tried for achieving dispersion.

1.5. Thermodynamic aspects

Exfoliation is optimal because it shows the maximum interfacial interaction between polymer and nanosilicate. Although complete exfoliation is impossible, we could get more exfoliated polymer layered silicate nanocomposites by managing the several conditions.

Polymer-nanosilicate structure is related with Gibbs-free energy. Thermodynamic of Gibbs-free energy [26] is

$$\Delta G = \Delta H - T \Delta S, \quad (1)$$

where G is Gibbs-free energy, T is temperature and S is entropy. When polymer chain is trying to open the clay gallery spacing, polymer chain should uncoil and follow insertion to get into spacing [27].

If considering the enthalpy term, there are three interactions, including polymer-polymer, polymer-nanosilicate, nanosilicate-nanosilicate in polymer-nanosilicate. In order to obtain the exfoliated polymer-nanocomposite, polymer-nanoparticle interaction should be stronger than the other two interactions [28-31]. In order to get the stronger interaction, cationic is exchanged to hydrophilic chains. This nanocomposite exfoliation could be achieved with heat and vigorously stirring [29].

In general, entropy is likely to increase when mixing occurs. However, entropy of polymer chain is likely to decrease during dispersing. This is because when polymer chains go through uncoiling at first, and is followed by intercalation or exfoliation they are affected by space limitation [28,32]. During in situ polymerization, monomer is used instead of polymer; the polymer uncoiling process is not necessary. However, during solution blending or melt blending, uncoiling is required. Accordingly, in terms of entropy, in-situ method is optimal choice.

Chapter 2. Experimental technique and theory

2.1. X-ray diffraction

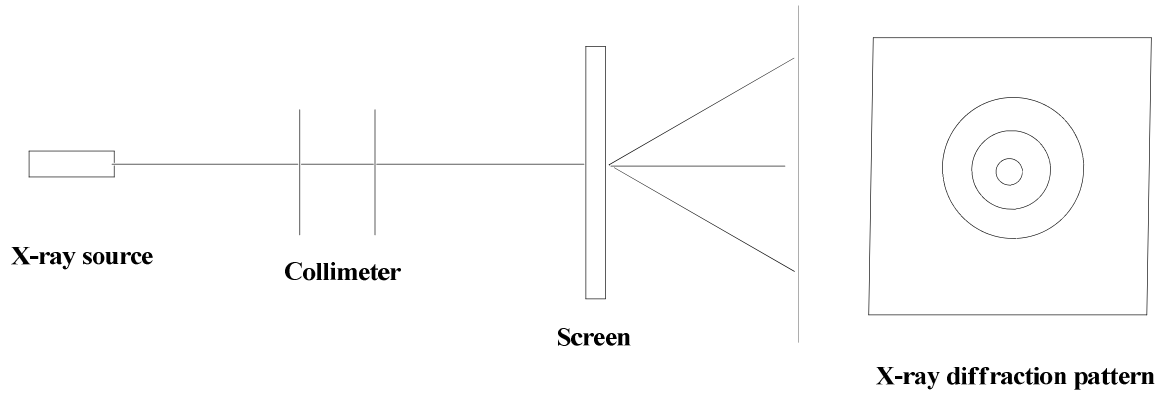


Figure 2-1. Basic x ray diffraction structure. After a collimated beam of x-rays have a collision with the samples, the signal could be received.

XRD is one of the attractive methods which can determine nanocomposites' morphology. As shown in the figure 6, x-ray is an electromagnetic radiation whose wavelength is from 0.01 and 10nm [34]. X-ray is generated when the high speed electron collide with target material (Cr,Fe,Co,Ni,Cu,Mo,W).

At first, a collimated beam of monochromatic x-rays go further on to the sample and incident x-rays have collision with crystals [35]. The signal can be detected by using goniometer which provides atomic arrangement of materials [34]. After collision, they are scattered at the specific angle. Depending on the θ , we can get the distance between atomic planes. This is called diffraction [36].

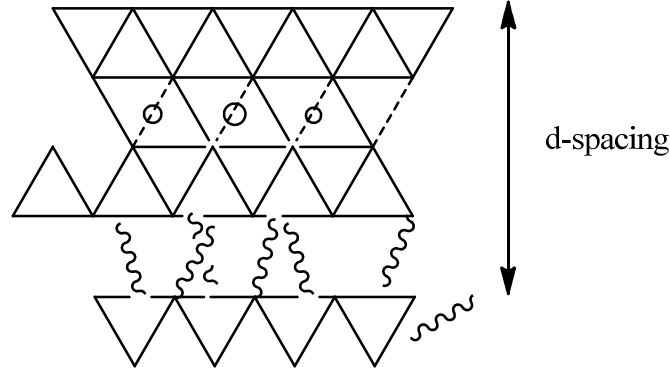


Figure 2-2. Interlayer spacing means distance between the layered silicates. The d-spacing means thickness of repeated units of polymer clay nanocomposites. This repeated structure includes layered silicates and interlayer spacing. It is also called as basal spacing.

From the experiment, d-spacing and crystallinity could be achieved from the xrd.

Bragg's law which helps to get interlayer spacing is

$$n\lambda = 2d \sin\theta, \quad (2)$$

where n is an interger and typically regarded as 1 when it has basic and 2 or 3 when it has higher sub-periodicity. λ is wavelength; θ is the scattering angle; d is the d spacing which is addition of interlayer distance and one layer thickness [37]. The incident beams have 90° with reflecting plane. Scattering angle means angle(θ) between the incident and scattered beam [7]. Generally, SAXS deals with $2\theta < 1^\circ$ meaning its d -spacing is larger than 8.8nm and WAXS deals with $2\theta > 1^\circ$ meaning its d -spacing is smaller than 8.8nm. From this law, interlayer spacing can be obtained [37].

Crystallinity can be determined using XRD. Diffraction happens when sample is crystalline, and scattering occurs when there are amorphous materials. The former gives

sharp peaks at a specific angle, while the latter provides smooth lines at the wide angle [34].

$$\text{Crystallinity}(\%) = \frac{A_c}{(A_c + A_a)} \times 100 \quad , \quad (3)$$

where A_c means area of crystallinity peak under diffraction curve and A_a refers to area of amorphous peak under diffraction.

Especially, at the polymer layered silicate nanocomposites, xrd leads to determine whether it is unmixed, intercalated or exfoliated. Specific information about the dispersed state is discussed in Chapter 4.

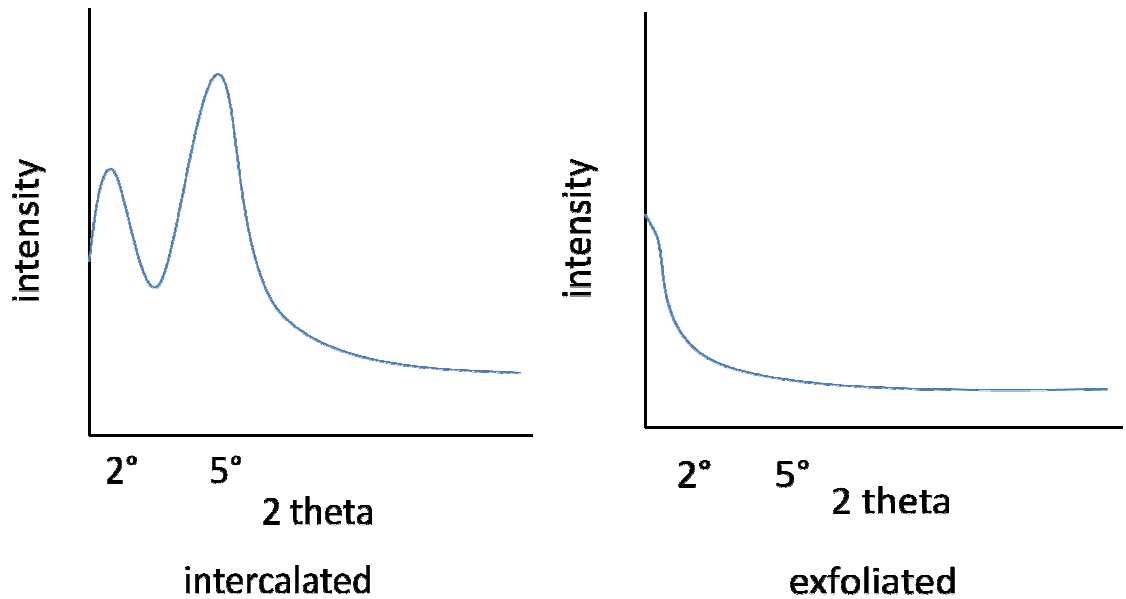


Figure 2-3. XRD of intercalated and exfoliated polymer layered silicates nanocomposites (a) Intercalated polymer layered silicate nanocomposites. The peak is shown when 2θ is 2, 5° (b) Exfoliated polymer layered silicate nanocomposites. There is no peak until 10°.

2.2. Thermal gravimetric analysis

Thermal gravimetric analysis (TGA) is simple method to measure the weight depending on temperature. As 10~15mg sample is heated with linearly temperature change on the TGA pan. Its weight also changed because of evaporation. From these phenomena, we could get the following two pieces of information.

The first result we obtain is inorganic filler concentration of the nanocomposites. As the temperature rises, organic contents disappear and only inorganic materials remain which implies inorganic concentration.

The second result from TGA is thermal stability of the nanocomposite. If sudden weight loss occurs either at a low temperature range or too fast rate, then it means its thermal stability is very low. However, if weight loss occurs at the high temperature range or its degradation rate is sufficiently slow, it has very strong thermal stability.

