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Circuits, Perfect Matchings and Paths in Graphs

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A Model for Permeability Reduction in Polymer Nanocomposites and Its Experimental Validation

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ABSTRACT

A Model for Permeability Reduction in Polymer Nanocomposites and Its Experimental Validation

Man Chio Tang

Environmental concerns have led to research interest in biodegradable plastics, especially polylactic acid (PLA). PLA, a bio-derived and biodegradable polymer which is readily available, is easy to process, and it can be a good substitute for conventional non-biodegradable polymers in food packaging applications. However, its poor gas barrier property has to be improved to make it competitive with more widely-used materials such as polyethylene terephthalate (PET) and polystyrene (PS). This can potentially be accomplished by dispersing nanoplatelets in the polymer as these additives act as impermeable barriers around which the diffusing molecules are forced to take a longer, tortuous path. The increased path length results in a reduction in the concentration gradient with a simultaneous reduction in the mass flux. A similar situation arises upon annealing the PLA which leads to the formation of crystals that again act as barriers to mass transfer. A combination of the two approaches may lead to further reductions in permeability.

To accomplish the goal of reducing permeability through PLA, an internal mixer was used to melt-mix nanoclay into the polymer matrix, and thin films were made using compression molding. Thermal measurements showed that these films were amorphous. Since the extent of hydrophobicity or hydrophilicity of the nanoclay surface influences the compatibility between the filler and the matrix, water vapor transmission rate experiments were conducted on nanocomposite films containing different commercially-available organically-modified nanoclays; a MOCON PERMATRAN W3/33 instrument was employed for this purpose. Based on the results obtained, it was found that Cloisite 30B was the most compatible clay with PLA. In other words, PLA containing Cloisite 30B had the largest reduction in water vapor permeability at a given clay loading level. Internal mixer operating conditions were then optimized to determine processing conditions that resulted in the best barrier properties for nanocomposite films made using Cloisite 30B. These were 200°C and 80 rpm for 5 mins. Under these conditions, it was found that, with an addition of 5.3 vol% (10 wt%) of Cloisite 30B, the water vapor permeability was reduced by 69% compared to neat PLA. The corresponding absolute value compares favorably to moisture permeability through PS. The solubility of moisture in the nanocomposites was measured in a separate set of experiments and was found to increase as the nanoclay loading increased. This was due to moisture adsorption on the nanofiller surface and not due to enhanced solubility within the polymer. Thus, the fractional reduction in water vapor diffusivity was the same as the fractional reduction in permeability.

The nanocomposite films were annealed to promote polymer crystallization, and the crystallinity level could be increased to 40% by annealing at 115°C for 40 hours. Under these conditions, the water vapor permeability was reduced by 45% compared to unannealed and unfilled PLA. When a nanocomposite film containing 2.6 vol% (5 wt) of Cloisite 30B was annealed under these same conditions, the water vapor permeability was reduced by a total of 66% compared to neat PLA. Annealed films containing more than 2.6 vol% clay were brittle, but
the addition of acetyl butyl citrate (ATBC) which is a plasticizer enhanced ductility. When 5 wt% of ATBC was added to PLA, an annealed sample containing 5.3 vol% (10 wt%) of Cloisite 30B exhibited a 74% reduction in water vapor permeability compared to unannealed and unfilled PLA.

A new model that builds on the tortuous path concept was developed based on the reduction in both the mass flux and area for mass transfer when nanoplatelets are dispersed in a polymer matrix. According to this theory, the ratio of the permeability in the absence of filler to that in the presence of filler is given by \( \left(1 + \frac{h}{2t}\phi\right)^2 \) where \( h/t \) is the aspect ratio of the nanoplatelets, and \( \phi \) is the filler volume fraction. When this theory was applied to moisture permeability results presented in this dissertation using an average aspect ratio determined from TEM pictures, there was quantitative agreement between the model prediction and the measured permeability value on PLA/clay nanocomposites at each filler loading level. By contrast, other theories available in the literature overpredicted the permeability values by a significant amount. Additionally, the theory predicts that the relative reduction in permeability is independent of the temperature of measurement and the concentration driving force, and this is again borne out by experimental results.
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1 OVERVIEW and OBJECTIVES

1.1 Introduction

Polymers are widely used as packaging materials. Most of them are typically derived from crude oil which is not a renewable resource. Also, the polymers are, in general, neither biodegradable nor compostable. Moreover, these non-degradable packaging materials are usually discarded after a single-use and end up in landfills as solid waste. As a consequence, concerns over pollution and sustainability have led to enormous scientific investigations on bio-derived and biodegradable polymers such as polyhydroxyalkanoate (PHA) and polylactic acid (PLA). They are largely used in packaging and biomedical applications (e.g., surgical sutures and ligaments). Among the biodegradable plastics, polylactic acid (PLA), behind the non-compostable bio-polyethylene and bio-polyethylene terephthalate, was the third (12.2%) in bioplastics production capacity in 2014 [Source: Bioplastics market data]. PLA is generally produced from agricultural resources (e.g., corn, sugar, food waste, etc.). The raw materials go through hydrolysis, and this yields dextrose. Then the dextrose is converted to lactic acid by fermentation. Finally PLA is obtained through either ring-opening polymerization or direct condensation of lactic acid. PLA has been considered as a good substitute for conventional synthetic non-biodegradable polymers because, unlike oil-based polymers, it can be produced from renewable resources and generates no solid waste at the end of the product life cycle. On the other hand, because of its biocompatibility and biodegradability, PLA has extensively been used in biomedical applications [Cha and Pitt, 1990; Coombes and Meikle, 1994; Duek et al., 1999; Ikada and Tsuji, 2000; Ouchi and Ohya, 2004]. However, the application of PLA as a packaging material has been limited to high-end products because of its high cost (greater than $2/lb) [Henton et al., 2005]. Due to the development of new technologies [Drumright et al.,
the production cost of PLA is decreasing, and world-scale plants have been set up. As a result, PLA can be used in a broader range of applications including food packaging which can increase the shelf life of food products and reduce the amount of food wasted. Advantages of PLA are its high strength, excellent transparency, and good processability [Rhim et al., 2009; Katiyar et al., 2011; Fukushima et al., 2013; Park et al., 2013; Wu et al., 2013] when compared to conventional polymers. However, compared to conventional packaging polymers, the poor gas barrier properties of PLA limit its application as a food packaging material. For example, oxygen can pass through PLA films and cause oxidation of heart-healthy unsaturated fat. On the other hand, baked products can absorb moisture from the environment and become soaked. Therefore, inappropriate packaging can reduce the value of food products. Among the oil-based plastics, there are two commonly used food packaging materials: polystyrene (PS) for rigid packaging and poly(ethylene terephthalate) (PET) for flexible packaging. Compared to PS and PET [Auras et al., 2005], the water vapor permeability through PLA [Siparsky et al., 1997] is 3.8 times and 5.6 times higher respectively. On the other hand, the oxygen permeability through PLA is 6 times higher than that through PET [Auras et al., 2005]. When PLA is considered as a food packaging material, these disadvantages limit its use to lower–value products like water bottles and food trays. Therefore, the gas barrier properties of PLA must be improved before it can be more widely used as a food packaging material.

A potential method to improve PLA barrier properties is through adding nanoparticles into the PLA matrix. Nanoparticles are materials that are between 1 and 100 nanometers in at least one dimension. They can be in different shapes: spheres (metal and metal oxide), rods (carbon nanotubes and nanofibers), and platelets (layered silicate and graphene). Nanoparticles are
widely used as additives in polymers to produce nanocomposites. The addition of nanoparticles can significantly improve material properties when distributed uniformly. One of the examples is nylon 6/clay nanocomposite developed by Toyota in 1993 [Kojima et al., 1993; Usuki et al., 1993]. The incorporation of clay into nylon 6 enhanced the mechanical properties, and the nanocomposite was later used in a timing belt cover in Camry cars.

In terms of improving gas barrier properties, the addition of nanoparticles into polymers is grounded in the tortuosity path concept proposed by Nielsen and by Cussler and coworkers [Nielsen, 1967; Cussler et al., 1988; Eitzman et al., 1996; Falla et al., 1996; Moggridge et al., 2003]. Figure 1.1 schematically depicts the tortuosity path concept in a polymer nanocomposite where high-aspect ratio platelets are dispersed in a polymer matrix through which diffusion takes place. The idea is that these virtually two-dimensional nanoplatelets act as impenetrable barriers and force the diffusing gas molecules to go around them. Consequently, the molecules diffusing through the polymer have to travel a much longer path resulting in significant reduction in the permeability. This is a purely geometric effect and is a consequence of a reduced concentration gradient. In this way, the permeability is significantly reduced with the incorporation of nanoplatelets into the polymer matrix.

The estimated diffusivity, a measurement of the rate of a substance passing through a medium by diffusion, based on Nielsen’s model, is derived in Chapter 3 [Nielsen, 1967]. This takes into account the increase in path length. The result is:

\[
\frac{D_0}{D} = 1 + \left( \frac{h}{2t} \right) \phi
\]  

(1.1)

where \(D_0\) is the diffusivity in the absence of any barriers and \(D\) is the diffusivity through the filled polymer. Other parameters are the barrier volume fraction \(\phi\), barrier thickness \(t\), and barrier width \(h\). The value of \(h/t\) is called the barrier aspect ratio.
On the other hand, the model proposed by Cussler and co-workers takes into account both the increase in path length and the reduction in the area for mass transfer. A variety of models have been employed, and a typical result of Cussler’s theory is given by [Cussler et al., 1988; Eitzman et al., 1996; Falla et al., 1996; Moggridge et al., 2003]:

\[
\frac{D_0}{D} = 1 + \left(\frac{h'}{l}\right)^2 \frac{\phi^2}{4(1-\phi)}
\]  

(1.2)

Results predicted by Eqs. (1.1) and (1.2) for typical values of aspect ratio and volume fraction are given in Table 1.1. These predictions depend on the equation used and have not been quantitatively tested for polymer nanocomposites in any significant way.

These models depend on the aspect ratio, which is affected by the extent of agglomeration. When nanoplatelets form agglomerates, the aspect ratio is reduced. Gas diffusion is only slightly reduced and diffusivity is not significantly lowered. Therefore, more nanoplatelets are needed to
obtain the same amount of reduction in diffusivity compared to a well-dispersed nanoplatelet system. The dispersion state of the nanoplatelets is a crucial factor for reducing the diffusivity. However, one needs to ensure that mechanical properties are not hurt in the process.

Table 1.1: $D_0/D$ predicted by Eqs. (1.1) and (1.2) for common aspect ratios and volume fractions.

<table>
<thead>
<tr>
<th>Vol %</th>
<th>$h/t=25$</th>
<th>$h/t=50$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Eq. (1.1)</td>
<td>Eq. (1.2)</td>
</tr>
<tr>
<td>0.5</td>
<td>1.06</td>
<td>1.00</td>
</tr>
<tr>
<td>1.0</td>
<td>1.13</td>
<td>1.02</td>
</tr>
<tr>
<td>1.5</td>
<td>1.19</td>
<td>1.04</td>
</tr>
<tr>
<td>2.0</td>
<td>1.26</td>
<td>1.06</td>
</tr>
<tr>
<td>2.5</td>
<td>1.32</td>
<td>1.10</td>
</tr>
<tr>
<td>3.0</td>
<td>1.39</td>
<td>1.14</td>
</tr>
<tr>
<td>3.5</td>
<td>1.45</td>
<td>1.20</td>
</tr>
<tr>
<td>4.0</td>
<td>1.52</td>
<td>1.26</td>
</tr>
<tr>
<td>4.5</td>
<td>1.59</td>
<td>1.33</td>
</tr>
<tr>
<td>5.0</td>
<td>1.66</td>
<td>1.41</td>
</tr>
</tbody>
</table>

Another method to reduce PLA permeability is by increasing the polymer crystallinity. Compared to the amorphous phase, the crystalline phase is more dense and impermeable to most gas molecules [Michaels and Parker, 1959; Michaels and Bixler, 1961; Rogers, 1985; Chrissafis et al., 2009; Compañ et al., 2010; Desobry and Arab-Tehrany, 2014]. According to the two-phase model proposed by Michaels et al. (1963), the reduction in diffusivity is due to the presence of crystals and proportional to the volume fraction of the crystalline phase [Michaels et al., 1963]. Therefore, the PLA barrier properties will be improved with an increase in PLA crystallinity. Again, the presence of crystals may affect mechanical properties, and this aspect has to be kept in mind.
1.2 Objectives of the Research

A proper packaging material should act as barrier against moisture and other gases. The emerging environmental concerns favor bio-derived and biodegradable polymers such as PLA. However, the limited gas barrier properties must be improved before PLA can be used as a food packaging material. In order to fulfill the task, it is proposed to study the effects of nanoclay and increased crystallization on water vapor diffusivity. The objectives are:

**Objective #1**: From the different commercially available nanomaterials, to identify the most compatible one with PLA.

**Objective #2**: To optimize the processing conditions to obtain the best dispersion level of the nanomaterials in PLA.

**Objective #3**: Under the optimized processing condition, to study the effect of nanomaterial loading on gas barrier properties with a view to reducing moisture diffusivity through nanocomposite films to a level observed for PET.

**Objective #4**: To develop and quantitatively test a theory that can relate observed reductions in diffusivity to nanocomposite morphology.

**Objective #5**: To improve mechanical properties by using plasticizer.

**Objective #6**: To study the effect of PLA crystallinity on gas barrier properties.

**Objective #7**: To study the effect of both nanoclay loading and PLA crystallinity on gas barrier properties.

**Objective #8**: To compare the value of moisture diffusivity through PLA nanocomposite with those of PS and PET.
2 LITERATURE REVIEW

2.1 Introduction

A review of the fundamentals of mass transfer is provided in this chapter along with techniques of measuring diffusivity and permeability of gases in polymer films. Also reviewed are available data on the influence of barriers and crystals on the reduction of the mass flux through polymer films.