2.3. Optical microscopy

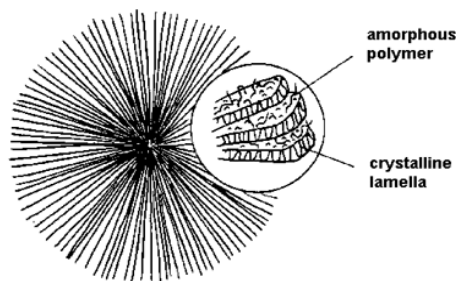


Figure 2-4. This structure is lamellar shape of a polymer. At the crystalline part, it is likely to be grown with nucleation sites. However, at the amorphous parts, definite spherulite form is not shown (www.doitpoms.ac.uk).

Optical microscopy (OP) is widely used for observing morphology of polymers with low cost compared to other techniques. Its coverage limit is approximately 1 μm . Its magnification is not strong compared to scanning electron microscope or transmission electron microscope; however, it helps observe spherulite polycrystalline polymer structure [38].

For my experiment, I use polarizing light microscopy. Under the polarizing light microscopy, isotropic shows dark field, however, anisotropic samples which have birefringence show a bright part.

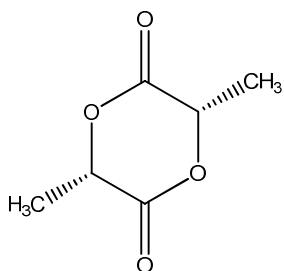
Polymer has amorphous parts and crystalline parts. The lamellar form is grown with spherulite shape related with the crystalline and amorphous parts. In particular, we could see spherulite form on polymer samples as shown in figure 2.4 [39]. Accordingly, if the crystalline parts are increased, its spherulite part is definite. However, if the amorphous form is increased, its shape is obscure. From the sphere, we could focus on number of nuclei and size of sphere. Nuclei are likely to grow into spherulite forms. From these information, the clay's role as the nucleation agent could be estimated.

Chapter 3. Experiment

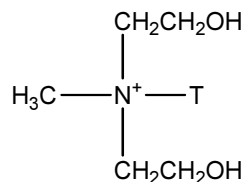
3.1. Materials

L-lactide ((3S,6S)-3,6-Dimethyl-1,4-dioxane-2,5-dione) is purchased from Sigma-Aldrich (1~5% PLA-OS) or Purac biomaterials. Cloisite® 30B(MT2EtOH, natural montmorillonite modified with a ternary ammonium salt) acts as an organic modifier which is from Southern clay products. Cloisite 30B (C-30B) is made from smectic phyllosilicate, montmorillonite which is organically modified with methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium (MT2EtOH) at 90 meq/100g clay. Its tallow distribution is 65% C₁₈, 35% C₁₆, and 5% C₁₄. A Sn(Oct)₂ (tin II ethylhexanoate) is from Sigma-Aldrich. For the solvent, toluene is used.

Monomer: L- lactide



Organosilicate : Cloisite® 30B(methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium lactide



T is tallow(~65%C₁₈;30%C₁₆;~5%C₁₄)

Catalyst : Sn(Oct)₂

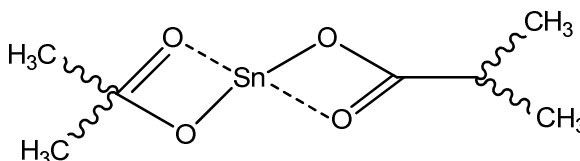


Figure 3-1. Structures of materials for synthesizing (a) L-lactide is used for monomer (b) Organophilic parts of Cloisite 30B. Exchangeable cations are exchanged by this materials (c) Sn(Oct)₂ is used for catalyst. It helps initiation of hydroxyl groups.

3.2. Method

3.2.1. Cleaning Cloisite 30B

The procedure is as follows: At first, disperse the clay in ethanol by stirring vigorously and sonication. Filter the clay solution with large Buchner funnel and the vacuum filtration pump. Take the collected solids and re-disperse in ethanol to repeat the steps above two to three times. During repeated process, consider stirring only. Take the final collected solids to the vacuum oven and dry for 24-48 hours at 60°C. In order to check water removal, take the 10~15mg sample to TGA. After drying the clay completely, it can then be added to final solvent and dispersed to polymer matrix.

3.2.2. Low concentration PLA-Layered silicate (1~5%)

Dry L-lactide in the vacuum oven at 25°C for overnight (at least more than 8 hours). Add dried L-lactide in a tri-necked flask, where one of the necks is connected with Argon/Vacuum line and Purge three times. During Argon atmosphere, add the toluene (volume of toluene = 3*mass of L-lactide, in ml) and purge 3times again. When the temperature increases up to 70~75°C, stir the solution vigorously. This step should be performed 100g per 1hour.

Simultaneously, dried Cloisite 30B is sonicated with toluene for 40 minutes at 60°C. After checking L-lactide to dissolve completely, mix L-lactide solution with sonicated Cloisite 30B solution. To add clay solution better, could use fresh toluene. Dissolve the CS30B into mixture at 70~75°C for at least 2 hours. Increase the

temperature to 120°C. When increasing the temperature, purge SnOct2/toluene mixture for 30 minutes. After purge, add SnOct2/Toluene mixture into original mixture. Let the polymerization sit for 24 hours at 130°C.

After polymerization, pour mixture into large amount of n-hexane slowly and let it precipitate. Wait overnight, and then run the vacuum filtration and collect retenerate. Dry the collected materials in the vacuum oven at 70°C.

3.2.3. High concentration PLA-MMT (11%)

Dry L-lactide in the vacuum oven at 25°C for overnight (at least more than 8 hours). Add dried L-lactide in a beaker and dissolve into toluene. As the temperature increases up to 70~75°C, let it dissolves for 3 hours.

Simultaneously, the dried Cloisite 30B is sonicated with toluene for 24 hours. After checking L-lactide dissolve completely, mix L-lactide solution with sonicated Cloisite 30B solution. The mixed solution is sonicated for 24 hours.

The mixture moves into a single flask in an oil bath and the temperature is set to 120°C. At the same time, purge SnOct2/toluene mixture for 30 minutes. After purge, add SnOct2/Toluene mixture into original mixture. Let the polymerization sit for 24 hour at 120°C. Wait until the single flask reaches the room temperature.

After polymerization, the mixture is poured into a large amount of n-hexane slowly and precipitates. Wait overnight and then run the vacuum filtration and collect retenerate. Dry the collected materials in the vacuum oven at 70°.

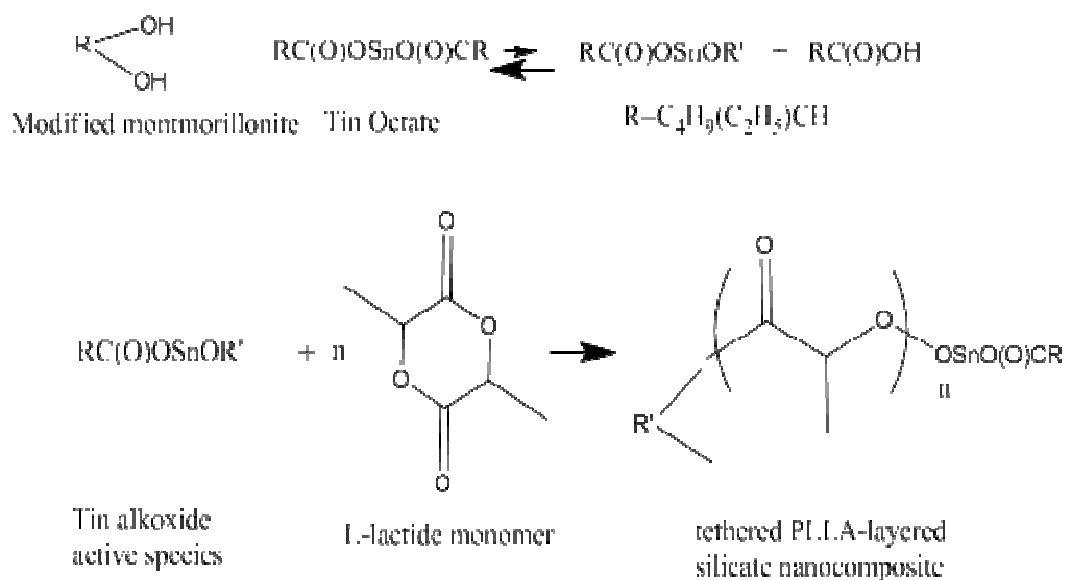


Figure 3-2. While the reaction occurs, the clay reacts with tin octate. After reaction of these two materials, tin alkoxide active species are made. Tin alkoxide active species react with L-lactide monomer to get the tethered PLLA-layered silicate nanocomposites. Remaining hydroxyl groups help polymerization continuously.



Figure 3-3. This sonicator is used for synthesizing 1~5% PLA layered silicate nanocomposites. When the 1~5% PLA layered silicate nanocomposites are synthesized, only one hour sonication is conducted for exfoliation samples.



Figure 3-4 .This sonicator is used in order to get the 11% concentration exfoliated PLA layered silicate nanocomposites. This machine provides stronger frequency and an automatic timer for sonication.

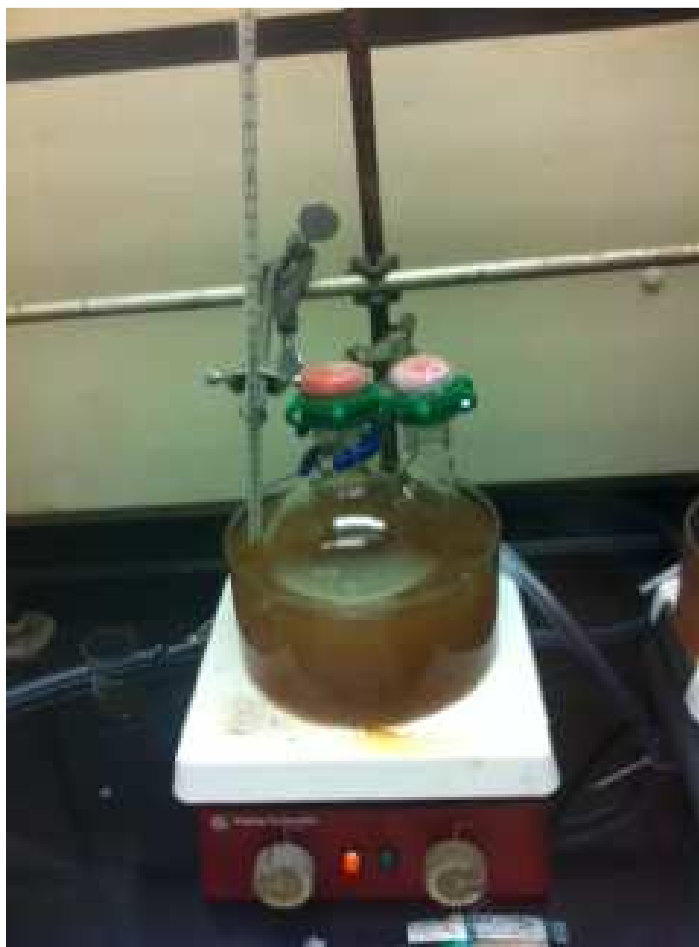


Figure 3-5. This picture is taken during polymerization. To prevent solvent evaporation, the flask is tightly sealed with the rubber plug using the clamp. The temperature is maintained at 120°C and polymerization is conducted for 24~48 hours.

3.3. Experimental

3.3.1. X ray diffraction

Using XRD, whether the sample is a result of intercalation or exfoliation can be determined. For the x-ray diffraction experiment, Siemen D5000 (Cu K α radiation ($\lambda=0.154\text{nm}$) is used.

For preparing XRD, annealing process is required. Dried polymer is placed on vacuum oven at 180°C for at least 3 hours (on DSC pan). After 3 hours, decrease the temperature and maintain it at 120 °C for at least 3 hours. During the process, pellet is formulated. XRD is conducted from 2° to 40°.

3.3.2. Thermal gravimetric analysis



Figure 3-6. This is TGA and TGA computer. At first, TGA pan is cleaned with flame and then calibrated for taring. If taring works well, sample is loaded to TGA. To prevent oxygen flow, argon is used during the experiment.

For TGA (Thermal analysis, In), temperature range is from 30° to 800°. The changing range is 10° /min. The measured sample quantity is 10~15mg on Argon atmosphere.

3.3.3. Optical microscopy

Optical microscopy from BX51 microscopy is used in this study. The idea is to melt the samples and watch them recrystallize. For checking birefringence, a polarized lens is used. One or two mg of dried sample made (as seen in the previous section) is prepared using the slide glass and cover glass. The darkest point is found by rotating the polarized lens to reach the point where the polarized lens is orthogonal to the analyzer. Once the appropriate spot was found, the lens is locked in position. Using Win Temp software from the computer, the temperature is increased by 10°C per minute until the temperature reaches 20°C or 30°C above the T_m of the material (at least) in order to ensure all the crystalline formed is dissolved once again. Any air bubble formed on the slide is removed by lightly pressing it with a cotton swab. Current temperature is maintained for 20 minutes and decreased to 120°C for 1 hour. The formation of crystals and spherulites is observed as the sample cooled down.

Chapter 4. Results and discussion

4.1. Synthesis of PLA-organic silicate nanocomposites

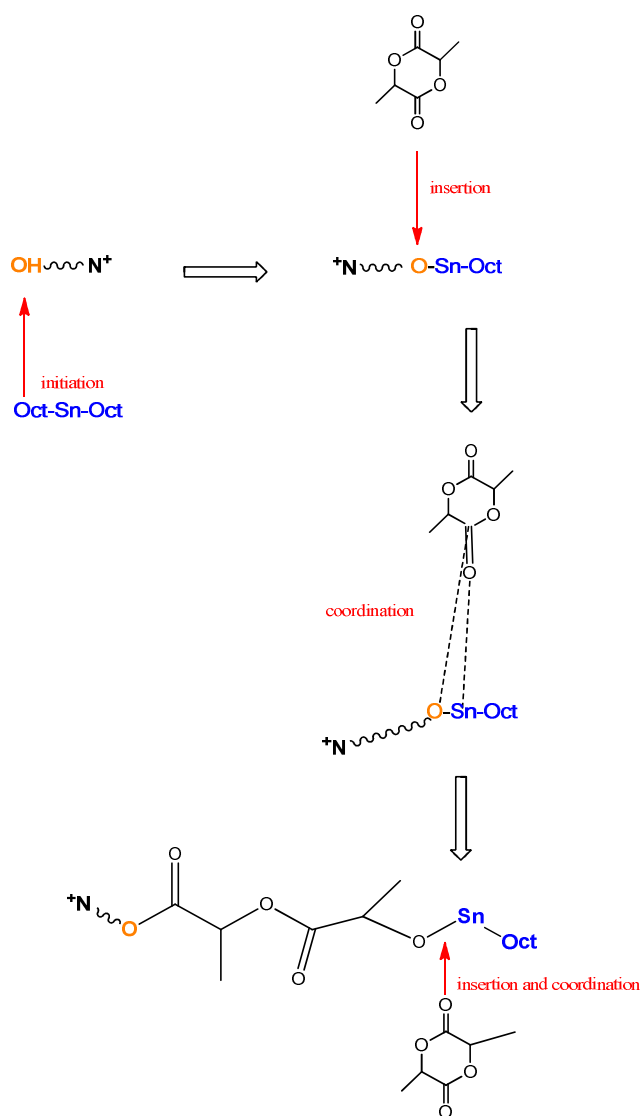


Figure 4-1. Reaction scheme. This picture shows in-situ ring opening polymerization. Initiation of hydroxyl groups occurs on the clay surface. Through the insertion and coordination, tethered layered silicate nanocomposites are synthesized.

The Figure 4-1 shows the clay structure and nanostructure during the synthesis. At first, tin octate reacts with the hydroxyl group of clay. Following the reaction, tin octate changes into tin alkoxide active group. L-lactide is inserted into these active sites and then coordinated between Sn and O linkage of the real initiator. After the ring is opened, it becomes the polymer through the insertion and coordination process, through which PLLA layered silicate nanocomposites are made.

While the polymerization is processing between layers, interlayer spacing is increased through in-situ-ring opening reaction. This is because the polymerization conducts within the clay galleries or extra galleries. The extension of polymer chains leads to exfoliation or intercalated structure. As shown in Chapter 1, if the direct condensation route is used, its molecular weight is low due to the condensation. However, higher molecular weight can be achieved through the ring-opening polymerization because the cyclic monomer has already gone through a condensation reaction prior to the formation of the ring [40].

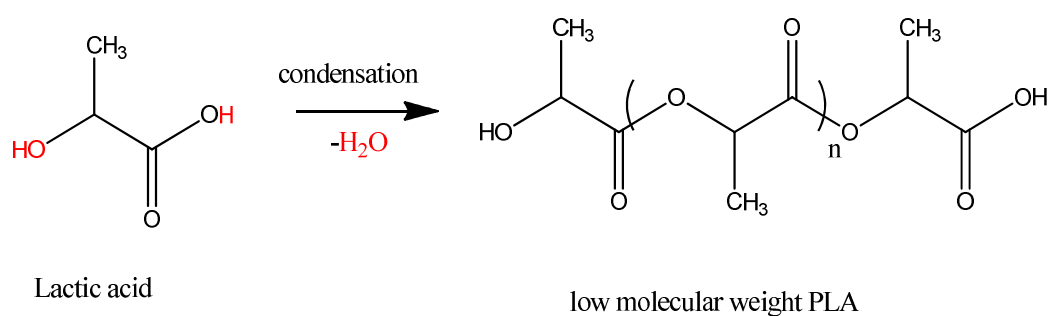


Figure 4-2. PLA is synthesized from Lactic acid or L-lactide (a) Direct condensation route makes low molecular weight.

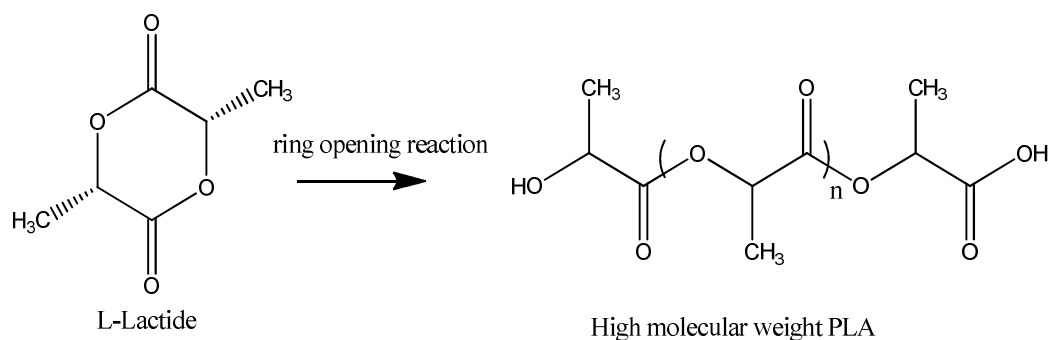


Figure 4-2. (b) Ring opening reaction could make high molecular weight because there is no condensation reaction. In case of cyclic L-lactide, condensation already occurs before forming the ring structure (continued).