2.2 Process of Mass Transfer

One of the goals of this work is to improve the barrier properties of PLA so that it may be used as a food packaging material. Reducing the mass transfer through this new material is critical to its being able to replace conventional petroleum-based polymers. As a consequence, the knowledge of mass transfer behavior—permeation, diffusion and solution—becomes very important. Once a concentration gradient exists across the two sides of a polymer, there is a natural tendency for material to diffuse through it to minimize this difference. There are three steps involved in mass transfer of gases through solid, non-porous polymers [Mukhopadhyay and Gupta, 2012]. In the first step, the gas dissolves in the polymer at the high-concentration side. Then it diffuses through the polymer to the low-concentration side. In the final step, it desorbs from the low-concentration side of the polymer. When the diffusion process is examined in a rectangular Cartesian coordinate system, it can be mathematically described by Fick’s “second law”:

\[ \frac{\partial c}{\partial t} = D \left( \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2} \right) \]  \hspace{1cm} (2.1)

in which \( C \) is the mass or molar concentration of the diffusing species, \( t \) is time, and \( D \) is the diffusion coefficient of the species in the polymer. In this case, \( D \) is assumed to be a constant.
For steady-state one-dimensional diffusion through a slab of thickness \( l \), Eq. (2.1) reduces to:

\[
\frac{d^2c}{dx^2} = 0
\]  

(2.2)

with boundary conditions \( C = C_1 \) at \( x = 0 \) and \( C = C_2 \) at \( x = l \).

Solving this equation by integrating and applying boundary conditions, one can get:

\[
\frac{c - c_1}{c_2 - c_1} = \frac{x}{l}
\]  

(2.3)

The steady-state flux \( J \) across the polymer film can be calculated by the following equation:

\[
J = -D \frac{dc}{dx} = -D \frac{c_2 - c_1}{l} = -D \frac{\Delta c}{l}
\]  

(2.4)

in which \( \Delta C \) is the concentration difference across the film.

The concentration difference can be expressed in terms of the partial pressure as the follows:

\[
\Delta C = S \Delta p
\]  

(2.5)

In which \( \Delta p \) is the partial pressure difference across the film and \( S \) is the gas solubility which is assumed to be a constant for simple gases.

Therefore, Eq. (2.4) can be rewritten as:

\[
J = -(D \times S) \frac{\Delta p}{l}
\]  

(2.6)

in which the product of \( D \) and \( S \) represents the permeability \( P \).

In a permeation experiment, the steady-state flux \( J \), the partial pressure difference across the polymer film \( \Delta p \), and the film thickness \( l \) are measured. The permeability \( P \) can be calculated by the following equation:

\[
P = \frac{J \times l}{-(\Delta p)}
\]  

(2.7)

If, on the other hand, we consider the transient one-dimensional form of Eq. (2.1) for mass transfer through an initially solute-free film [Kumar and Gupta, 2003]:

\[
\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}
\]  

(2.8)
The initial and boundary conditions are:

\[ C(0, t) = C_1 \]
\[ C(l, t) = 0 \]
\[ C(0 < x < l, 0) = 0 \]

The solution to the above equation provides the time-dependent concentration profile as [Daynes, 1920; Crank, 1975]:

\[ C = C_1 \left( 1 - \frac{x}{l} \right) - \frac{2C_1}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} \sin \left( \frac{n\pi x}{l} \right) \exp \left( \frac{-Dn^2\pi^2 t}{l^2} \right) \] (2.9)

The flux of gas leaving the film is \(-D \left( \frac{\partial C}{\partial x} \right)\), and this is evaluated at \(x = l\). When this term is integrated over time, we get \(Q(t)\), the amount of material that has actually passed through unit area of the film in time \(t\):

\[ \frac{Q(t)}{lC_1} = \frac{Dt}{l^2} - \frac{1}{6} - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp \left( \frac{-Dn^2\pi^2 t}{l^2} \right) \] (2.10)

which reduces to the equation of a straight line as \(t \to \infty\); i.e.,

\[ Q(t) = \frac{DC_1}{l} t - \frac{lC_1}{6} \] (2.11)

This straight line intersects the \(t\) axis at the point \(\theta = \frac{l^2}{6D}\), and this is called the time lag. This is shown in Figure 2.1, and it allows for the calculation of the diffusivity \(D\) from a plot of \(Q(t)\) versus time. A measurement of flux from the permeation experiment is used to generate a plot of cumulative gas permeated through the film versus time. The diffusivity can be obtained from the plot by extending backwards the steady-state portion of cumulative water permeated till it intersects the time axis. Permeability, however, is obtained from the steady state portion of the plot using Eq. (2.7). This “time-lag” method is the basis of commercial instruments. Solubility can be calculated as the ratio of the measured permeability to the computed diffusivity. All of
this is true for a homogeneous material. However, Eq. (2.9) is not likely to be valid for composite materials.

An alternative method of measuring transport properties is the sorption method. In a sorption experiment, the weight of a solute-free sample is measured. Then it is placed in an environmental chamber at the desired temperature and relative humidity (RH). The weight of the sample is measured on a regular basis until it reaches equilibrium. The governing equation for this process is again Eq. (2.8). However, the initial and boundary conditions are:

\[
C(0,t) = C_1 \\
C(l,t) = C_1 \\
C(-l < x < l,0) = 0
\]

The solution to the above equation is [Crank, 1975]:

\[
C = C_1 - \frac{4C_1}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \cos \left(\frac{(2n+1)\pi x}{2l}\right) \exp\left[-\frac{D(2n+1)^2\pi^2 t}{4l^2}\right]
\]

(2.12)

The amount of material \(Q(t)\) that has entered the sample in time \(t\) is given by integrating the flux over time [Crank, 1975]:

\[
\frac{Q(t)}{Q_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \exp\left[-\frac{D(2n+1)^2\pi^2 t}{4l^2}\right]
\]

(2.13)

where \(Q_\infty\) is the sample mass at equilibrium.
At the initial stage of the process, the corresponding solution for small time is [Crank, 1975]:

$$C = C_1 \sum_{n=0}^{\infty} (-1)^n \text{erfc} \left( \frac{2n+1)l-x}{2\sqrt{Dt}} \right) + C_1 \sum_{n=0}^{\infty} (-1)^n \text{erfc} \left( \frac{2n+1)l+x}{2\sqrt{Dt}} \right)$$  \hspace{1cm} (2.14)

The amount of material $Q(t)$ that has entered the sample at the initial stage is given by [Crank, 1975]:

$$\frac{Q(t)}{Q_\infty} = 2\left(\frac{Dt}{l^2}\right)^{\frac{1}{2}} \left[\frac{\pi}{2} - \frac{1}{2} + 2 \sum_{n=1}^{\infty} (-1)^n \text{erf} c \left( \frac{2nl}{\sqrt{Dt}} \right) \right]$$  \hspace{1cm} (2.15)

At the early stage of the sorption process defined by $\frac{Dt}{4l^2} < 0.05$, Eq. (2.15) reduces to [Crank, 1975]:

$$\frac{Q(t)}{Q_\infty} = 4\left[\frac{Dt}{\pi (2l)^2}\right]^{\frac{1}{2}}$$  \hspace{1cm} (2.16)

Eq. (2.16) can be rearranged as:

$$D = \frac{\pi}{16} \left[\frac{2Q_t}{Q_\infty \sqrt{t}}\right]^2$$  \hspace{1cm} (2.17)

where $\frac{2Q_t}{Q_\infty \sqrt{t}}$ is the slope of the straight line drawn up to $\frac{Q_t}{Q_\infty} < 0.5$ as shown in Figure 2.2. $D$ can be calculated from Eq. (2.17). Again, this method is theoretically correct only for homogeneous materials.

![Figure 2.2: Moisture sorption curve for vinyl ester resin [Shah, 2001].](image-url)
2.3 Water Vapor Permeability through Various Polymers

A food packaging material should act as a good barrier against water vapor and also gases such as oxygen and carbon dioxide. An appropriate food packaging material can increase the shelf life of the food and reduce the amount of food that is wasted. To compare the water vapor barrier properties of different polymers, water vapor permeability can be used. Table 2.1 shows the water vapor permeability through various polymers used in the packaging industry [Siparsky et al., 1997; Brandrup et al., 1999; Auras et al., 2005]. For example, compared to PET, which is another polyester, the water vapor permeability through PLA is significantly higher. From the values given in Table 2.1, it is apparent that for PLA to be competitive with PET, the water vapor permeability must be reduced by more than 80%. This is one of the goals of the present research. In the following section, a thorough literature review is presented to show what other researchers have done to improve the water vapor barrier properties of PLA.

Table 2.1: Water vapor permeabilities through various packaging polymers [Siparsky et al., 1997; Brandrup et al., 1999; Auras et al., 2005].

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Water vapor permeability at 25°C and 100% RH (kg/m/s/Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>High Density Polyethylene (HDPE)</td>
<td>7.24x10^{-17}</td>
</tr>
<tr>
<td>Polypropylene (PP)</td>
<td>3.06x10^{-16}</td>
</tr>
<tr>
<td>Low Density Polyethylene (LDPE)</td>
<td>5.47x10^{-16}</td>
</tr>
<tr>
<td>Poly(ethylene terephthalate) (PET)</td>
<td>2.82x10^{-15}</td>
</tr>
<tr>
<td>Polystyrene (PS)</td>
<td>4.18x10^{-13}</td>
</tr>
<tr>
<td>Polylactic acid (PLA)</td>
<td>1.60x10^{-14}</td>
</tr>
</tbody>
</table>
2.4 Improvement of Polymer Gas Barrier Properties with the Incorporation of Nanofillers

2.4.1 Synthesis of Nanocomposites

Before presenting how the addition of fillers into a polymer improves polymer properties, one needs to understand how polymer nanocomposites are processed. There are two major methods: solvent-casting and melt-processing. In solvent-casting, the polymer is dissolved in a solvent and the filler is added to form a suspension. This suspension is then spread out and placed onto an inert medium. The polymer chains and the filler form an intimate mixture giving a nanocomposite. Finally, the material is dried to remove the solvent. The advantage of this method is that it requires a relatively low processing temperature and the possibility of polymer degradation is minimized. However, this method requires a large amount of solvent and is not considered environmentally-friendly. On the other hand, in melt-processing, the polymer and the filler are heated to a desired temperature, typically in an extruder. The polymer chains bond with the filler in the molten state and form a polymer nanocomposite. This method often employs high temperatures which lead to possible polymer degradation. However, it does not involve solvent in the process. So it is greener compared to solvent-casting.

2.4.2 Structure of Nanoclay

Nanoclay is a commonly-used filler for polymers due to its widespread availability and relatively low cost. The structure of nanoclay is composed of two types of layers: a silicon-oxygen tetrahedral sheet and an aluminum/magnesium-oxygen-hydroxyl octahedral sheet. In the tetrahedral sheet, each silicon atom is linked to four oxygen atoms at the four corners of a tetrahedron [Shah, 2001]. The tetrahedral shares three corners with the adjacent tetrahedral sheets to form a hexagonal network [Uddin, 2008]. In the octahedral sheet, each aluminum or
magnesium atom is coordinated with six oxygen atoms or hydroxyl groups at the corners of an octahedron [Shah, 2001]. These two sheets form a layer by sharing four corners in their structures [Uddin, 2008]. Nanoclay found in nature consists of many layers joined together by van der Waals force. Figure 2.3 shows the typical structure of nanoclay [Kornmann et al. 1998].

Figure 2.3: Montmorillonite structure [Kornmann et al. 1998].

Nanoclay is neutral in charge in the presence of silicon oxide. However, in general, the silica cations (Si\(^{4+}\)) in most of the clays are replaced by cations like aluminum cations (Al\(^{3+}\)), and this leaves the clay negative in charge. The negative charge is neutralized by the adsorption of cations such as sodium cations (Na\(^+\)). When the clay is dissolved in a solution, these cations can be exchanged by the substances present in the solution [Shah, 2001]. The amount of cations that can be exchanged is called the cation exchange capacity (CEC).

2.4.3 Effect of Unmodified Nanoclay on Gas Barrier Properties

To reduce gas permeability through a polymer, one of the popular methods is to incorporate fillers, especially nano-additives, into the matrix. Among all the possibilities, nanoclays are most frequently used. This is because, with the incorporation of a small amount of nanoclay, the gas permeability through the polymer can be dramatically reduced [Choudalakis and Gotsis, 2009; Tan and Thomas, 2016].
Cloisite Na⁺, a montmorillonite (MMT) or an unmodified nanoclay, is proven to be effective in reducing water vapor permeability. Strawhecker and Manias (2000) investigated the water vapor permeability through polyvinyl alcohol containing Cloisite Na⁺. As shown in Figure 2.4, with the incorporation of 6 wt% of clay, the permeability was reduced by 60% compared to the unfilled polymer.

![Figure 2.4: Water vapor permeability through polyvinyl alcohol containing Cloisite Na⁺](image)

Figure 2.4: Water vapor permeability through polyvinyl alcohol containing Cloisite Na⁺

[Strawhecker and Manias, 2000].

Another group of researchers also studied the effect of Cloisite Na⁺ on water vapor permeability through polyvinyl alcohol [Liu et al., 2014]. As shown in Table 2.2, the permeability was reduced by 25% when 4.8 wt% of clay was added. In the literature, the barrier property improvement by adding Cloisite Na⁺ is shown not only for polyvinyl alcohol but also other polymers. Reduction in water vapor permeability was also observed when Cloisite Na⁺ was incorporated into fish gelatin [Bae et al. 2009], red algae [Jang et al., 2011], hydroxypropyl methylcellulose (HPMC) [Moura et al., 2011; Mondal et al., 2013], agar [Rhim, 2011], starch [Slavutsky et al., 2012], banana flour and rice flour films [Rodríguez-Marín et al., 2013],
chicken feather protein [Song et al., 2013], and quince seed edible film [Shekarabi et al., 2014]. It is clear that the incorporation of Cloisite Na⁺ can significantly reduce the water vapor permeabilities through various polymers. However, Cloisite Na⁺ is not compatible with hydrophobic polymers and surface modification is required.

Table 2.2: Water vapor permeability through polyvinyl alcohol containing Cloisite Na⁺ [Data from Liu et al., 2014].