When the reaction occurs, we can estimate the molecular weight. In general, molecular weight can be estimated by the monomer/initiator ratio. In this work, if ratio of L-lactide is increased, its molecular weight is increased. However, if the ratio of clay is increased, its molecular weight is decreased as the OH group of the clay acts as an initiator by combining to the tin oxide. As shown in figure 2, if there are a remaining OH groups, it can help the initiation continuously. As the amount of the catalyst is increased, its reaction rate can also be increased. However, its molecular weight is decreased because the catalyst also helps in making the initiator. Accordingly, it can be estimated that as the clay concentration is increased, its molecular weight is likely to be decreased.

To get the exfoliated PLA layered silicate nanocomposites, sonication is conducted. Ultrasound energy of sonication agitates the particles and can dissolve an intermolecular interaction. In my work, sonic waves make acoustic cavitations that go through formation, growth, and collapse of bubbles in the toluene. The process helps dispersing the clay platelets into toluene. Interlayer spacing which is interacted by van der Waals force can be broadened and dispersed well in toluene because it has a relatively weak force than other parts.

4.2. Inorganic concentration of clay

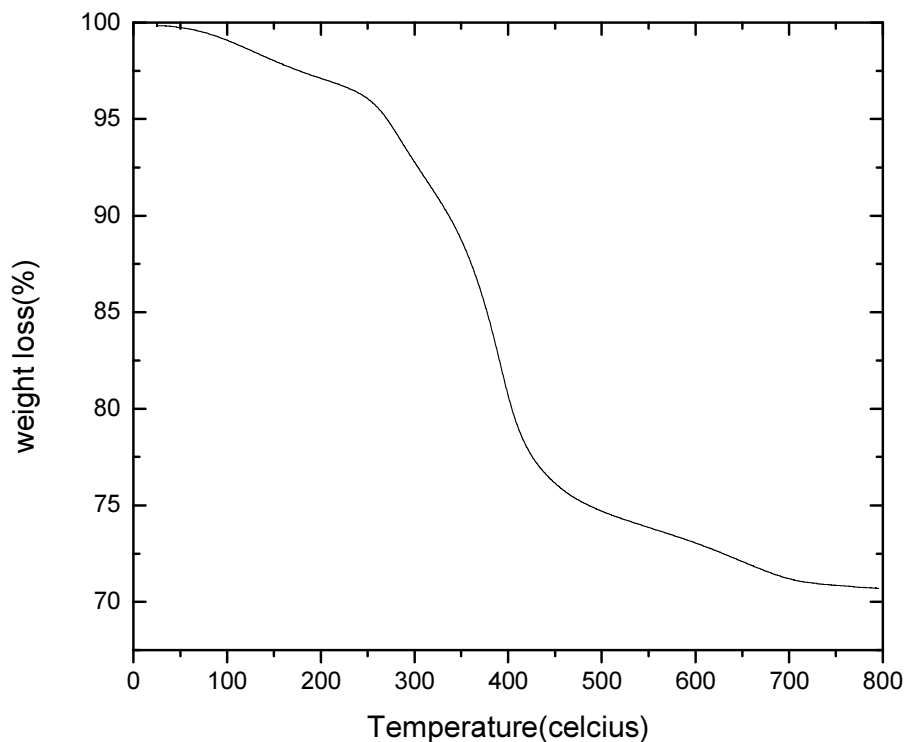
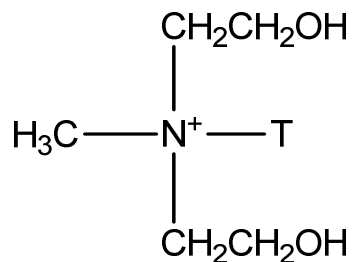


Figure 4-3. TGA of Cloisite 30B is run because we should know how much inorganic concentration is included. This graph shows that its inorganic concentration is around 71%.

Thermo gravimetric analysis (TGA) is used to check how much inorganic concentration of the clay is included. This occurs under an inert gas flow, a non-oxidative degradation. The remaining inorganic concentration weight percent at 800°C is 71%. During the heating, the weight loss in Cloisite 30B occurs. At the first stage, moisture loss can lead to weight loss with slight change. When sudden weight loss takes place, the organic modifier either in a physically adsorbed form or in the interlayer spacing is decomposed. The organomodifier part is shown in figure 4-4. Ammonium cations of Cloisite 30B can be thermally degradable with Hoffmann

elimination reaction, which decomposes ammonia and matched olefin, and then vaporizes as CO₂, C₂H₂, NH₃ or H₂O [41]. Finally, a char of nanoclay, the inorganic concentration is 71% which corresponds to the original nanoclay before the modification of alkylammonium cation.



T is tallow(~65%C18;30%C16;~5%C14)

Figure 4-4. This is the organic modifier part of clay. It has an ammonium ion and it goes through Hoffman elimination when heat is applied to the materials.

4.3. Dispersibility

4.3.1. Comparison between intercalated and exfoliated nanocomposites

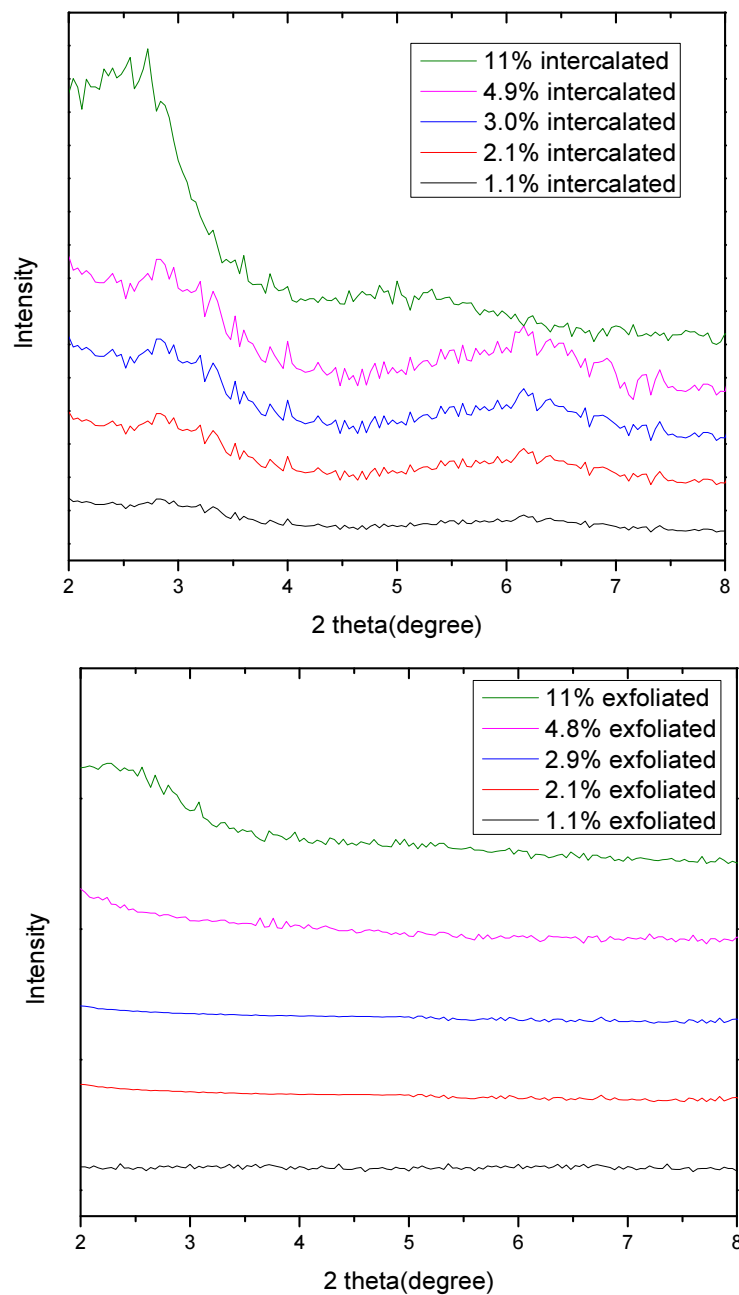


Figure 4-5. XRD data of all samples (a) Non-exfoliated PLA layered silicate nanocomposites. In these cases, there are broad shoulder peak from $2\Theta = 2^\circ$ to 5° . As the concentration increases, its intensity becomes stronger (b) Exfoliated PLA layered silicate nanocomposites. They have no peaks around from $2\Theta = 2^\circ$ to 5° .

From the XRD peak, we can determine whether it is intercalated or exfoliated. From the figure 4.3, the intercalated samples show wide and less intense shoulders. As the inorganic concentration increases, the more intense peaks appear at $2\Theta = 3, 6^\circ$. These peaks prove that they are not completely dispersed, yet partially aggregated. In the case of intercalated samples, polymer chains penetrate into the gallery spacing of layered silicate as shown figure 4.4. The intensity of x-ray diffraction means the number of photons per second; so the higher the intensity, the more atoms or molecules are at a specific place. Moreover, d-spacing, the addition of interlayer spacing and one layer thickness, has increased while decreasing of the x-axis as shown in Chapter 2. At the intercalated samples, higher intensity peaks at the low specific angle show that the many number of clay platelets (multi-layers) are placed parallel to each other while having the same d-spacing value, due to the ordered clay structure. Accordingly, these peaks show that it has many parallel clay platelets with specific d-spacing. The calculation of d-spacing will be shown below. In addition, as the inorganic concentration increases, their intensity of x-ray diffraction is increased because there are more portions of clay which have the regular structure with specific d-spacing. As a result, higher concentration samples show higher intensive peaks. Except for the peak at d-spacing, it has unstable y intensity because clay platelets aggregate.

Basal spacing of intercalated PLA-layered silicate nanocomposite is shown in the Table 1. The d-spacing is a distance of addition of interlayer spacing and the one layer thickness, and it is dispersed well if it is broadened. This value is calculated by Bragg's law. As shown in Table 1, d-spacing of intercalated PLA layered silicate nanocomposites is broadened to $30 \sim 35\text{\AA}$ compared to the clay d-spacing (around 17\AA) because polymer

chains disperse into the gallery between layered silicate [42]. From the data, we can reach the conclusion that the polymer chains into the silicate galleries expand clay structure by similar distance in the intercalated samples.

Table 1. d-spacing of non-exfoliated PLA layered silicate nanocomposites

Intercalated	
1.1% PLA-OS nanocomposite	31.51 Å
2.1% PLA-OS nanocomposite	31.07 Å
3% PLA-OS nanocomposite	31.07 Å
4.9% PLA-OS nanocomposite	31.07 Å
11.01% PLA-OS nanocomposite	32.44 Å

However, exfoliated samples do not show peak at low angle because they have much broaden interlayer spacing and respective layer is dispersed with disordered structure as shown in figure 4.6. Because layered silicate is individually dispersed in the resin in case of exfoliated samples, it is difficult to show the peaks at $2\Theta = 3, 6^\circ$ for exfoliated samples [43]. In other words, no peak between these angles means that they are dispersed well. In these cases, the radius of gyration of PLA could be regarded as the interlayer spacing, in that it is dispersed well individually. Especially, up to 2.9%, peaks at $2\Theta = 3, 6^\circ$ completely disappear. However, there are small and broad shoulder above 4.9% PLA-OS nanocomposites. The disappearance of peak at the low angle shows the well separation between clay platelets. In case of high inorganic concentration (11% inorganic concentration) exfoliated sample, it has broad shoulder at the low angle since it is not completely exfoliated. In that case, partially intercalated and exfoliated structures are mixed because of its strong viscosity at high inorganic concentration samples. Most

parts are exfoliated; however, there are remaining ordered structures with parallel multilayer clay structures. Additionally, partially multilayer in parallel leads to make broad shoulder peaks because they have some parts with ordered clay structure with d-spacing. Because the numbers of parallel multi-layers in the high exfoliated samples are smaller than those of intercalated and its interlayer spacing is irregular, intensity of high inorganic concentration exfoliated samples is much smaller and broader than that of intercalated samples.

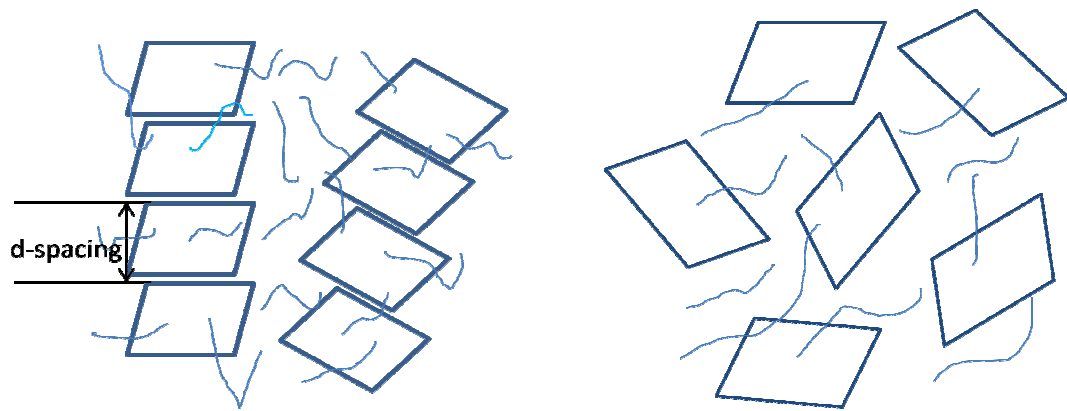


Figure 4-6 (a) Structure of intercalated samples have d-spacing which is combination of interlayer spacing and one layer thickness. This shows ordered structure. (b) Structure of exfoliated samples. In this case, they have disordered structure.

4.3.2. Crystallinity

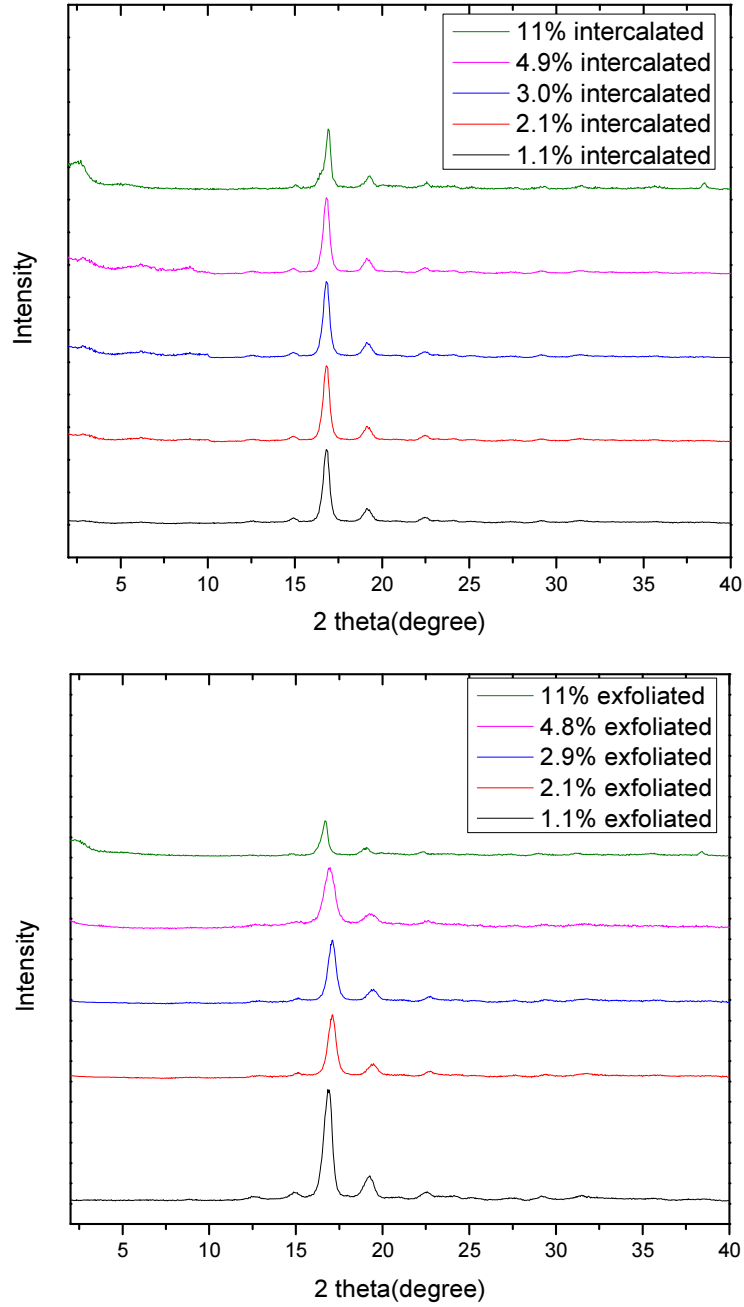


Figure 4-7. XRD data of all samples (a) Non-exfoliated PLA layered silicate nanocomposites. (b) Exfoliated PLA layered silicate nanocomposites. All samples maintain PLLA α -form after synthesizing. Most intensive peak could be observed around 16.8° among all samples. This peak means 200 peak of typical orthorhombic crystal. In addition, they have small peaks around 19.3° , 22.9° , which respectively means 203, 105 peaks [44].

Table 2. Crystallinity(%) respect to d₂₀₀ peak

Intercalated		Exfoliated	
1.1% PLA-Nanosilicate	38.32%	1.1% PLA-Nanosilicate	45.84%
2.1% PLA-Nanosilicate	33.65%	2.1% PLA-Nanosilicate	34.13%
3% PLA-Nanosilicate	29.84%	2.9% PLA-Nanosilicate	34.14%
4.9% PLA-Nanosilicate	26.73%	4.8% PLA-Nanosilicate	32.39%
11.01% PLA-Nanosilicate	22.26%	11.5% PLA-Nanosilicate	21.41%

Crystallinity respect to d₂₀₀ is calculated in Table 2. The atoms or molecules could be arranged within periodic manner. Crystallinity refers to how many crystalline parts are included. As the inorganic concentration increases, crystallinity is decreased in both cases.