<table>
<thead>
<tr>
<th>Sample</th>
<th>Permeability (×10⁻¹⁰ g m/m² s Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyvinyl alcohol</td>
<td>3.15±0.62</td>
</tr>
<tr>
<td>Polyvinyl alcohol/Cloisite Na⁺</td>
<td>2.36±0.39</td>
</tr>
</tbody>
</table>

2.4.4 Surface Modification of Nanoclay

Unmodified nanoclay is hydrophilic. To make it compatible with hydrophobic polymers, surface treatment is required. The surface modification can be achieved in two ways: ion exchange method and ion dipole method. The ion exchange method involves replacing the natural cations (e.g. sodium cation) on the clay surface by the organocations (e.g. ammonium salt). On the other hand, the ion dope method is to leave positively charged sodium atoms on the nanoclay surface [Shah, 2001]. These atoms can then interact with the negatively charged functional groups on polymers. Both of these methods can minimize the interaction between each nanoclay layer. Moreover, the spacing between the nanoclay layers increases, and this allows better interactions between the clay surface and the surrounding polymer chains. Therefore, a better dispersion state of the nanoclay can be achieved, and the final properties of the nanocomposites can be improved. Table 2.3 shows some commercially available modified nanoclays, and the relative hydrophobicity of these nanoclays is shown in Figure 2.5.
Table 2.3: Nanoclays and their surfactants.

<table>
<thead>
<tr>
<th>Name</th>
<th>Surfactant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cloisite 15A</td>
<td>Dimethyl dihydrogenated tallow quaternary ammonium salt</td>
</tr>
<tr>
<td>Cloisite 20A</td>
<td>Dimethyl dehydrogenated tallow quaternary ammonium salt</td>
</tr>
<tr>
<td>Cloisite 93A</td>
<td>Methyl dehydrogenated tallow ammonium salt</td>
</tr>
<tr>
<td>Cloisite 25A</td>
<td>Dimethyl dehydrogenated tallow 2-ethylhexyl quaternary ammonium salt</td>
</tr>
<tr>
<td>Cloisite 30B</td>
<td>Methyl tallow bis-2-hydroxyethyl quaternary ammonium salt</td>
</tr>
<tr>
<td>Cloisite 10A</td>
<td>Dimethyl benzyl hydrogenated tallow quaternary ammonium salt</td>
</tr>
<tr>
<td>Cloisite Na⁺</td>
<td>No surfactants</td>
</tr>
</tbody>
</table>

Figure 2.5: Hydrophobicity of different MMTs [Info from Southern Clay Products].

2.4.5 Characterization of Morphology of Polymer Nanocomposites

The dispersion state of nanoclay in the polymer can be investigated by means of a scanning electron microscope (SEM) and a transmission electron microscope (TEM). In SEM, the electron beam interacts with the atoms in the sample and produces signals that include the information of the sample surface. The resolution of SEM can be around 10 nm. On the other hand, in TEM, the electron beam passes through an ultra-thin sample and interacts with the sample. TEM provides images with a typical resolution of 0.2 nm. This imaging technique can be used to investigate the gallery spacing and the dispersion of nanoclay in the polymer.
2.4.6 Effect of Modified Nanoclay on Gas Barrier Properties

Various modified nanoclays have been used to reduce the water vapor permeability through polymers. Jang et al. (2011) investigated the water permeability through red algae containing Cloisite 30B (natural montmorillonite modified with methyl tallow bis-2-hydroxyethyl quaternary ammonium) at 38°C and 90% relative humidity. As shown in Table 2.4, when 3 wt% of clay was added, the water permeability was reduced by 12% compared to the unfilled polymer. The incorporation of modified nanoclays is also proven to improve water vapor barrier properties through other polymers. Reduction in water vapor permeability was observed with poly(styrene-co-butyl acrylate) containing encapsulated Cloisite 30B [Mirzataheri et al., 2011], PLA containing Cloisite 20A (natural montmorillonite nanoclay modified with dimethyl dehydrogenated tallow quaternary ammonium) [Chee et al., 2013], PLA containing Cloisite 30B [Singh et al., 2010; Duan et al., 2013; Tenn et al., 2013], gelatin film containing Cloisite 20A [Farahnaky et al., 2014], and starch containing Cloisite 30B [Abreu et al., 2015]. The incorporation of modified nanoclays can improve the water vapor barrier properties of various polymers.

Table 2.4: Water vapor permeability through red algae containing Cloisite 30B [Data from Jang et al., 2011].

<table>
<thead>
<tr>
<th>Cloisite 30B wt%</th>
<th>Permeability (ng m/m² s Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.29±0.02</td>
</tr>
<tr>
<td>1</td>
<td>1.20±0.08</td>
</tr>
<tr>
<td>3</td>
<td>1.14±0.05</td>
</tr>
</tbody>
</table>

Not surprisingly, nanoclay can also be used to improve oxygen barrier properties. Frounchi and Dourbash (2009) investigated the oxygen permeability through PET containing Cloisite 15A (natural montmorillonite nanoclay modified with dimethyl dihydrogenated tallow quaternary
ammonium). As shown in Table 2.5, at a loading of 2 wt% of clay, the oxygen permeability was reduced by 30% compared to the unfilled polymer. Such behavior was also observed on fish gelatin containing Cloisite Na⁺ [Bae et al., 2009], PLA containing Cloisite 30B [Singh et al., 2010], HPMC containing Cloisite Na⁺ [Moura et al., 2011], PLA containing Cloisite 20A [Chee et al., 2013], quince seed edible film containing Cloisite Na⁺ [Shekarabi et al., 2014], and starch containing Cloisite 30B [Abreu et al., 2015]. The addition of nanoclay can reduce not only water vapor permeability but also oxygen permeability. The incorporation of nanoclay is an effective way of improving gas barrier properties of various polymers. Note, though that the extent of improvement has been found to depend also on the chemical nature of the diffusing molecule.

Table 2.5: Oxygen permeability through PET containing Cloisite 15A [Frounchi and Dourbash, 2009].

<table>
<thead>
<tr>
<th>Cloisite organoclay</th>
<th>Permeability</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt.-%</td>
<td>cm³ · cm · m⁻² · day⁻¹ · bar⁻¹</td>
</tr>
<tr>
<td>0</td>
<td>0.223</td>
</tr>
<tr>
<td>1</td>
<td>0.179</td>
</tr>
<tr>
<td>2</td>
<td>0.157</td>
</tr>
</tbody>
</table>

The discussion above shows that nanoclay is an effective additive for polymers and can significantly improve gas barrier properties. However, commercial nanoclays have different surface treatments which change the nanoclay hydrophobicity. This change can make the nanoclay be compatible with a chosen polymer and thus further improve the dispersion state of nanoclay particles in the polymer. The effect of nanoclay hydrophobicity on gas barrier properties will be discussed in the following section.
2.4.7 Effect of Nanoclay Hydrophobicity on Gas Barrier Properties

The previous section shows that the addition of nanoclay can significantly improve gas barrier properties of polymers. However, the surface of the unmodified nanoclay is hydrophilic. In its natural form, the separation or exfoliation of nanoclay particles cannot be accomplished in hydrophobic polymers due to poor interaction between the nanoclay surface and polymer chains. However, when natural sodium cations on the clay surface are replaced by organocations such as ammonium salt, the hydrophobicity of the nanoclay can be tuned to match a specific polymer. Therefore, a better dispersion state of the nanoclay can be achieved and the final properties of the nanocomposites can be improved.

Park et al. (2002) tested the water vapor permeability through thermoplastic starch film containing four different nanoclays: Cloisite Na\(^+\), Cloisite 30B, Cloisite 10A and Cloisite 6A. Cloisite 10A and Cloisite 6A are natural montmorillonite nanoclays modified with dimethyl benzyl hydrogenated tallow quaternary ammonium and dimethyl dehydrogenated tallow quaternary ammonium chloride respectively. The permeation test was carried at 24°C. As shown in Figure 2.6, with the incorporation of 5 wt% of different clays, samples containing Cloisite Na\(^+\) showed the lowest permeability among all the clays. It was because Cloisite Na\(^+\) was the most hydrophilic clay and the most compatible with the hydrophilic starch. Therefore, samples with Cloisite Na\(^+\) had the best intercalated structure.

Similar results were reported on agar films containing various nanoclays (Cloisite 20A, Cloisite 30B and Cloisite Na\(^+\)) [Rhim et al., 2011] and sesame seed meal protein films containing two kinds of nanoclays (Cloisite 10A and Cloisite Na\(^+\)) [Lee et al., 2014]. In these cases, different nanoclays showed different reductions in gas permeability through the polymer.
It was because the compatibility of the nanoclay and the polymer determined the dispersion state of the nanoclay and thus the final properties of the nanocomposite.

![Water vapor permeability through starch containing various nanoclays](image)

Figure 2.6: Water vapor permeability through starch containing various nanoclays [Park et al., 2002].

Rhim et al. (2009) tested the water vapor permeability through PLA containing Cloisite Na⁺, Cloisite 30B and Cloisite 20A at 25°C and 100% relative humidity. Cloisite 20A is nanoclay modified with dimethyl dehydrogenated tallow quaternary ammonium. With the addition of Cloisite 30B and Cloisite 20A, the water permeability through the nanocomposites was lower than that of neat PLA. As shown in Table 2.6, in their study, the permeability through PLA containing Cloisite 20A was lower than that through PLA containing Cloisite 30B because the more hydrophobic Cloisite 20A was dispersed better in PLA. The permeability through PLA containing Cloisite 20A was reduced by 36%.

From the discussion above, one can see that filler hydrophobicity plays an important role in influencing the dispersion state of nanoclay in the polymer. If the polymer is hydrophobic, nanoclay has to be modified to make it compatible with that specific polymer. When the
nanoclay is not compatible with the polymer, the nanoclay particles most likely agglomerate, and this negatively affects the gas barrier property of the nanocomposite. Thus, a thorough study of the effect of nanoclay hydrophobicity on polymer properties is necessary. On the other hand, the loading of nanoclay also affects gas barrier properties because the number of barriers increases as the loading increases. However, nanoclay particles can agglomerate at high loadings, and one may not obtain the full benefit of the added filler. Thus the effect of nanoclay loading on gas barrier properties will be discussed in the following section.

Table 2.6: Water vapor permeability through PLA containing different nanoclays (5 parts clay per 100 parts PLA) [Rhim et al., 2009].

<table>
<thead>
<tr>
<th>Films</th>
<th>WVP (×10⁻¹¹ g m/m² s Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PLA film</td>
<td>1.80 ± 0.01SUPBC</td>
</tr>
<tr>
<td>PLA/Cloisite Na⁺</td>
<td>2.08 ± 0.01ID</td>
</tr>
<tr>
<td>PLA/Cloisite 30B</td>
<td>1.70 ± 0.03B</td>
</tr>
<tr>
<td>PLA/Cloisite 20A</td>
<td>1.15 ± 0.02A</td>
</tr>
</tbody>
</table>

2.4.8 Effect of Nanoclay Loading on Gas Barrier Properties

When the loading of nanoclay increases, there are more nanoclay particles acting as barriers. Therefore, the permeability is expected to decrease as the loading of nanoclay increases. However, nanoclay tends to agglomerate at high loadings because there is less free volume for the particles to disperse [Peter and Woldesenbet, 2008]. This aspect is considered in detail in the section on use of plasticizers.

Duan et al. (2013) studied water vapor transmission rate through PLA containing Cloisite 30B at 38°C and 90% relative humidity. The water vapor transmission rates of two different PLA polymers containing 1-6 wt% of Cloisite 30B were measured. These two polymers have
different molecular weights (89,000 and 94,000 g/mol). As shown in Figure 2.7, water transmission rate decreased as the amount of Cloisite 30B increased. For a 3.7 vol% addition of nanoclay, the water transmission rate was reduced by around 43% comparing to unfilled PLA. In this study, the water transmission rate continued to decrease in the range of nanoclay loadings tested. In addition, the water transmission rate was independent of molecular weight in this study. Similar behavior was also observed on fish gelatin containing Cloisite Na\(^+\) [Bae et al., 2009], PLA containing Cloisite 20A [Rhim et al., 2009], poly(styrene-co-butyl acrylate) containing encapsulated Cloisite 30B [Mirzataheri et al., 2011], PLA containing Cloisite 20A [Chee et al., 2013], chicken feather protein film containing Cloisite Na\(^+\) [Song et al., 2013], gelatin film containing Cloisite 20A [Farahnaky et al., 2014], and quince seed edible film containing Cloisite Na\(^+\) [Shekarabi et al., 2014]. In these studies, the nanoclay content was around 1-10 wt%.

Figure 2.7: Water vapor transmission rates through two different PLAs [Duan et al., 2013].
However, further improvement in gas barrier properties may not be achieved when the loading of nanoclay increases because of potential agglomeration. Singh et al. (2010) investigated oxygen and water permeabilities through different PLA samples containing Cloisite 30B at 37.8°C and 90% relative humidity. As shown in Table 2.7, the oxygen permeability was reduced by 33% compared to the unfilled polymer with the incorporation of 3 wt% of Cloisite 30B. However, the oxygen permeability was lower at the loading of 3 wt% of clay than 5 wt% of clay. On the other hand, the reduction of water permeability started to level off when the clay content reached 5 wt%. The water permeability was reduced by 39% at this level compared to the unfilled polymer. The result implied that the clay was not well-dispersed at high loadings. In this study, one can see that the permeability leveled off or even increased after a certain loading. This meant that the dispersion of nanoclay in the polymer was not well accomplished at high loadings. Similar behavior was also observed with PET containing Cloisite 15A [Frounchi and Dourbash, 2009], red algae containing Cloisite Na⁺ and Cloisite 30B [Jang et al., 2011], agar film containing Cloisite Na⁺ [Rhim, 2011], starch containing Cloisite Na⁺ [Slavutsky et al., 2012], HPMC containing Cloisite Na⁺ [Mandal et al., 2013], and PLA containing Cloisite 30B [Tenn et al., 2013].

Table 2.7: Oxygen permeability and water permeability through PLA nanocomposites [Data from Singh et al., 2010].

<table>
<thead>
<tr>
<th>Cloisite 30B wt%</th>
<th>Oxygen permeability</th>
<th>Water permeability</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1586</td>
<td>73.8</td>
</tr>
<tr>
<td>1</td>
<td>1323</td>
<td>59.0</td>
</tr>
<tr>
<td>3</td>
<td>1057</td>
<td>45.9</td>
</tr>
<tr>
<td>5</td>
<td>1131</td>
<td>45.0</td>
</tr>
</tbody>
</table>

From the discussion above, one can see that the gas barrier property is improved as the loading of nanoclay increases because there are more nanoclay particles acting as barriers and
forcing the diffusing molecules to travel a longer path. However, the permeability does not necessarily decrease at high loadings because of particle agglomeration. Later in this chapter, methods of improving nanoclay dispersion will be discussed. In addition, the loading of nanoclay affects the water vapor solubility in the nanocomposite because the increased surface area can immobilize more water vapor molecules. In the following section, the effect of nanoclay loading on water vapor solubility is discussed.