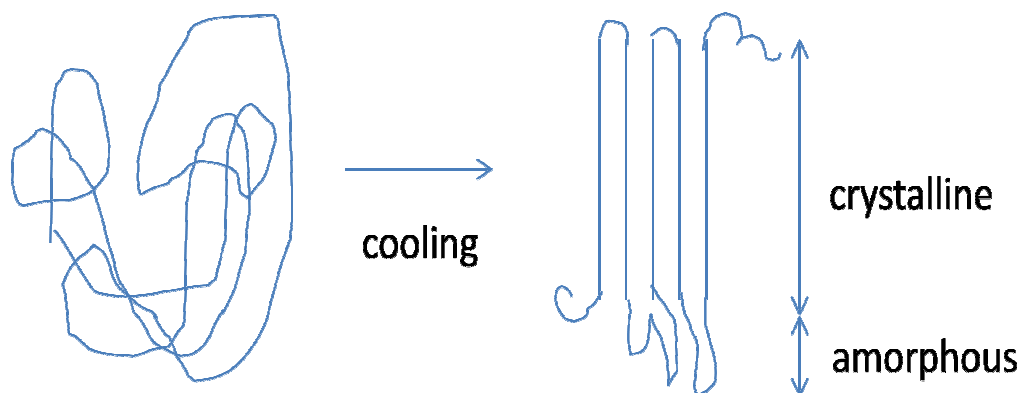


Figure 4-8. After holding polymer at the high temperature, its polymer chain is fully extended. After slow cooling, its chain rearranges orderly and makes lamellar structure. Regular parts are crystalline parts and irregular parts are amorphous parts.

Considering the tendency of decreasing crystallinity, clay is likely to play a role of barrier obstruction while crystallization arises. Decreasing crystallinity means that their crystalline parts are decreased, while there is an increase in amorphous parts. For

preparing the xrd samples, chains of polymer sample are annealed. After precipitation and drying process, polymer chain becomes irregular. To anneal the polymer chains, hold the material at 170°C for 3 hours to make chains to be extended fully and then decrease the temperature slowly. Through this process, polymer chains become ordered structure and form lamellar structures which have crystalline parts and amorphous parts. While the chains of polymer are extended to ordered structure, clay could interfere with these rearranging processes as obstruction. Accordingly, it has more irregular parts which mean high amorphous parts with low crystallinity. High inorganic concentration has more number of clays. As a result, more and more obstruction occurs during rearranging the chains and its crystallinity is decreased with increasing the inorganic concentration.

In conclusion, although the large surface area of polymer-nanocomposite gives more crystallization property, clay may prohibit flowing more and more during crystallization at higher miscibility samples. Lastly, as the inorganic concentration increases, crystallinity of polymer layered silicate nanocomposites decreases due to clay role as physical obstruction.

4.4. Thermal stability

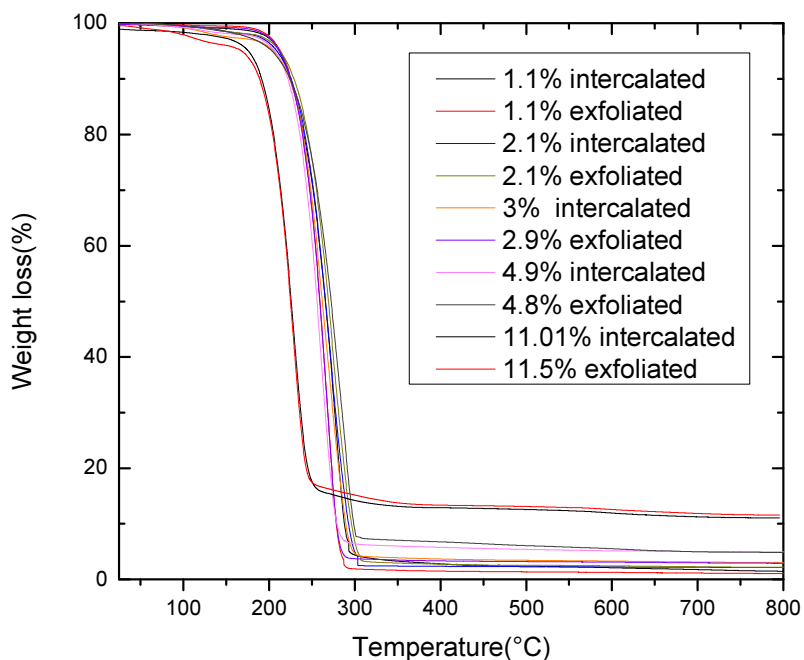


Figure 4-9. Thermo gravimetric analysis (TGA) data of all PLA layered silicate nanocomposites. Final concentration and degradation rate are obtained from the graph. To get data on thermal stability, picked up the data when 10% temperature loss occurs.

Thermo gravimetric analysis process is run under the nitrogen atmosphere. This heating process without the oxygen is called pyrolysis, which means that thermochemical decomposition of organic material happens with the increase of temperature. As the temperature increases, generated volatile materials evaporate, and inorganic parts remain after the process. As the temperature increases, pyrolysis of ester group of PLA leads to the cleavage of polyester chains with releasing of CO_2 and H_2O . After that, cyclic dimmer such as lactide is made due to unzipping depolymerization. The heating continuously makes CO , acetaldehyde and H_2O as volatile material [45]. From the figure 4.9, we can see that the final inorganic concentrations remain at 800°C. Respective result

about final concentration is given Table 3. Although there is little difference between the intended concentrations, it approaches the intended value.

Table 3. Comparison between targeted inorganic concentration and synthesized inorganic concentration

Intercalated		Exfoliated	
targeted	synthesized	Targeted	synthesized
1%	1.1%	1%	1.1%
2%	2.1%	2%	2.1%
3%	3%	3%	2.9%
5%	4.9%	5%	4.8%
11%	11.01%	11%	11.5%

From the data shown in figure 4-9 data, pick the T10% weight loss data in order to measure thermal stability. Figure 4.6 is based on information from figure 4.5 data and we could compare thermal stability between non-exfoliated and exfoliated PLA layered silicates nanocomposites.

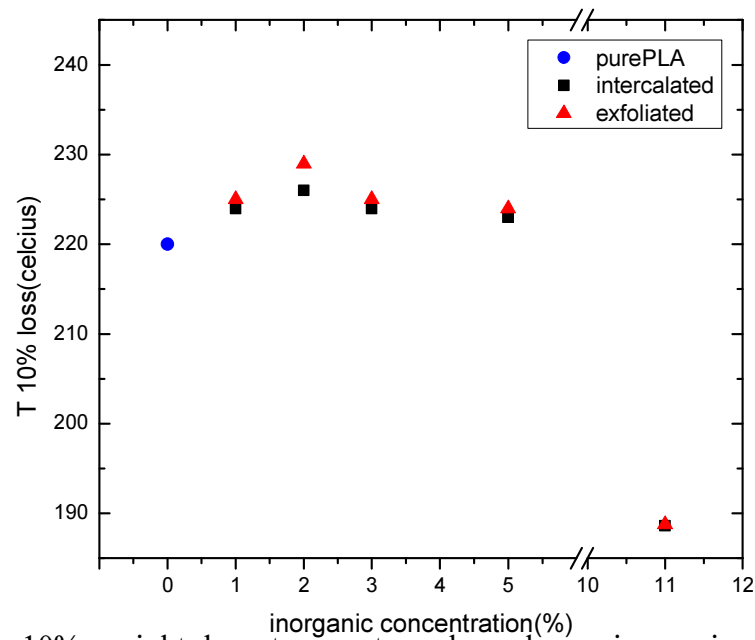


Figure 4-10. 10% weight loss temperature depends on inorganic concentration and dispersion state. The black dot is non-exfoliated data and the red dot is exfoliated data. T10% loss data is dramatically decreased when the concentration is 11%.

As shown in figure 4-11, T10% weight loss of all samples from 1 to 5% is similar. However, T10% weight loss dramatically decreases above 11% inorganic concentration. Higher T10% weight loss means higher thermal stability. PLA is degradable materials and its thermal stability is related to molecular weight. If the molecular weight is low, it is likely to be easily volatilized. Therefore, polymers with low molecular weight show low thermal stability and we need to know the degradation information to understand the thermal stability.

At first, pure PLA is degraded by chain-scission reaction and transesterification reaction. These two phenomena decrease molecular weight during the process. In figure 4-7, it represents the possible chain-scission reaction of PLA. Two susceptible linkages, carbonyl carbon-carbon linkages and carbonyl carbon-oxygen go through the reaction at the polyester. In addition, the mechanism of degradation is also located at the end of the chain. Transesterification reactions decrease the molecular weight because intramolecular transesterification or back-biting make polymer degradation by making cyclic oligomers[46] as shown in figure 4.11. The existence of monomers, oligomers and hydroxyl groups helps the transesterification reaction.

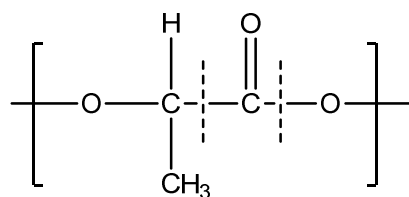


Figure 4-11. This picture shows the degradation of PLA. (a) Chain scission helps cleaving of carbonyl carbon-carbon linkages and carbonyl carbon-oxygen. This cleavage can happen at the chain end.