### 2.4.9 Effect of Nanoclay Loading on Water Vapor Solubility

When hydrophilic nanoclay is incorporated into a polymer matrix, the water vapor solubility is believed to increase compared to the unfilled polymer because the hydrophilic nanoclay surfaces can interact with and immobilize water molecules. Chung et al. (2010) studied the water vapor solubility in starch containing Cloisite Na⁺. The sorption test was carried out at 25°C and 100% relative humidity. As shown in Figure 2.8, when 5 wt% of clay was added to the polymer, the solubility increased by 38% compared to the unfilled polymer. Similar behavior was reported by others on HDPE/thermoplastic starch containing Cloisite 20A [Sharif et al., 2011], ethylene-vinyl alcohol copolymer containing bentonite nanoclay [Cerisuelo et al., 2012], and thermoplastic polyurethane containing Cloisite 30B [Benali et al., 2014]. The discussion above shows that the solubility increases as the loading of hydrophilic nanoclay increases. This suggests that permeability and solubility should be measured independently, and the diffusivity can be obtained as the ratio of these two quantities. In other words, one should avoid the time-lag method for diffusivity calculation.
2.5 Improvement in Nanoclay Dispersion with the Use of a Plasticizer

2.5.1 Effect of Plasticizer on Nanoclay Dispersion

In Section 2.4.8, it was seen that the dispersion of nanoclay deteriorates at high loadings. The nanoclay platelets agglomerate and form stacks. This leads to preferred pathways for gas diffusion and results in poor gas barrier property. One of the solutions is to add a plasticizer to the polymer matrix, and this can increase the free volume in the polymer [Queiroz et al., 2001; Yave et al., 2009]. It is also believed to improve the interaction between the polymer chains and the nanoclay particles during processing [Tang et al., 2008]. Therefore, the dispersion of clay in the polymer matrix can be improved.

Chivrac et al. (2008) investigated the effect of glycerol as a plasticizer on the dispersion of cationic starch-modified-Cloisite Na\(^+\) in starch. SAXD showed that the intensity of the clay peak
was reduced with the addition of glycerol. In addition, TEM pictures shown in Figure 2.9 exhibited a homogeneous dispersion of clay in the starch. This observation implies that the dispersion of modified Cloisite Na\textsuperscript{+} in starch was accomplished.

Figure 2.9: TEM pictures of wheat starch-Cloisite Na\textsuperscript{+}-glycerol nanocomposite: (a) low magnification; (b) medium magnification; (c) high magnification [Chivrac et al., 2008].
Another set of experiments was done on starch/glycerol/Cloisite Na\(^+\) by Chiou et al. (2007). The TEM picture in Figure 2.10 shows that there are intercalated and exfoliated nanoclay platelets in the polymer matrix. An intercalated structure is one where the polymer chains insert themselves into the layered nanoclay structure, but the nanoclay retains its layered structure. On the other hand, an exfoliated structure is one where the nanoclay layers completely separate from each other and interact with the polymer matrix. The exfoliated structure gives a larger surface area, so it is the preferred structure. The dispersion of Cloisite Na+ was well accomplished in starch after the addition of glycerol as plasticizer. Such improvement was also seen in thermoplastic starch/urea/montmorillonite nanoclay modified with ammonium [Chen et al., 2005], starch/water/Cloisite Na\(^+\) [Dean et al., 2007], thermoplastic starch/\textit{N-}(2-hydroxyethyl) formamide/montmorillonite nanoclay [Dai et al., 2009], corn starch/glycerol/Cloisite Na\(^+\) [Wang et al., 2009], poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV)/acetyl tributyl citrate (ATBC)/Cloisite 30B [Corrêa et al., 2012], PLA/polyethylene glycol/Cloisite 30B [Gumus et al., 2012], polyvinyl chloride/dioctyl phthalate/Cloisite 30B [Saad and Dimitry, 2012], and thermoplastic starch-PLA/glycerol/Cloisite Na\(^+\) [Ayana et al., 2014].

Figure 2.10: TEM picture of starch/glycerol/Cloisite Na\(^+\) nanocomposite [Chiou et al., 2007].
The preceding literature review shows that the addition of plasticizer can have a positive effect on reducing nanoclay agglomeration. Both XRD and TEM data reveal that a more homogeneous dispersion of nanoclay was achieved with the aid of a plasticizer. With the exfoliated nanoclay structures in the polymer matrix, the polymer will have improved thermal properties, mechanical properties and gas barrier properties. On the other hand, there are many chemicals that can be used as plasticizers. To obtain enhanced polymer properties, one must select an appropriate plasticizer which can improve the dispersion state of the nanoclay in the polymer matrix. In the next section, the effect of plasticizer type on nanoclay dispersion is discussed. However, it should be noted that the presence of a plasticizer can increase molecular diffusion and permeation through the neat polymer.

2.5.2 Effect of Plasticizer Type on Nanoclay Dispersion

As discussed above, the addition of a plasticizer can improve the dispersion state of nanoclay in the polymer matrix and lead to enhanced polymer properties. However, there are many substances available as plasticizers. Because different plasticizers have different chemical structures, this results in different interactions between the polymer and the nanoclay. Tang et al. (2008) studied the effect of different plasticizers on the water vapor permeability through starch containing 6 wt% of montmorillonite nanoclay. The plasticizers used in the study were glycerol, urea, and formamide. The permeation test was carried out at 25°C and 75% relative humidity. The effect of different plasticizers on the water vapor permeability was determined. 15 wt% of glycerol, urea or formamide were added to a starch film containing 6 wt% of montmorillonite nanoclay. As shown in Figure 2.11, among the three different samples, the film with formamide showed the lowest permeability because the formamide was the most compatible with starch. This resulted in the best dispersion state of clay in starch.
Figure 2.11: Water vapor permeability through starch containing 6 wt% of montmorillonite nanoclay and different plasticizers [Tang et al., 2008].

Chivrac et al. (2010) also investigated the effect of different plasticizers on the dispersion of Cloisite Na⁺ modified with cationic starch in wheat starch. The plasticizers used in the study were: glycerol, sorbitol, and Polysorb (a glycerol/sorbitol mixture 59/41 by weight). In the small angle X-ray diffraction (SAXD) scan shown in Figure 2.12, the peak at 3.6° corresponded to Cloisite Na⁺. When glycerol was added, the peak disappeared and completely exfoliated structures of clay in the polymer matrix were obtained. On the other hand, for samples with sorbitol and Polysorb, small peaks at around 3.6° were present, and this revealed that there was a combination of intercalated/exfoliated structures in the polymer matrix. This suggested that there was strong interaction between clay and starch when glycerol was present. Therefore, the dispersion of clay was well accomplished.
As discussed above, one can see that the addition of plasticizer can enhance the dispersion of nanoclay in polymer. In addition, the choice of plasticizer is important. An appropriate plasticizer can enhance the bonding between the polymer and the nanoclay surface. Thus exfoliated nanoclay structures can be obtained, and the polymer properties can be improved. On the other hand, not only the plasticizer type but also the plasticizer concentration affects the dispersion state of nanoclay in the polymer matrix. Excess plasticizer may compete with nanoclay to bond with the polymer, and this behavior results in poor interaction between the nanoclay and the polymer. In the next section, the effect of plasticizer concentration on nanoclay dispersion is discussed.
2.5.3 Effect of Plasticizer Concentration on Nanoclay Dispersion

As discussed in the previous subsection, the use of plasticizer can enhance interaction between the polymer and the nanoclay surface, improving the dispersion of nanoclay in the polymer. However, use of a large amount of plasticizer may lead to an increase in plasticizer-polymer interactions and competition with the polymer-nanoclay interactions. Then the final properties are affected. Here the effect of plasticizer concentration on nanoclay dispersion is discussed.

Chiou et al. (2007) investigated the effect of plasticizer concentration on the dispersion state of Cloisite Na⁺ in starch. Glycerol was used as plasticizer. When 5 wt% of glycerol was added, TEM pictures, as shown in Figure 2.13, revealed that the clay had both exfoliated and intercalated structures in the starch matrix. As the concentration increased to 10 wt%, there were more intercalated structures. This was because initially plasticizer could promote interaction between polymer chains and clay nanoplatelets, but the polymer-clay interaction was inhibited when the plasticizer concentration was increased.

Another set of studies was done on starch-glycerol-Cloisite Na⁺ system [Tang et al., 2008]. TEM pictures, as shown in Figure 2.14, demonstrate that a small amount of glycerol (5 wt%) can enhance interaction between the polymer and the nanoclay, leading to exfoliated nanoclay structures in the polymer. However, when the glycerol concentration is increased to 10 wt%, the glycerol competes with Cloisite Na⁺, and this results in less interaction between the polymer and the nanoclay, resulting in poor nanoclay dispersion in the starch.

This literature review shows that sufficient plasticizer can improve the dispersion state of nanoclay in the polymer and thus the gas barrier properties. However, excess plasticizer inhibits the interactions between the polymer and the nanoclay. The gas permeability increases under this
latter condition. Therefore, finding the optimized concentration of plasticizer is critical in obtaining good dispersion of nanoclay in the polymer.

Figure 2.13: TEM pictures of starch containing 5 wt% of Cloisite Na⁺ and: (a) 10 wt% of glycerol; (b) 15 wt% of glycerol; (c) 5 wt% of glycerol [Chiou et al., 2007].
Figure 2.14: TEM pictures of starch containing Cloisite Na⁺: (a) 5 wt% of glycerol; (b) 10 wt% of glycerol [Tang et al., 2008].

2.6 Polymer Crystallization

As mentioned above, the other way to improve gas barrier properties is by increasing the polymer crystallinity. Therefore, it is necessary to understand the crystallization behavior of polymer. The theory of crystallization and PLA crystallization will be covered in this section.

2.6.1 Theory of Polymer Crystallization

Polymer crystallization is a process of polymer chains rearranging into a regular order and lowering the Gibbs free energy [Kumar and Gupta, 2003]. This process takes place in the temperature range between the glass transition temperature and melting point, in which the polymer chains are able to move. Polymer crystallization consists of nucleation (homogeneous or heterogeneous) and growth. These steps are relatively slow. Polymer crystallization depends on temperature and time. It can be quantified by the Avrami expression [Avrami, 1940]:
\[ V(t) = 1 - e^{-kt^n} \]  \hspace{1cm} (2.18)

where \( V(t) \) is the fraction of the crystalline phase at time \( t \), \( k \) is the kinetic parameter which is a function of temperature, and \( n \) is an integer value between 1 and 4. There are two terms in \( n \): nucleation (\( N \), 0 or 1 based on heterogeneous or homogeneous nucleation) and crystallization (\( C \), 1-3 depends on the dimension of the growth) [Avrami, 1941]. \( n \) is equal to the sum of \( N \) and \( C \).

Figure 2.15 shows Eq. (2.18) with different \( n \). Thanks to the development of new technologies, today people can use instruments such as X-ray diffraction (XRD) or polarized optical microscope to investigate the crystal structures. These analyses give more detailed quantitative information about the crystalline nature of materials.

Figure 2.15: Crystal growth as a function of time [Avrami, 1940].
2.6.2 Crystallization of PLA

Before investigating the crystallization of PLA, it is better to understand the structure of PLA first. PLA can be synthesized from either L-lactic acid or D-lactic acid. Therefore, when producing PLA, there are three possible forms: LL from two L-lactic acids, DD from two D-lactic acids, and LD from one L-lactic acid and one D-lactic acid [Saeidlou et al., 2012]. Figure 2.16 shows the structures of these compounds.

![Structures of different lactic acids and lactides](image)

**Figure 2.16: Structures of different lactic acids and lactides [Saeidlou et al., 2012].**

Different structures have been reported for PLA crystals. The first form discovered is the more packed $\alpha$ form when annealed above 120°C [De Santis and Kovacs, 1968; Hoogsteen et al., 1990]. On the other hand, a less packed $\alpha'$ form is produced when annealed below 100°C [Zhang et al., 2005]. When the crystallization temperature is between 100°C and 120°C, $\alpha$ and $\alpha'$ forms coexist [Kawai et al., 2007; Zhang et al., 2008]. Since $\alpha'$ form has a less ordered structure, it has lower gas barrier properties and higher elongation at break [Cocca et al., 2011]. In addition, others reported that not only annealing temperature but also annealing time affected the properties of crystallized PLA. Table 2.8 shows the properties of PLA annealed at different temperatures and different amounts of time. One could see that increasing annealing temperature and annealing time led to increase in crystallinity, melting temperature, tensile strength and Young’s modulus while the elongation at break decreased [Tsuji and Ikada, 1995].
Table 2.8: Thermal and mechanical properties of annealed PLA [Tsuji and Ikada, 1995].

<table>
<thead>
<tr>
<th>$T_h$ (°C)</th>
<th>$t_k$ (min)</th>
<th>$T_i$ (°C)</th>
<th>$T_e$ (°C)</th>
<th>$T_{wb}$ (°C)</th>
<th>$\varepsilon_c^a$ (%)</th>
<th>$\sigma_{tu}^b$ (kg mm$^{-2}$)</th>
<th>$E^c$ (kg mm$^{-2}$)</th>
<th>$\varepsilon_b^d$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>600</td>
<td>59</td>
<td>178</td>
<td>46</td>
<td>5.0</td>
<td>181</td>
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</tr>
<tr>
<td>100</td>
<td>600</td>
<td>59</td>
<td>178</td>
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<tr>
<td>120</td>
<td>600</td>
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<td>51</td>
<td>5.7</td>
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</tr>
<tr>
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<td>59</td>
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<td>47</td>
<td>5.2</td>
<td>190</td>
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</tr>
<tr>
<td>140</td>
<td>60</td>
<td></td>
<td>178</td>
<td>49</td>
<td>5.3</td>
<td>170</td>
<td>23</td>
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<tr>
<td>140</td>
<td>600</td>
<td></td>
<td>179</td>
<td>52</td>
<td>5.7</td>
<td>200</td>
<td>10</td>
<td>10</td>
</tr>
</tbody>
</table>

*Crystallinity: $\varepsilon_c = 100 \times (\Delta H_m + \Delta H_e)/93$

*Tensile strength

*Young’s modulus

*Elongation at break

2.7 Improvement in Gas Barrier Properties by Increasing Polymer Crystallinity

As discussed earlier, the improvement in gas barrier properties can be accomplished not only by the addition of nanoclay but also by an increase in polymer crystallinity. There are two reasons behind this phenomenon [Michaels and Parker, 1959]. The first one is that the crystalline regions in the polymer can act as barriers and force the gas molecules to diffuse through the constricted amorphous region in the polymer. The second is that the crystals lower the polymer chain mobility and raise the activation energy for gas diffusion. Thus the increase in polymer crystallinity can reduce the gas permeability. In the following section, the effect of crystallinity on gas permeability will be discussed.

Lasoski and Cobbs (1959) studied the effect of polymer crystallinity on water vapor permeability through PET. The permeation test was carried out at 39.5°C. As shown in Figure 2.17, the permeability was reduced by 63% when the crystallinity increased from 0 to 40%. Clearly, an increase in crystallinity can reduce the gas permeability dramatically.
Another set of work was done on PLA [Shogren, 1997]. The water vapor transmission rate of PLA with different crystallinities was measured at 25°C and 100% relative humidity. As shown in Table 2.9, the water vapor transmission rate was reduced by 52% when the crystallinity increased to 66%. The increase in impermeable crystalline region limited the diffusion of water vapor molecules and led to a decrease in water transmission rate.

Table 2.9: Water vapor transmission rate of PLA with different crystallinities [Data from Shogren, 1997].

<table>
<thead>
<tr>
<th>Crystallinity</th>
<th>Water vapor transmission rate (g/m²/d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>172</td>
</tr>
<tr>
<td>66%</td>
<td>82</td>
</tr>
</tbody>
</table>
Compañ et al. (2010) studied the effect of PE crystallinity on gas diffusivity. As shown in Figure 2.18, the diffusivities of carbon dioxide, ethylene and propane all decreased as the crystallinity increased. It was because there were crystals acting as barriers against gas diffusion. Similar behavior was also reported by others on PET [Polyakova et al., 2001; Liu et al., 2004], 1,4-polybutadiene [Cowling and Park, 1979], poly(p-phenyleneterephthalamide) [Weinkauf et al., 1984], PLA [Tsuji et al., 2006; Drieskens et al., 2009; Tsuji and Tsuruno, 2010; Guinault et al., 2012; Duan and Thomas, 2014], PE [Wang et al., 1998; Pauly, 1999], polyethylene naphthalate [Hu et al., 2002], and PEN [Hardy et al., 2003].

From the discussion above, one can see that the improvement in gas barrier properties can be accomplished by increasing the crystallinity. Increasing the crystalline regions can constrain the gas molecules to diffuse through irregular amorphous regions and raise the activation energy for gas diffusion [Michaels and Parker, 1959]. Therefore, the gas permeability is reduced.

![Figure 2.18: Effect of crystallinity on gas diffusivities through PE [Compañ et al., 2010].](image-url)
2.8 Improvement in Gas Barrier Properties by the Combination of Nanoclay and Polymer Crystallinity

As discussed earlier, a reduction in gas permeability and diffusivity can be accomplished by either the addition of nanoclay or an increase in polymer crystallinity. In this section, the effect of a combination of nanoclay and polymer crystallinity on gas barrier properties is investigated. Adewole et al. (2012) studied the effect of crystallinity on natural gas permeability through a polyethylene (PE) nanocomposite where 1 wt% of Cloisite 15A was incorporated into PE. The permeability was measured at different volume fractions of amorphous phase ($\Phi_a$). As shown in Figure 2.19, the permeabilities of methane ($\text{CH}_4$) and methane ($\text{CH}_4$)/carbon dioxide ($\text{CO}_2$) mixture were reduced as $\Phi_a$ decreased. A further decrease in permeability was observed when nanoclay was incorporated in PE. This suggests that the combination of nanoclay and increased crystallinity has a positive effect on gas barrier properties.

Figure 2.19: Gas permeability as a function of polymer crystallinity [Adewole et al., 2012].
Bartel et al. (2017) investigated the effect of Cloisite 30B and crystallinity on oxygen permeability through PLA containing Cloisite 30B. The oxygen permeability decreased with the incorporation of Cloisite 30B as shown in Figure 2.20. Moreover, the annealing treatment resulted in increase in polymer crystallinity and further reduction in oxygen permeability. With the incorporation of 6 wt% nanoclay and thermal treatment, the permeability was reduced by 66% compared to neat PLA.

**Figure 2.20:** Oxygen permeability through PLA containing Cloisite 30B [Bartel et al., 2017].

In the same study by Bartel et al. (2017), the effect of Cloisite 30B and crystallinity on water vapor permeability through PLA containing Cloisite 30B was studied. As shown in Figure 2.21,
The addition of nanoclay reduced the water vapor permeability. In addition, the annealing treatment increased the crystallinity of PLA nanocomposite and led to further improvement in water vapor permeability. The permeability was reduced by 66\% compared to neat PLA when 6 wt\% of nanoclay and thermal treatment were applied.

![Graph showing water vapor permeability through PLA containing Cloisite 30B](graph.png)

Table 2.21: Water vapor permeability through PLA containing Cloisite 30B [Bartel et al, 2017].

2.9 Summary of Literature Review

The literature review shows that the incorporation of nanoclay can significantly improve the gas barrier properties of PLA. Indeed, nanofillers are able to provide relevant performance gain even at low loadings because of their shape and high specific surface areas. The reduction in permeability and diffusivity is often explained using Nielsen’s model and Cussler’s model.
According to these models, the diffusivity should continue to decrease as the filler concentration or filler aspect ratio is increased provided that the fillers are completely exfoliated. However, these materials can agglomerate at high loadings, and an effort has to be made to prevent this from happening. This can be done with the use of mechanical shear and the addition of plasticizer. In addition, polymer crystallinity can also play an important role in improving gas barrier properties of semi-crystalline polymers. A combination of clay and crystals can offer additional benefits.
3 MODELS OF GAS PERMEABILITY AND DIFFUSIVITY THROUGH POLYMER NANOCOMPOSITES

When impermeable fillers such as nanoplatelets are incorporated into the polymer matrix, the diffusivity of gases through the polymer is expected to decrease because molecules follow a tortuous path. This is a complex phenomenon which involves many factors. However, there exist some simple quantitative models which can show the minimum diffusivity that can be obtained for polymer nanocomposites. In the following sections, two of these widely-used mathematical models will be introduced. Also introduced is a new model that is expected to represent data better than models available in the literature.

3.1 Derivation of Nielsen’s Model

The simplest model which seeks to quantitatively predict the reduction in diffusivity when impermeable nanoplatelets are added to the polymer was proposed by Nielsen [Nielsen, 1967]. Nielsen’s model is the one of the first few models to apply the tortuous path concept to a filled polymer system. This is a two-dimensional model that assumes that the fillers are rectangular in shape and uniformly dispersed in the polymer matrix [Nielsen, 1967]. Figure 3.1 shows the essential idea behind the model. Molecules diffuse in the x direction through a film of thickness $d$ under the influence of an imposed concentration gradient. It is assumed that the barriers are infinitely long in the z direction.

The flux of a solute diffusing through a polymeric membrane is given by Fick’s law, Eq. (3.1):

$$ J = -D \frac{\Delta C}{L} $$

(3.1)
where \( J \) is the flux in units of mass or moles per unit time per unit area, \( D \) is the diffusivity, \( \Delta C \) is the concentration difference across the membrane, and \( L \) is the distance traveled by the diffusing molecules.

For an unfilled polymer, therefore, the flux can be written as:

\[
J = -D_0 \frac{\Delta C}{d}
\]  

(3.2)

where \( J \) is the flux, \( D_0 \) is the diffusivity through the unfilled polymer, \( \Delta C \) is the concentration difference across the membrane, and \( d \) is the thickness of the polymeric membrane.

On the other hand, for a filled polymer, the flux is:

\[
J = -D_0 \frac{\Delta C}{d'}
\]  

(3.3)

where \( d' \) is the length of path traversed by the molecules in the filled polymeric membrane.

One normally knows the membrane thickness \( d \), imposes a concentration difference \( \Delta C \) and measures \( J \) for the filled membrane. One then says that:
\[ J = -D \frac{\Delta C}{d} \]  

(3.4)

in which \( D \) is the diffusivity through the filled polymer.

By equating the right hand side of Eq. (3.3) to that of Eq. (3.34),

\[ \frac{D_0}{d'} = \frac{D}{d} \]  

(3.5)

or

\[ D = D_0 \frac{d}{d'} \]  

(3.6)

Since \( d' \gg d \), the diffusivity through the filled polymer is significantly less than that through the unfilled polymer.

The ratio \( \frac{d'}{d} \) is generally called the tortuosity factor \( \tau \), so that:

\[ \frac{D_0}{D} = \tau \]  

(3.7)

The following derivation can be found in Shah’s thesis [Shah, 2001] for estimating \( \tau \). With reference to Figure 3.1, for each layer of nanoplatelets in the polymer, \( d' \) is \( \frac{h}{2} \) larger than \( d \).

Assuming there are \( n \) layers of nanoplatelets, the following equation is obtained:

\[ d' = d + n \frac{h}{2} \]  

(3.8)

The unit cell, which is indicated by the bold rectangle, has a total of one nanoplatelet in a given layer. If there are a total of \( n \) layers, the volume fraction of the nanoplatelets in the control volume is given by the following equation:

\[ \phi = \frac{n t}{d} \frac{h}{h} \]  

(3.9)

where \( t \) is the thickness of a single nanoplatelet. Also, \( \phi \rightarrow \frac{n t}{d} \) as \( h' \rightarrow h \).

In view of the above, the number of layers \( n \) can be expressed as:

\[ n = \frac{d}{t} \phi \]  

(3.10)

Eq. (3.8) can be rewritten as:
\[ d' = d + d \frac{h}{2t} \phi \]  

(3.11)

Dividing both sides of Eq. (3.11) by \( d \), and noting the definition of tortuosity,

\[ \tau = 1 + \left( \frac{h}{2t} \right) \phi \]  

(3.12)

By combing Eq. (3.7) and Eq. (3.12), the desired result is obtained:

\[ \frac{D_0}{D} = 1 + \left( \frac{h}{2t} \right) \phi \]  

(3.13)

While Eq. (3.13) can give an estimate of the diffusivity that can be obtained for a polymer containing nanoplatelets, it neglects factors such as the reduction in the area of mass transfer and a horizontal concentration gradient around the fillers. Consequently, the predicted diffusivity is expected to be larger than the actual value [Nielsen, 1967]. Note that the right hand side of Eq. (3.13) is often divided by a factor of \((1-\phi)\) [Choudalakis and Gotsis, 2009]. This may not be correct.

**3.2 Derivation of Cussler’s Model**

Besides the model of Nielsen discussed above, another popular model for estimating the reduction in diffusivity through a polymer containing plate-like fillers is the one that was developed by Cussler and co-workers [Cussler et al., 1988; Eitzman et al., 1996; Falla et al., 1996; Moggridge et al., 2003]. In this model, the impermeable fillers are again assumed to be rectangular-plate in shape and periodically dispersed in the polymer matrix as before, but the structure is characterized slightly differently. This is shown in Figure 3.2. Based on this structure, Cussler and coworkers used a resistances-in-series approach to determine the rate of mass transfer through the filled polymer.
The following derivation can be found in this paper [Cussler et al., 1988]. Considering mass transfer through area $h'W$ in the y-z plane, the rate of mass transfer $N_0$ when there are no fillers can be expressed as follows:

$$N_0 = D h' W \frac{\Delta C}{l}$$

(3.14)

where $D$ is the diffusivity, $\Delta C$ is the concentration difference across the film assumed positive, $l$ is the thickness of the film, and $W$ is the width in the z direction. Note that $N_0$ has units of mass or moles per unit time.

By rearranging Eq. (3.14), the following equation is obtained:

$$R_0 = \frac{D \Delta C}{N_0} = \frac{l}{h'W}$$

(3.15)

where $R_0$ is the resistance for diffusion through this unit cell. It is proportional to the thickness of the film and inversely proportional to the area of the unit cell.
Now considering the same unit cell filled with \( n \) layers of nanoplatelets, there are three different resistances for diffusion through this filled cell.

The first one is the resistance of the polymer itself. As demonstrated by Eq. (3.15), this is proportional to the thickness of the film and inversely proportional to the area of the unit cell:

\[
R_p = \frac{l}{h'W} \tag{3.16}
\]

The second one is the resistance exerted by presence of gaps between the nanoplatelets. This term is proportional to the thickness of the nanoplatelet and inversely proportional to the area of the platelet gap. Since there are \( n \) layers, this resistance is:

\[
R_f = \frac{nt}{sw} \tag{3.17}
\]

where the distance \( s \) is defined in Figure 3.2.

The third one is the resistance due to the tortuosity created by \( n \) layers of nanoplatelets. It is proportional to the length of the nanoplatelet and inversely proportional to the area between each layer of nanoplatelets:

\[
R_t = \frac{1}{2} (n - 1) \frac{h'}{2bw} \tag{3.18}
\]

The factor \( \frac{1}{2} \) indicates that the diffusing molecules can pass through the nanoplatelet either from the left or from right. \((n-1)\) represents the fact that there are \((n-1)\) wiggles for each nanoplatelet of \( h'/2 \) in length. The quantity \( b \) is again defined in Figure 3.2.

The total resistance for diffusion through this filled unit cell is the sum of the above three terms:

\[
R = \frac{D\Delta C}{N} = R_p + R_f + R_t = \frac{l}{h'W} + \frac{nt}{sw} + \frac{1}{2} (n - 1) \frac{h'}{2bw} \tag{3.19}
\]

Dividing the left side of Eq. (3.19) by the left side of Eq. (3.15) and the right side of Eq. (3.19) by the right side of Eq. (3.15), the following equation can be obtained:
\[
\frac{N_0}{N} = 1 + \frac{nh't}{sl} + \frac{1}{2} (n - 1) \frac{h'^2}{2bl} \tag{3.20}
\]

Since the film thickness \(l\) is equal to \(n(b+t)\) and the volume fraction of the nanoplatelets \(\phi\) as \(s \to 0\) is equal to \(\frac{nt}{l}\) or \(t/(b+t)\), Eq. (3.20) can be rearranged to give:

\[
\frac{N_0}{N} = 1 + \frac{h'\phi}{s} + \frac{1}{4} \frac{(n-1)}{n} \frac{h'^2 \phi^2}{1 - \phi} \tag{3.21}
\]

When there are many layers, \((n-1)\) is close to \(n\), and Eq. (3.21) reduces to:

\[
\frac{N_0}{N} = 1 + \frac{h'\phi}{s} + \frac{(h'/t)^2 \phi^2}{4(1-\phi)} \tag{3.22}
\]

This equation is identical to the upper portion of Eq. (6) in the corresponding paper [Cussler et al., 1988].