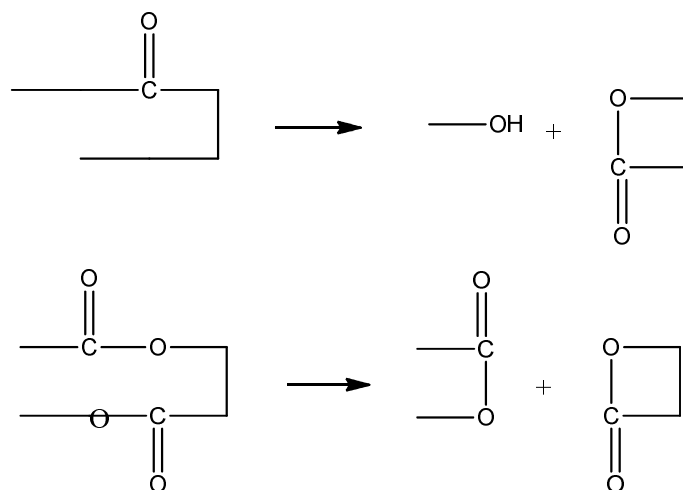


Figure 4-11. (b) Transesterification reaction can lead to degradation of PLA. It changes to cyclic oligomers (continued).

The filler like Cloisite 30B is likely to reinforce thermal stability since it acts as thermal insulator or mass transport barrier when the volatile products is generated [21]. It also helps the formation of char. At the same time, the clay also accelerates thermal decomposition as silicate layers help hold accumulated heat at early steps and its hydroxyl group of organic modifier parts which affect to molecular weight [47].

From these experiments, pyrolysis of ester group leads to the cleavage of polyester chains with releasing of CO_2 and H_2O and then cyclic dimmer is formed due to unzipping depolymerization as mentioned above. Considering clay and PLA, its role as reinforcing thermal stability is more prominent on 2~5% inorganic concentration samples because its T 10% weight loss is around 200° . This is because thermal insulator and mass transport barrier properties of clay. However, in the case of 10% inorganic concentration, the clay working as assisting the degradation is dominant because its T 10% weight loss dramatically decreased compared to 2~5% inorganic concentration samples. In particular,

increasing of hydroxyl group on the clay surface leads to low molecular weight because hydroxyl group acts as an initiator during polymerization and the number of monomers is decreased. Generally, monomer/initiator ration is correlated with molecular weight. Thus, low ratio of monomer and high ratio of initiator implies low molecular weight. In addition, hydroxyl groups of clay help transesterfication reactions which decrease the molecular weight as mentioned above. Accordingly, low molecular weight ends up with the decreases of the low thermal stability since low molecular weight materials is readily volatile. In addition, stacked silicate layers are able to hold accumulated heat which helps decomposition from outside heat. Thus, thermal stability of high inorganic concentration is decreased.

In conclusion, heat barrier property is dominant at the low inorganic concentration samples. However, as the inorganic concentration increases, its reverse role is dominant because of low molecular weight and heat accumulator of the clay.

4.5. Morphology

Ordered polymer chain is likely to be oriented perpendicular to the radius of the spherulite that is correlated with the crystalline and amorphous parts. With the nucleation site as the starting point the lamellar arises and grows away from the nucleation site. In addition to this effect, polarizability anisotropy of individual polymer molecules makes different refractive index which is called birefringence. The two components of polarizer of lamellar transmit on a different orientation causing it to have lighter or darker parts.

When the temperature of hot plate is increased to around 230°C ~240°C, all birefringence disappear. After confirming that all the birefringence has disappeared, the hot plate is turned off so that it can be cool down. The pictures from figure 4-12 below have been taken when the hot plate temperature indicated around 120°C, and they show birefringence after isothermal crystallization at 120°C. At the semicrystalline polymers, it is not transparent because there are light scattering boundaries between the crystalline and amorphous parts. If these boundaries were to be decreased, then it becomes transparent. When the samples are cooled down slowly, certain orderly configurations (crystalline lamellar) are present [48].

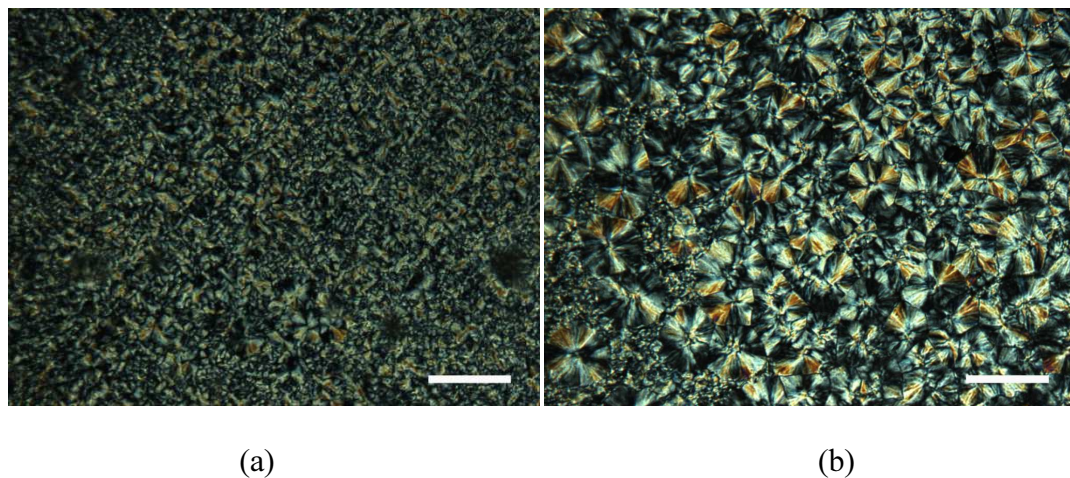
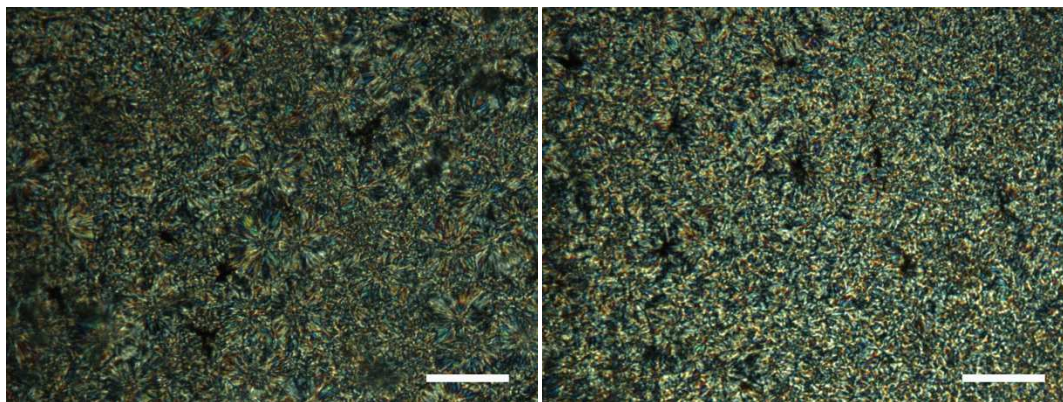
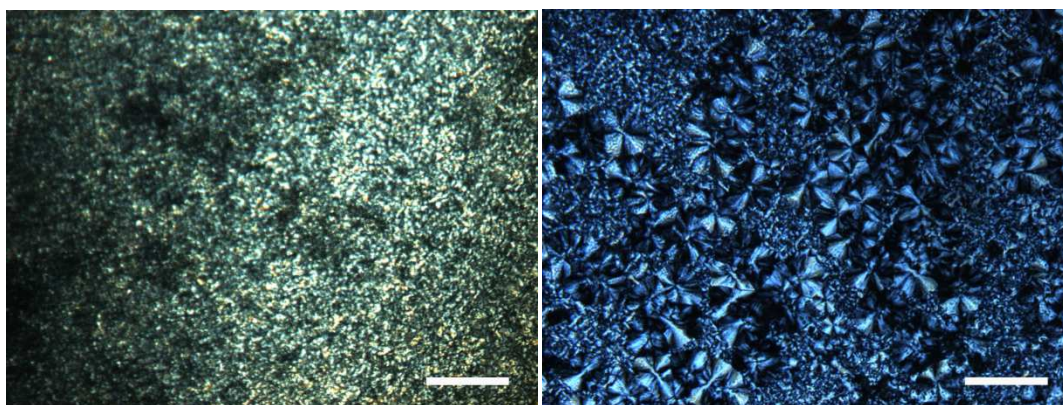


Figure 4-12. Optical microscopy pictures are taken after isothermal crystallization at 120°C. The scale bar is 100μm. From these pictures, spherulite form could be observed. Its shape and size is different depending on the concentration and dispersibility (a) 2.1% non-exfoliated (b) 2.1% exfoliated



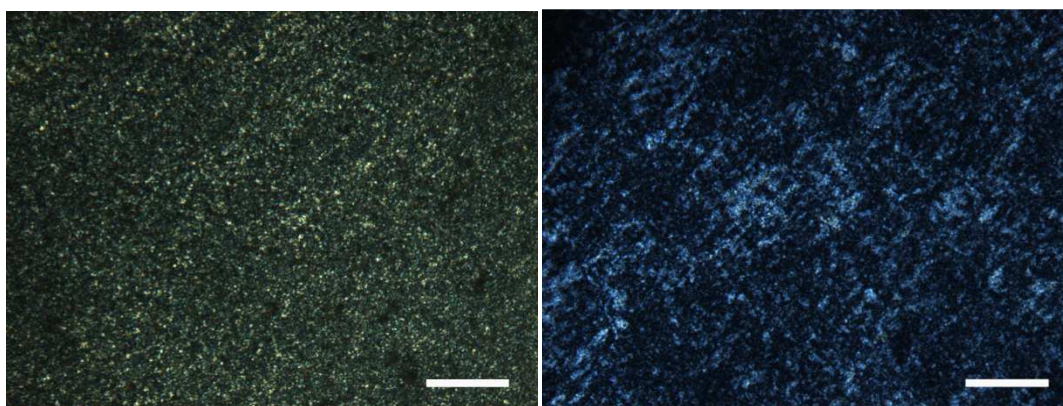
(c)

(d)



(e)

(f)



(g)

(h)

Figure 4-12. Optical microscopy pictures are taken after isothermal crystallization at 120°C. The scale bar is 100um. From these pictures, spherulite form could be observed. Its shape and size is different depending on the concentration and dispersibility (a) 2.1% non-exfoliated (b) 2.1% exfoliated (c) 2.9% non-exfoliated (d) 2.8% exfoliated (e) 4.9% non-exfoliated (f) 4.8% exfoliated (g) 11.01% non-exfoliated (h) 11.5% exfoliated.