It is only when the platelet gap \(s\) is comparable to the platelet width \(h'\), that Eq. (3.22) reduces to (but note our earlier assumption of \(s \to 0\)):

\[
\frac{N_0}{N} = 1 + \frac{(h'/t)^2 \phi^2}{4(1-\phi)} \tag{3.23}
\]

and clearly an inconsistency is involved.

Because the rate of mass transfer \(N\) is proportional to diffusivity \(D\), Eq. (3.23) becomes:

\[
\frac{D_0}{D} = 1 + \frac{(h'/t)^2 \phi^2}{4(1-\phi)} \tag{3.24}
\]

Eq. (3.24) is the final result of the Cussler analysis. Note that in the paper by Cussler et al., \(h'\) is denoted by \(2d\). They, therefore, do not have a factor of 4 as we do in Eq. (3.23) and Eq. (3.24).

### 3.3 Proposed Model

Instead of using a model that relies on combining resistances to mass transfer, one may build on the idea originally proposed by Nielsen. The essential concept is illustrated in Figure 3.3.
Here it is recognized that if the diffusion path length increases from $d$ to $d'$, the area for mass transfer must reduce correspondingly.

Figure 3.3: Illustration of the new model showing reduction in the area for mass transfer with an increase in path length.

As shown in Figure 3.3, the polymer is essentially divided into $n$ channels by the nanoplatelets. The number of channels $n$ is:

$$n = \frac{d'}{d}$$

(3.25)

where $d'$ is the distance that the diffusing molecules have to travel inside the polymer with nanoplatelets, and $d$ is the thickness of the polymer film.

From Eq. (3.11), one knows that:

$$\frac{d'}{d} = 1 + \frac{h}{2t} \phi$$

(3.26)

where $\phi$ is the barrier volume fraction.

Since the flux is inversely proportional to the distance traveled, the following equation is obtained:

$$\frac{j_0}{j} = 1 + \frac{h}{2t} \phi$$

(3.27)
where $J_0$ is the flux in the polymer without nanoplatelets, and $J$ is the flux in the polymer with nanoplatelets.

On the other hand, the area of mass transfer is inversely proportional to the number of channels:

$$\frac{A_0}{A} = 1 + \frac{h}{2t} \phi$$  \hspace{1cm} (3.28)

where $A_0$ is the area of mass transfer in the polymer without nanoplatelets, and $A$ is the area of mass transfer in the polymer with nanoplatelets.

The rate of mass transfer $N$ is:

$$N = J \times A$$  \hspace{1cm} (3.29)

where $N_0$ is the rate of mass transfer in the polymer without nanoplatelets, and $N$ is the rate of mass transfer in the polymer with nanoplatelets.

Combining Eqs. (3.27)-(3.29), the following equation can be obtained:

$$\frac{N_0}{N} = (1 + \frac{h}{2t} \phi)^2$$  \hspace{1cm} (3.30)

Since rate of mass transfer is proportional to the diffusion coefficient, Eq. (3.30) can be rewritten as follows:

$$\frac{D_0}{D} = (1 + \frac{h}{2t} \phi)^2$$  \hspace{1cm} (3.31)

where $D_0$ is the diffusivity in the polymer without nanoplatelets, and $D$ is the apparent diffusivity through the polymer with nanoplatelets.

Again, the reduction in diffusivity depends on the filler volume fraction and the filler aspect ratio, but the final result differs significantly from both Eqs. (3.13) and (3.24).
4 EXPERIMENTAL DETAILS

4.1. Materials

Polylactic acid PLA 6752D (L:D=96:4) was provided by NatureWorks LLC (Minnetonka, MN). Its melting point is 150-160°C while its glass transition temperature is 55-60°C. The molecular weight is 65000 g/mol [Tenn et al., 2013]. The nanoclays (primary thickness: 1-2 nm) used in this study were from Southern Clay Products (Austin, TX): Cloisite 15A, Cloisite 20A, Cloisite 93A, Cloisite 25A, Cloisite 30B, Cloisite 10A and Cloisite Na⁺. Note that Cloisite 30B is a natural montmorillonite that was modified with methyl tallow bis-2-hydroxyethyl quaternary ammonium salt. The organic fraction was determined to be 20.2% using thermal gravimetric analysis (TGA) measurement. Plasticizers acetyl tributyl citrate (ATBC) 98% and palm oil analytical standard were obtained from Sigma-Aldrich (St. Louis, MO). Plasticizer glycerol 99+% was obtained from Acros Organics (Pittsburgh, PA).

4.2 PLA Nanocomposite Preparation

All materials used in this work were dried (90°C in an oven for 4h) before use. The desired concentrations of Cloisite 30B (inorganic content) were mixed with PLA in a Haake Polydrive counter-rotating internal mixer at various mixing conditions. Variables for mixing conditions were temperature, rotor rpm and mixing time. Unfilled PLA was also melt-processed under the same conditions to prepare a reference material. The PLA nanocomposite was then compression molded into 0.5 mm-thick films at 220°C and 10 ton load for 5 min.
4.3 Thermal Treatment

PLA containing Cloisite 30B was processed by different thermal treatments to increase the polymer crystallinity in order to see the effect of crystallinity on the permeability.

4.4 Differential Scanning Calorimetry

The glass transition temperature (T_g), melting temperature (T_m), enthalpy of cold crystallization (H_{cc}), and enthalpy of melting (H_m) of PLA and PLA nanocomposites were determined using a DSC Q100 system from TA Instruments (New Castle, DE). The molded samples, which were from 5 mg to 10 mg, were heated at a scanning rate of 10°C/min from 10°C to 200°C, held for 5 min and cooled to 10°C at the same rate. The thermal properties were measured with individually prepared films in triplicate. The crystallinity (\(\chi_c\)) was calculated using the following equation:

\[
\chi_c = \frac{\Delta H_m - \Delta H_c}{\Delta H_m^0 (1 - \phi)} \times 100
\]

where \(\Delta H_m\) is the melting enthalpy, \(\Delta H_c\) is the cold crystallization enthalpy, \(\Delta H_m^0\) is the theoretical value of the melting enthalpy of a 100% crystalline PLA (93 J/g) [Fisher et al. 1973], and \(\phi\) is the nanofiller mass fraction. DSC measurements were carried out on compression molded films unless otherwise stated.

4.5 Measurement of Water Vapor Permeability

Before being used, the PLA film was dried in a desiccator for 7 days. The water vapor barrier property of the film was determined by PERMATRAN W3/33 purchased from MOCON (Minneapolis, MN) which measures the water transmission rate across the film. Figure 4.1 shows the picture of the test cell.
Figure 4.1: Test cell of PERMATRAN W3/33.

In the MOCON instrument, the sample film in the test cell was exposed to a continuous flow of dry nitrogen gas on the inside and 100% relative humidity on the outside by the use of a sponge soaked with HPLC grade water. The gas stream leaving the cell via the exhaust port consisted of a mixture of nitrogen and water vapor. When the nitrogen flow rate was kept constant, the resulting water vapor density changed due to the water vapor transmission through the sample film. The exhaust gas was sent to a pressure-modulated, infrared detection system. The absorption rate of the infrared energy was proportional to the water vapor density. The detection system measured the change in infrared energy and calculated the water vapor density in the exhaust stream. The water vapor transmission rate across the film was obtained based on the water vapor density, and the water vapor permeability was determined by the methods described in Section 2.2. All the values reported are the average of results of at least 3 samples.

4.6 Solubility Experiments

In a solubility experiment, the initial weight of a dried sample is measured. Then the sample is placed in an environmental chamber at the desired temperature and relative humidity (RH). The weight of the sample is measured on a regular basis until it reaches equilibrium. Since the
volume of one mole of any gas is 22.414 L at STP, the equilibrium moisture concentration in the sample $C_{eq}$ in units of cc of water vapor at STP per cc of sample is calculated by the following equation [Siparsky et al. 1997]:

$$C_{eq} = \frac{(W-W_0)22414\rho}{18W_0} \quad (4.2)$$

where $C_{eq}$ is the equilibrium concentration of gas in the polymer, $W$ is the weight in grams of the polymer and absorbed water at equilibrium, $W_0$ is the weight in grams of the dried polymer, and $\rho$ is the density of PLA nanocomposite which is about the same as PLA (1.2 g/cm$^3$).

The gas solubility can be obtained from the following equation (see Appendix 8):

$$S = \frac{0.803C_{eq}}{p} \quad (4.3)$$

where $S$ is the solubility of water vapor in units of (kg/Pa/m$^3$), $C_{eq}$ is the equilibrium concentration of moisture in the polymer, and $p$ is the saturated water vapor pressure measured in Pa. All the values reported are the average of results of at least 3 samples.

4.7 Transmission Electron Microscopy

The nanofiller dispersion was examined by a CM200 Transmission Electron Microscope (TEM) from Philips (Amsterdam, Netherlands). A cryo-ultramicrotome was used to prepare thin samples.

4.8 Rheological Measurements

Oscillatory shear rheological analyses were conducted with a rotational rheometer Rheometrics RMS 800 from Rheometric Scientific (Piscataway Township, NJ). The measurements were performed with a plate and plate geometry (sample of 25 mm in diameter sample and 0.5 mm in thickness) at 180°C and strain of 5%. All the values reported are the average of 5 measurements.
4.9 X-Ray Diffraction Pattern

X-ray diffraction (XRD) analysis was carried out with X’Pert Pro XRD from PANalytical (Almelo, Netherlands) with a Cu Kα source (λ=0.15418 nm) at 35 kV and 40 mA. The patterns were recorded at 25°C in the range of 5°-30°.

4.10 Mechanical Properties Measurement

Mechanical properties were measured on a DMTA V from Rheometric Scientific (Piscataway Township, NJ). Single cantilever bending geometry (14×8×0.1mm) was used. The strain rate was 1×10⁻⁵/s.
5 RESULTS AND DISCUSSION

5.1 Introduction

In this chapter, the results of the current research are presented. At the beginning, the most appropriate nanoclay for PLA is identified. The processing condition for this particular nanoclay is optimized. Also, the effects of loading, temperature and relative humidity on water vapor barrier properties are presented. Then the ability of the proposed model to fit the experimental data is examined and compared to the existing models. The effect of plasticizer on the nanoclay dispersion is shown. Finally, the effect of crystallinity on water vapor barrier properties of PLA and PLA nanocomposites is presented.

5.2 Effect of Nanoclay Surface Character on Properties of PLA Nanocomposites

5.2.1 Effect of Nanoclay Surface Character on Thermal Properties of PLA Nanocomposites

2.6 vol% of each clay was incorporated into PLA via the use of an internal mixer at 180°C and 80 rpm for 5 minutes. These processing conditions were based on experience. Figure 5.1 shows representative data of the first heating scan of material taken from films made from as-received PLA pellets, PLA directly from the mixer, compression molded PLA and compression molded PLA containing 2.6 vol% of Cloisite 30B. The step change at around 58°C represents \( T_g \), the glass transition temperature. The peak after the glass transition is the polymer relaxation [Pluta, 2004; Picard et al., 2005]. The exothermic peak in the region of 110-120°C can be attributed to cold crystallization. The values of the glass transition temperature and cold crystallization temperature are similar to those reported in the literature [Mohapatra et al., 2012]. The two endothermic peaks in the temperature range of 145-155°C are the two melting peaks of the sample. Similar behavior and values were reported by others as well [Pan et al., 2008;
Mohapatra et al., 2012; Duan et al., 2013). The lower peak corresponds to the less ordered \( \alpha' \) form, while the higher peak corresponds to the more ordered \( \alpha \) form. It is clear that the incorporation of clay did not have a qualitatively significant impact on the PLA heating curve as compared to neat PLA.

![DSC heating curve of PLA and PLA containing 2.6 vol% of Cloisite 30B](image)

Figure 5.1: DSC 1\textsuperscript{st} heating curve of PLA and PLA containing 2.6 vol\% of Cloisite 30B.

Table 5.1 shows the thermal properties based on the 1\textsuperscript{st} heating scan of the different samples examined. An examination of this table shows that the as-received PLA had a crystallinity of 42\%, so there was no cold crystallization temperature in the sample. In addition, the processing of PLA led to increase in the glass transition temperature and the melting temperature. Compared to the PLA directly from the mixer, compression molded PLA had lower glass transition temperature, cold crystallization temperature and melting temperatures. The PLA directly from
the mixer had a crystallinity of 1.8%. As expected, the compression mold eliminated the thermal history and resulted in amorphous PLA sample, so the compression molded PLA had similar cold crystallization enthalpy and melting enthalpy. Moreover, the addition of nanoclays increased the glass transition temperature slightly. The reason could be that the polymer chain mobility was restricted in the presence of the nanoclay particles [Das et al., 2010]. In addition, the cold crystallization temperature and the melting temperatures also slightly increased after the incorporation of nanoclay. The increase in the cold crystallization temperature is unusual because others have reported that the addition of nanoclay facilitated the crystallization process and reduced the cold crystallization temperature [Duan et al., 2013; Tenn et al., 2013]. The increase in the cold crystallization temperature in this study might be due to the presence of clay hindering crystal growth. On the other hand, the cold crystallization enthalpy and the melting enthalpy were clearly higher for pure PLA because the intensities of those peaks are proportional to the amount of organic phase [Tenn et al., 2013]. The glass transition temperature and the cold crystallization temperature did not vary much among the nanoclays tested. The two melting temperatures were similar for all the nanoclays except for PLA containing Cloisite 93A. In particular, Cloisite 93A-PLA nanocomposite did not have a first melting peak. This implied that there was only one crystal type in this material. The cold crystallization enthalpy $H_{cc}$ and the melting enthalpy $H_m$ of each sample were the same. This implied that the nanocomposites were amorphous.

Table 5.2 shows results from the 2nd heating scan of the samples. Compared to the PLA directly from the mixer, compression molded PLA had lower glass transition temperature, cold crystallization temperature and melting temperatures. In addition, neat PLA again had similar glass transition temperature and melting temperature compared to the PLA nanocomposites. The
cold crystallization temperature was lower for pure PLA. It was because the incorporation of nanoclay hindered the crystal growth as discussed above. Moreover, the cold crystallization enthalpy and the melting enthalpy were higher for pure PLA because the organic content decreased when nanoclay was added. All the PLA nanocomposites had similar properties except the one made with Cloisite 93A. PLA containing Cloisite 93A was not able to crystallize after melting at the first heating scan. Therefore, this material showed a higher cold crystallization temperature $T_{cc}$ and a smaller melting enthalpy $H_m$ compared to the others. Such unusual behavior has also been reported by others [Darie et al., 2014]. In their study, the cold crystallization temperature of PLA containing Cloisite 93A ($131.9^\circ C$) was much higher than that of other PLA nanocomposites ($114.2$-$120.4^\circ C$).

In summary, based on the thermal data presented in this subsection, all the nanocomposite films used in this work are likely to be amorphous in nature.

Table 5.1: Thermal properties of 1st heating scan of PLA containing 2.6 vol% of nanoclays.

<table>
<thead>
<tr>
<th>Clay</th>
<th>$T_g$ ($^\circ C$)</th>
<th>$T_{cc}$ ($^\circ C$)</th>
<th>$H_{cc}$ (J/g)</th>
<th>$T_{m1}$ ($^\circ C$)</th>
<th>$T_{m2}$ ($^\circ C$)</th>
<th>$H_m$ (J/g)</th>
<th>Crystallinity (%)</th>
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<td>58±1</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>39.4±0.5</td>
<td>42.1±0.6</td>
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<td>26.4±0.5</td>
<td>1.8±0.5</td>
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<tr>
<td>PLA</td>
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<td>33.8±0.5</td>
<td>~0%</td>
</tr>
<tr>
<td>15A</td>
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<td>110±3</td>
<td>29.6±0.4</td>
<td>147.1±0.6</td>
<td>154.9±0.2</td>
<td>29.2±0.2</td>
<td>~0%</td>
</tr>
<tr>
<td>20A</td>
<td>61.0±0.3</td>
<td>110.8±0.1</td>
<td>29.9±0.3</td>
<td>147.5±0.3</td>
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</tr>
<tr>
<td>93A</td>
<td>61.7±0.1</td>
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<td>13.4±0.6</td>
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</tr>
<tr>
<td>25A</td>
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<td>27.2±0.5</td>
<td>148.1±0.3</td>
<td>154.4±0.1</td>
<td>26.8±0.2</td>
<td>~0%</td>
</tr>
<tr>
<td>30B</td>
<td>60.5±0.2</td>
<td>111.2±0.2</td>
<td>27±1</td>
<td>147.5±0.3</td>
<td>154.2±0.1</td>
<td>26±1</td>
<td>~0%</td>
</tr>
<tr>
<td>10A</td>
<td>60.0±0.2</td>
<td>109.6±0.5</td>
<td>27.1±0.4</td>
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<td>~0%</td>
</tr>
<tr>
<td>Na$^+$</td>
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<td>109.6±0.1</td>
<td>28±1</td>
<td>147.3±0.3</td>
<td>154.6±0.1</td>
<td>27±1</td>
<td>~0%</td>
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</tbody>
</table>
Table 5.2: Thermal properties of 2\textsuperscript{nd} heating scan of PLA containing 2.6 vol% of nanoclays.

<table>
<thead>
<tr>
<th>Clay</th>
<th>$T_g$ (°C)</th>
<th>$T_{cc}$ (°C)</th>
<th>$H_{cc}$ (J/g)</th>
<th>$T_{m1}$ (°C)</th>
<th>$T_{m2}$ (°C)</th>
<th>$H_m$ (J/g)</th>
</tr>
</thead>
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<td>PLA mixer</td>
<td>58.9±0.7</td>
<td>110.3±0.1</td>
<td>26.4±0.7</td>
<td>147.8±0.4</td>
<td>155.0±0.2</td>
<td>25.9±0.5</td>
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<tr>
<td>PLA</td>
<td>58.9±0.2</td>
<td>108.2±0.1</td>
<td>34.9±0.8</td>
<td>145.7±0.1</td>
<td>153.1±0.1</td>
<td>34.2±0.4</td>
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<tr>
<td>15A</td>
<td>59.9±0.1</td>
<td>116.2±0.4</td>
<td>29.9±0.6</td>
<td>148.7±0.2</td>
<td>155.6±0.1</td>
<td>30.4±0.4</td>
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<tr>
<td>20A</td>
<td>59.9±0.2</td>
<td>112.8±0.1</td>
<td>30.4±0.2</td>
<td>148.0±0.1</td>
<td>155.5±0.1</td>
<td>30.4±0.1</td>
</tr>
<tr>
<td>93A</td>
<td>61.0±0.2</td>
<td>132.5±0.1</td>
<td>2.1±0.4</td>
<td>-</td>
<td>153.6±0.1</td>
<td>1.9±0.1</td>
</tr>
<tr>
<td>25A</td>
<td>60.5±0.1</td>
<td>115.2±0.1</td>
<td>27.7±0.3</td>
<td>148.9±0.1</td>
<td>155.1±0.1</td>
<td>27.4±0.1</td>
</tr>
<tr>
<td>30B</td>
<td>60.1±0.1</td>
<td>113.4±0.2</td>
<td>28±1</td>
<td>148.4±0.1</td>
<td>154.9±0.1</td>
<td>27±1</td>
</tr>
<tr>
<td>10A</td>
<td>59.8±0.1</td>
<td>112.4±0.2</td>
<td>27.7±0.5</td>
<td>147.4±0.2</td>
<td>154.7±0.1</td>
<td>27.8±0.3</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>60.8±0.1</td>
<td>112.6±0.1</td>
<td>28±1</td>
<td>147.8±0.1</td>
<td>154.7±0.2</td>
<td>27±1</td>
</tr>
</tbody>
</table>

5.2.2 Effect of Nanoclay Surface Character on Water Vapor Barrier Properties of PLA Nanocomposites

Figure 5.2 shows the water transmission rate through a 0.49 mm-thick PLA sample measured at 25°C by MOCON. Using Eq. (2.7), the rate of 9.44 g/(m$^2$×d) gives 1.67×10$^{-14}$ kg/(m×Pa×s) as water vapor permeability. The sample calculation can be found in Appendix 8. Figure 5.3 shows the cumulated water vapor permeated through that sample. The straight line intersects the t-axis and gives a time-lag of 1.77 hrs. The time-lag method described in Section 2.2 gives 6.12×10$^{-12}$ m$^2$/s as water vapor diffusivity. Siparsky et al. (1997) reported 1.61 kg/(m×Pa×s) as permeability and 5.2×10$^{-12}$ m$^2$/s as diffusivity at 20°C and 90% RH. The MOCON instrument could measure permeability accurately but the time-lag method gave slightly lower diffusivity as compared to the literature value.

Figure 5.4 shows the water vapor transmission rate through a 0.5 mm-thick PLA film containing 2.6 vol% Cloisite 30B measured by MOCON. Using Eq. (2.7), the rate of 6.02 g/(m$^2$×d) gives 1.09×10$^{-14}$ kg/(m×Pa×s) as water vapor permeability. Figure 5.5 shows the cumulated water vapor permeated through that sample. The straight line intersects the t-axis and
gives a time-lag of 2.39 hrs. The time-lag method described in Section 2.2 gives $4.71 \times 10^{-12}$ m$^2$/s as water vapor diffusivity.

Figure 5.2: Water vapor transmission rate through PLA.

Figure 5.3: Cumulated water permeated through PLA.
Figure 5.4: Water vapor transmission rate through PLA containing 2.6 vol% of Cloisite 30B.

Figure 5.5: Cumulated water permeated through PLA containing 2.6 vol% of Cloisite 30B.

The water vapor barrier properties through PLA containing a fixed amount of different nanoclays were investigated using the MOCON instrument. Figure 5.6 shows the water vapor permeability through these PLA nanocomposites. From the DSC data, it was found that all the samples have zero crystallinities. Therefore, the reduction in water vapor permeability was due to the barrier effect of the nanoclays alone. The permeability was reduced for all the PLA
nanocomposites except for Cloisite Na\textsuperscript{+}. The result matched the expectation that the coated nanoclays could be dispersed in the PLA matrix. The impermeable nanoplatelets acted as barriers which increased the diffusion pathway and the time spent in the PLA matrix. Thus, the water vapor permeability was reduced. As the hydrophilicity increased from Cloisite 15A to Cloisite 30B, the water vapor permeability decreased. This was because the nanoclays became more compatible with PLA and presumably dispersed better in the PLA matrix. However, increasing the hydrophilicity from Cloisite 30B to Cloisite Na\textsuperscript{+} did not reduce the water vapor permeability because Cloisite 10A and Cloisite Na\textsuperscript{+} were not as compatible as Cloisite 30B was in PLA. Among all the nanoclays, Cloisite 30B showed the lowest water permeability because it was the most compatible with PLA and possibly had the best dispersion in PLA. In this regard, Rhim et al. (2011) measured the water vapor permeability through agar films containing three different nanoclays, and found that an inappropriate nanoclay might even cause an increase in permeability. Our study showed that the sample with Cloisite Na\textsuperscript{+} did not have any reduction in permeability because it did not have any surface treatment and did not disperse at all in PLA. Thus, it showed no barrier effects. In other words, the permeability depended on the surface character of the nanoclay. In this study, Cloisite 30B was the best nanoclay in terms of reducing water vapor permeability. This kind of behavior has also been reported by the others. The water transmission rates of these samples can be found in Appendix 1.

The dispersion state of nanoclays in PLA can be evaluated by the use of a TEM. Figure 5.7 shows the TEM images of PLA containing 2.6 vol\% of Cloisite Na\textsuperscript{+} and Cloisite 30B respectively. It is seen that the sample containing Cloisite Na\textsuperscript{+} had agglomerates which was an indicator of poor dispersion. When nanoplatelets aggregated, a preferred pathway formed for diffusion of gas molecules, and the nanoclay had no impact on reducing gas permeability.
Compared to untreated Cloisite Na⁺, the organo-modified Cloisite 30B showed a higher homogeneity in the nanoclay dispersion. Both intercalated and exfoliated structures can be seen in the PLA containing Cloisite 30B. With the well dispersed Cloisite 30B nanoplatelets in the PLA matrix, the diffusing water vapor molecules had to travel a tortuous path and thus the permeability was reduced. The TEM pictures help explain the permeability results in Figure 5.6.

![Figure 5.6: Water vapor permeability through PLA containing 2.6 vol% of nanoclays](image)

\[\text{Permeability} \times 10^{14} \text{ kg/(m-Pa-s)}\]

**Figure 5.6:** Water vapor permeability through PLA containing 2.6 vol% of nanoclays

\[\times 10^{14} \text{ kg/Pa/m/s} \]

![Figure 5.7: TEM images of PLA containing 2.6 vol% of: (a) Cloisite Na⁺; (b) Cloisite 30B.](image)
5.3 Optimization of Processing Conditions for PLA and PLA Containing Cloisite 30B

5.3.1 Effect of Mixer Screw Speed on Water Vapor Permeability through PLA and PLA Containing Cloisite 30B

The previous section showed that Cloisite 30B was the most effective additive in terms of lowering the water vapor permeability through PLA. Therefore, further investigation was done to improve the dispersion of Cloisite 30B in PLA. The processing conditions in the internal mixer should affect the dispersion state of Cloisite 30B in PLA. Here there are three main factors: mixing screw speed, mixing temperature, and mixing time. Raising the mixing screw speed, mixing temperature or mixing time may lead to better dispersion state of Cloisite 30B in PLA. However, this action might also result in PLA degradation, damage to Cloisite 30B and decrease in the aspect ratio of nanoplatelets in PLA [Logakis et al., 2010; Pollatos et al., 2015]. Therefore, a systematic study was conducted to determine the optimum processing conditions for PLA nanocomposites.

Figure 5.8 shows the water vapor permeability through PLA and PLA containing 2.6 vol% Cloisite 30B as a function of mixing screw speed. The samples were processed at 180°C and different mixing screw speeds for 5 minutes. As expected, the incorporation of Cloisite 30B into the PLA matrix significantly reduced the water vapor permeability through PLA. Since the DSC result showed that the films were amorphous, the decrease in permeability of PLA nanocomposite was attributed solely to the presence of the nanoclay. In addition, one could see that mixing screw speeds had, at best, only a slight impact on the water vapor permeability of PLA nanocomposites. This behavior was also observed by the others working on starch containing Cloisite Na⁺/Cloisite 30B [Chiu et al., 2006]. XRD scans showed that the samples processed at various screw speeds had similar 2θ peak values. This implied that the screw speed
had little impact on nanoclay dispersion in the starch. In addition, Frounchi and Dourbash (2009) reported similar behavior on PET containing Cloisite 15A. When the screw speed was varied, thermal, mechanical and gas barrier properties did not change. This implied that increasing the screw speed had no beneficial effect on the nanoclay dispersion. In our study, it was found that the dispersion state was not a strong function of the screw speed. In other words, the shear force had only a minor effect on the nanoclay dispersion in the polymer matrix once a certain screw speed had been obtained.

Figure 5.8: Effect of mixer screw speed on water vapor permeability through PLA and PLA nanocomposites (×10^{14} kg/Pa/m/s).

5.3.2 Effect of Mixing Temperature on Water Vapor Permeability through PLA and PLA Containing Cloisite 30B

Another factor affecting the dispersion of Cloisite 30B in PLA is mixing temperature. Figure 5.9 shows the effect of nanocomposite processing temperature on water vapor permeability through PLA and PLA containing 2.6 vol% Cloisite 30B. The samples were processed at
different temperatures but at a fixed 80 rpm for 5 minutes. At 200°C, the water vapor permeability through PLA containing 2.6 vol% Cloisite 30B was the lowest. A further increase in processing temperature to 220°C did not lead to additional reduction in permeability compared to the corresponding neat PLA. This implied that the dispersion of Cloisite 30B into PLA was well achieved at 200°C. Similar behavior was reported for starch containing Cloisite 30B [Chiou et al., 2006]. When the temperature increased, the XRD spectrum showed that the nanocomposite became more intercalated at higher temperature. The increase in temperature had a positive impact on the nanoclay dispersion in the polymer. Thus the permeability would be improved because of the enhanced dispersion state of nanoclay in the polymer.