At the low concentration, the definite spherulite structure can be obtained, but as the concentration increases, the spherulite structure becomes obscure. Based on data of the x-ray diffraction, crystallinity is decreased as inorganic concentration is increased in contrast. This means that area of crystalline part is decreased and area of amorphous part is increased. When there are more amorphous parts present, the formation of lamellar structure is less likely to occur. Therefore, it is difficult for us to find spherulite structures at the high inorganic concentration.

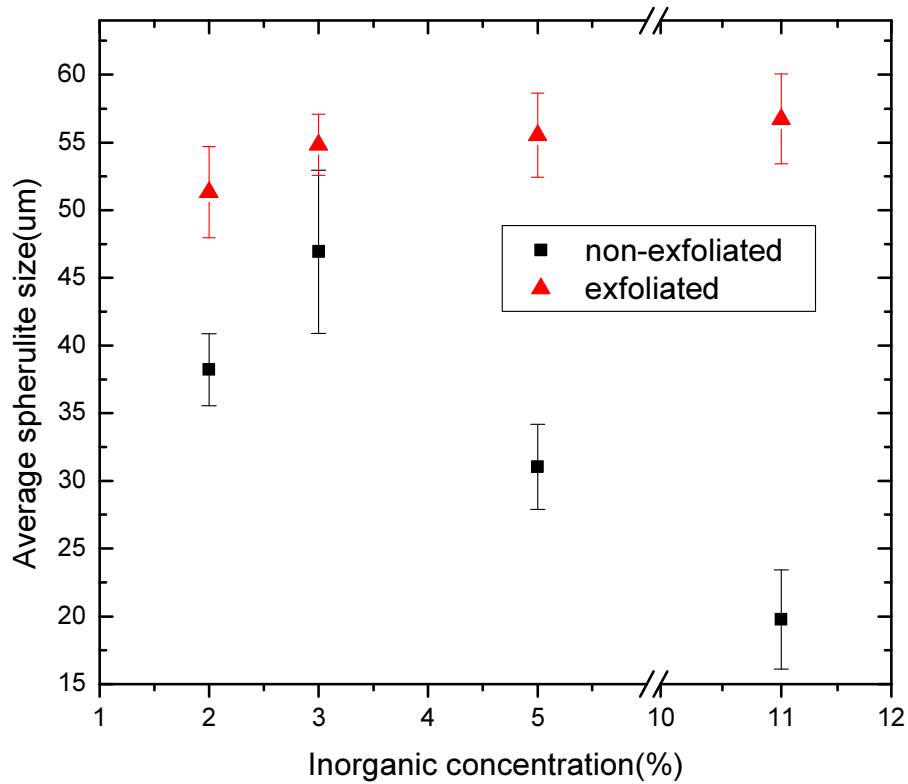


Figure 4-13. Average spherulite sizes depend on the inorganic concentration and dispersibility. The sizes of exfoliated samples are larger than that of non-exfoliated samples.

In figure 4.13 above, the average sizes of spherulite are calculated from figure 4.12. This procedure is done in order to observe morphology of polymer layered silicate nanocomposites. Figure 4.13 shows a tendency of spherulite size depending on the inorganic concentration and clay dispersibility into resin. In order to get the average of spherulite size, a series of spherulite photos' were taken, as shown in figure 4.12 above, and a diameter of each definite spherulite's was measured manually by constructing a circle around each spherulite and using a ratio of 100 micrometers scale bar. For diameter measurement, each circle is estimated from the center to tip of growth point of the spherulite from figure 4.12.

If the Cloisite 30B acts as nucleating agent, it makes a large amount of nucleation sites. If nucleation site is increased, then the spherulite size will decrease due to interference of each spherulite form. For detailed analysis, we need to consider non-exfoliated and exfoliated separately.

In case of the non-exfoliated samples, spherulite size (or circle size) decreases as the concentration increases in the most polymer layered silicate nanocomposites. These intercalated samples show lower miscibility between polymer and organic modifier of the clay, and the low miscibility of two materials increases bulk crystallization and makes smaller spherulites [49]. This is because the growth of new nucleating sites prohibits spherulite growth continuously and it leads to finer spherulites. As the inorganic concentration increases, there are many layered silicates and lower miscibility which obstruct spherulite growth, so it has finer spherulites. Thus, the clay acts as nucleating agent in the non-exfoliated PLA layered silicate nanocomposites.

However, in case of the exfoliated samples at figure 4-13, spherulite size (or circle size) is likely to be similar among all inorganic concentration within error bars. Moreover, spherulite size of exfoliated ones is larger than that of non-exfoliated ones through all inorganic concentration from figure 4-13. If the samples with similar inorganic concentration are compared, the non-exfoliated samples have more number of nuclei sites, but in the exfoliated samples, polymer has high miscibility with organic modifier of the clay. In that case, bulk crystallization is slower than that of non-exfoliated samples. The reason is that when samples have high miscibility it causes superstructure templating effect with fully extended clay platelets and it may obstruct local lamellar crystallization [50,51]. These low spherulite nucleation leads to larger spherulite in the exfoliated samples. In most cases, the CS30B does not have positive role as nucleating agent in the PLA. This analysis also supports the claim that the Cloisite 30B role as nucleating agent is stronger in the non-exfoliated PLA layered silicate nanocomposites than in the exfoliated ones.

In conclusion, the clay does not affect to nucleation action positively in the exfoliated samples. But, considering the size of spherulite shape in the intercalated samples, the clay does play its part as the nucleating agent due to low miscibility. From these results, I conclude that clay platelets are not ruled out when the spherulite form is grown and locked in the spherulites during isothermal crystallization in the non-exfoliated samples.

Chapter 5. Conclusion and future work

PLA (Poly-lactic acid) is an interesting eco-friendly material that researchers and practitioners as well as the government are increasingly targeting to develop and improve for its use. In addition, layered silicates are usually mixed with polymer to reinforce its property such as mechanical properties, thermal stability and barrier property. By mixing these two materials, the PLA can overcome its disadvantages such as brittleness and low thermal stability. However, strong interaction between individual sheets of layered silicate makes it difficult to be dispersed in the polymer.

In this work, in-situ ring opening method, organic-modified layered silicate and sonication are applied to get more exfoliated polymer layered silicate nanocomposites. In case of low concentration of PLA layered silicates nanocomposites, its exfoliation could be achieved with 1 hour sonication. In case of high concentration polymer nanocomposites, complete exfoliation is difficult. The exfoliation can be achieved through 48 hours of clay sonication and 24 hours of mixture sonication. In this experiment, 1, 2, 3 and 5 % inorganic concentration is for low concentration nanocomposites and 11% inorganic concentration is for high concentration polymer layered silicate nanocomposites.

Dispersibility, morphology, and thermal stability are evaluated by x-ray diffraction, thermal gravimetric analysis and optical microscopy. The result of x-ray diffraction shows whether polymer layered silicate nanocomposites is exfoliated or not and allows to calculate the crystallinity. There are peaks around 3° with intercalated samples because it is partially aggregated. However, there is no peak

around $2\theta = 2\sim 5^\circ$ with exfoliated samples because each layer is dispersed into the resin polymer. However, as the inorganic concentration increases, there are broadened peaks at the low angle. This is because it is difficult for layered silicates to be dispersed individually at the high inorganic concentration, so, partially aggregated and individual layers are mixed. In addition, crystallinity decreases as the concentration increases since clay plays a role of physical obstruction during the crystallization process.

Through the TGA data, we can reach the conclusion that real inorganic concentration is approximates the intended inorganic concentration. Furthermore, thermal stability is increased at low concentration and decreased at high concentration. It shows that the function of clay as heat barrier works well at the low inorganic concentration and thermal stability is decreased at high inorganic concentration because of low molecular weight of PLA and heat accumulator role of clay.

The morphology of PLA layered silicate nanocomposites shows different results depending on the dispersion state. At the same concentration, the non-exfoliated polymer nanocomposites show smaller spherulite size than the size of exfoliated samples. In the exfoliated PLA layered silicate nanocomposites, spherulite size is similar across all inorganic concentrations, which implies that clay does not affect the nucleation reaction. With the non-exfoliated PLA layered silicate nanocomposites, higher inorganic concentration leads to smaller spherulite size. Also, it is a nucleation agent in the non-exfoliated samples.

When the polymer is mixed with the clay, its molecular weight is decreased because clay leads to degradation and ratio of monomer/initiator is correlated with

molecular weight. Low molecular weight leads to poor mechanical property. In the future, high concentration PLA organic layered silicates will be mixed with high molecular weight commercial PLA to prevent overly low molecular weight. Through this method, high molecular weight of PLA layered silicates will be achieved with enhanced mechanical property.

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