![Figure 5.9](image-url)

Figure 5.9: Effect of mixing temperature on water vapor permeability through PLA and PLA containing 2.6 vol% of Cloisite 30B ($\times 10^{14}$ kg/Pa/m/s).
5.3.3 Effect of Mixing Temperature on Rheological Properties of PLA and PLA Containing Cloisite 30B

The melt viscosity of polymer is proportional to its molecular weight. Thus, by measuring the melt viscosity of PLA, it is possible to determine if its molecular weight is changing. Figure 5.10 shows the complex viscosity measurement of PLA processed under different mixing temperatures and 80 rpm for 5 minutes. The viscosity was measured at 180°C. It shows that the PLA processed at higher temperature has lower viscosity. The result indirectly implies that the molecular weight decreased when the mixing temperature was raised. It was because higher temperature accelerated the degradation reaction. Similar behavior was reported on poly(methyl methacrylate) (PMMA) [Kashiwagi et al., 1985] and PLA [Signori et al., 2009]. It was found that the degradation was accelerated and the molecular weight decreased when the temperature was raised.

![Effect of mixing temperature on viscosity of PLA.](image.png)

Figure 5.10: Effect of mixing temperature on viscosity of PLA.

Figure 5.11 shows the viscosity measurements of PLA and PLA nanocomposites mixed under different mixing temperatures and 80 rpm for 5 minutes. The viscosity measurement was
done at 180°C. Compared to PLA, PLA containing Cloisite 30B had higher viscosity because of filler effect of the nanoclay platelets. There was also more pronounced shear-thinning behavior at low frequencies for PLA nanocomposites as can be expected for nanoclay filled polymers. However, the viscosity difference narrowed at high frequencies for all the samples. Such behavior was also reported for methyl methacrylate (MMA)/poly-methyl methacrylate (PMMA)/Cloisite 30B nanocomposites [McAlpine et al., 2006] and PLA/poly-hydroxybutyrate-valerate (PHBV)/Cloisite 30B nanocomposites [Zhao et al., 2013]. The shear-thinning response was similar for the nanocomposite processed at different temperatures because the dispersion state of Cloisite 30B did not change significantly by raising the mixing temperature [Pluta et al., 2007]. The rheological behavior matched the permeability measurement.

![Figure 5.11: Effect of mixing temperature on viscosity of PLA and PLA nanocomposites.](image)

On the other hand, the rise in mixing temperature aggravated the degradation reaction and reduced the molecular weight of PLA containing Cloisite 30B. The PLA nanocomposites were subject to polymer decomposition. Therefore, the viscosity of PLA nanocomposites decreased as the mixing temperature increased. Thermal degradation of polymer nanocomposites during melt processing was also reported on PLA containing Cloisite 30B [Zhou and Xanthos, 2008; Meng et
Both the temperature and the nanoclay acted as catalysts of the degradation reaction which led to a decrease in the molecular weight and complex viscosity [Meng et al., 2012].

5.3.4 Effect of Mixing Time on Water Vapor Permeability through PLA and PLA Containing Cloisite 30B

The third factor that affects the dispersion of Cloisite 30B in PLA is the mixing time in the internal mixer. Figure 5.12 shows the effect of mixing time on water vapor permeability through PLA and PLA containing 2.6 vol% Cloisite 30B. The samples were processed at 180°C and 80 rpm for different lengths of time. At 5 minutes, the water vapor permeability through PLA containing 2.6 vol% Cloisite 30B was the lowest. The increase in mixing time beyond 5 minutes did not reduce the water vapor permeability in any significant manner. This implied that the dispersion of Cloisite 30B in PLA was well accomplished at 5 minutes. Further increase to 7 minutes in mixing time did not have a positive impact on improving the dispersion of Cloisite 30B in PLA. Such behavior was reported by the others including Lertwimolnun and Vergnes (2005). Cloisite 20A was incorporated into PP via an internal mixer. When the mixing time increased, the complex viscosity and the storage modulus increased. It was because the dispersion state of the nanolcay was improved with the increase in mixing time. However, further increase in mixing time had no significant effect on enhancing the nanoclay dispersion. Moreover, de Abreu et al. (2007) studied the effect of mixing time on the dispersion of Cloisite 15A in LDPE. XRD showed that the intensities of 2θ peaks corresponding to the Cloisite 15A on the XRD spectrum decreased when the mixing time increased. This meant that the increase in the mixing time had a positive impact on the dispersion of nanoclay in the polymer matrix.
Figure 5.12: Effect of mixing time on water vapor permeability through PLA and PLA containing 2.6 vol% of Cloisite 30B ($10^{14}$ kg/(Pa·m·s)).

### 5.3.5 Effect of Mixing Time on Rheological Properties of PLA and PLA Containing Cloisite 30B

It is known that the viscosity of PLA is strongly dependent on the molecular weight of PLA. Thus, the viscosity measurement method was used to see the effect of mixing time on the molecular weight of PLA. The measurement was taken at 180°C. Figure 5.13 shows the viscosity measurement of PLA mixed at 180°C and 80 rpm for different amounts of time, where it can be seen that the viscosity of PLA decreased as the mixing time increased. It was because longer mixing time facilitated the degradation reaction and reduced the molecular weight of PLA. Similarly, Nugay and Tincir (1994) reported that the oxidative degradation of HDPE and LDPE became more severe as the mixing time increased. The longer the residence time was, the less the molecular weight would be.
Figure 5.13: Effect of mixing time on viscosity of PLA.

Figure 5.14 shows the viscosity measurement of PLA and PLA nanocomposites mixed at 180°C and 80 rpm for different amounts of time. The viscosity was measured at 180°C. The presence of the filler results in a higher viscosity for the nanocomposites and a shear thinning effect. Consistent with the results obtained for pure PLA, for PLA nanocomposites also, increased mixing times result in decreased viscosity which indicates reduction in molecular weight due to increased degradation at longer mixing time.

Figure 5.14: Effect of mixing time on viscosity of PLA and PLA nanocomposites.
5.3.6 Optimized Processing Conditions for PLA and PLA Containing Cloisite 30B

Several factors were investigated in order to get the best dispersion state of Cloisite 30B in PLA. There was little dependence of water vapor permeability on mixing screw speed. However, change in the mixing temperature from 180°C to 200°C reduced the water vapor permeability through PLA containing 2.6 vol% Cloisite 30B. The water vapor permeability decreased when the mixing time was increased up to 5 minutes. Further increases in mixing temperature to 220°C and mixing time to 7 minutes did not have a positive impact on the water vapor permeability through PLA nanocomposite. But as the rheological measurements showed, there was a reduction in molecular weight with the rise in mixing temperature and mixing time. Thus, based on data obtained from the permeability and rheology measurements, the optimized mixing conditions for Cloisite 30B-PLA nanocomposites were chosen as 200°C and 80 rpm for 5 minutes.

5.4 Effect of Cloisite 30B Loading Level on Properties of PLA Nanocomposites

5.4.1 Effect of Cloisite 30B Loading Level on Thermal Properties of PLA Nanocomposites

Since the previous test showed that Cloisite 30B was the best additive for PLA, a study was conducted to investigate the effect of loading level of Cloisite 30B on thermal properties of PLA under the optimized processing conditions. Different amounts of Cloisite 30B were incorporated into PLA at 200°C and 80 rpm for 5 minutes. Figure 5.15 shows the first heating scan using films of PLA and PLA containing 2.6 vol% Cloisite 30B. The transition at around 58°C was the glass transition temperature. The peak following the step change was the polymer relaxation, while the exothermic peak in the region of 110-120°C represents the cold crystallization temperature. The two endothermic peaks in the temperature range of 145-155°C are the two
melting peaks of the sample. It is evident that the incorporation of Cloisite 30B did not change the heating curve significantly.

Figure 5.15: DSC 1st heating curve of PLA and PLA containing 2.6 vol% Cloisite 30B.

Table 5.3 shows the thermal properties obtained from the 1st heating scan of PLA containing different loading levels of Cloisite 30B. The glass transition temperature \( T_g \) of PLA containing Cloisite 30B was slightly lower than that of PLA except for PLA containing 0.5 vol% Cloisite 30B. Similar behavior was reported on PLA containing Cloisite 30B by others [Pluta et al., 2007; Fukushima et al., 2009], and it was because of the plasticization effect of the surfactant in Cloisite 30B (20 wt% in Cloisite 30B). Thus, the polymer chain mobility was enhanced, and the glass transition temperature was reduced. Another possible reason was that the surfactant of Cloisite 30B acted as a catalyst for the degradation reaction and resulted in a loss of molecular weight of PLA [Gamez-Perez et al., 2011]. Therefore, the glass transition temperature of sample containing Cloisite 30B was reduced. The addition of Cloisite 30B did not have a significant impact on the cold crystallization temperature \( T_{cc} \) or the melting temperature \( T_m \). The cold crystallization enthalpy \( H_{cc} \) and the melting enthalpy \( H_m \) decreased as the loadings of Cloisite
30B increased. As expected, however, these values were proportional to the PLA content in the nanocomposite. After being processed in the internal mixer, all the samples showed two melting peaks because they formed two types of crystals of different sizes and perfections. On the other hand, the samples had similar cold crystallization enthalpy and melting enthalpy. This implied that all the samples were largely amorphous.

Table 5.3: Thermal properties of 1st heating scan of Cloisite 30B-PLA films.

<table>
<thead>
<tr>
<th>Clay vol%</th>
<th>T_g (°C)</th>
<th>T_cc (°C)</th>
<th>H_cc (J/g)</th>
<th>T_m1 (°C)</th>
<th>T_m2 (°C)</th>
<th>H_m (J/g)</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>59.6±0.5</td>
<td>110.2±0.1</td>
<td>27.8±0.5</td>
<td>147.4±0.2</td>
<td>154.7±0.1</td>
<td>28.4±0.7</td>
<td>~0%</td>
</tr>
<tr>
<td>0.5</td>
<td>59.9±0.4</td>
<td>109.5±0.9</td>
<td>27.1±0.6</td>
<td>147.6±0.3</td>
<td>154.4±0.1</td>
<td>27.9±0.4</td>
<td>~0%</td>
</tr>
<tr>
<td>1.5</td>
<td>58.6±0.6</td>
<td>110.6±0.1</td>
<td>26.4±0.2</td>
<td>147.8±0.1</td>
<td>154.3±0.1</td>
<td>26.7±0.2</td>
<td>~0%</td>
</tr>
<tr>
<td>2.6</td>
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<td>111.6±0.4</td>
<td>25.8±0.3</td>
<td>148.0±0.3</td>
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<tr>
<td>5.3</td>
<td>57.8±0.1</td>
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<td>153.5±0.1</td>
<td>24.7±0.7</td>
<td>~0%</td>
</tr>
</tbody>
</table>

Table 5.4 shows the thermal properties obtained from the 2nd heating scan of the above samples. The glass transition temperatures T_g were lower for all the PLA nanocomposites compared to the neat PLA, and the reason has already been discussed above. The cold crystallization temperature T_cc and the melting temperatures T_m did not change much for PLA nanocomposites compared to neat PLA. Similar to the 1st heating scan, the 2nd heating scan showed decreases in cold crystallization enthalpies and melting enthalpies as the loading of Cloisite 30B increased. It was because there was a decrease in the organic content.

Table 5.4: Thermal properties of 2nd heating scan of Cloisite 30B-PLA films.

<table>
<thead>
<tr>
<th>Clay vol%</th>
<th>T_g (°C)</th>
<th>T_cc (°C)</th>
<th>H_cc (J/g)</th>
<th>T_m1 (°C)</th>
<th>T_m2 (°C)</th>
<th>H_m (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>60.8±0.1</td>
<td>111.5±0.1</td>
<td>28.2±0.8</td>
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<td>155.0±0.2</td>
<td>28.5±0.5</td>
</tr>
<tr>
<td>0.5</td>
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<td>111.7±0.1</td>
<td>27.6±0.4</td>
<td>148.0±0.1</td>
<td>154.8±0.1</td>
<td>28.0±0.3</td>
</tr>
<tr>
<td>1.5</td>
<td>59.3±0.1</td>
<td>112.9±0.2</td>
<td>27.1±0.3</td>
<td>148.6±0.2</td>
<td>154.6±0.1</td>
<td>27.2±0.4</td>
</tr>
<tr>
<td>2.6</td>
<td>58.7±0.5</td>
<td>113.5±0.1</td>
<td>27.1±0.3</td>
<td>148.6±0.1</td>
<td>154.5±0.2</td>
<td>26.2±0.1</td>
</tr>
<tr>
<td>5.3</td>
<td>58.0±0.1</td>
<td>113±1</td>
<td>25.2±0.6</td>
<td>148.2±0.5</td>
<td>154.2±0.3</td>
<td>24.8±0.8</td>
</tr>
</tbody>
</table>
5.4.2 Effect of Cloisite 30B Loading Level on Water Vapor Barrier Properties of PLA Nanocomposites

The effect of Cloisite 30B loading on the water vapor barrier properties of PLA was investigated, and this is the main objective of the research. Figure 5.16 shows the water vapor permeability through PLA and PLA containing Cloisite 30B. As expected, the permeability decreased with the incorporation of Cloisite 30B due to the tortuous effect created by the dispersed Cloisite 30B nanoplatelets. The impermeable nanoplatelets acted as barriers and forced the diffusing water molecule to travel a longer path in the PLA matrix. Thus the permeability was reduced. In addition, the permeability decreased significantly as the Cloisite 30B loading increased and more Cloisite 30B particles were available as barriers. This behavior is expected and was also reported for PLA containing Cloisite 20A [Rhim et al., 2009] and PLA containing Cloisite 30B [Duan et al., 2013; Tenn et al., 2013]. The difference between the present work and the prior work in the literature is in the extent of permeability reduction that is observed. For PLA and PLA containing 5.3 vol% of Cloisite 30B, the permeabilities were 1.58±0.03 and 0.49±0.04 ×10^{-14} kg/(m×Pa×s) respectively. Thus, the permeability through PLA containing 5.3 vol% of Cloisite 30B was reduced by 69% compared to neat PLA. These results are superior to the literature data. Since the DSC result showed that the films were amorphous, the decrease in permeability of PLA nanocomposite is attributed solely to the presence of dispersed Cloisite 30B. On the other hand, there was a linear relationship between the loading of Cloisite 30B and permeability for loading up to 2.6 vol%. However, the slope decreased at a loading of 5.3 vol%. This might be due to some agglomeration of Cloisite 30B in the PLA matrix. Water vapor transmission rates of these samples can be found in Appendix 2.
TEM was used to investigate the dispersion state of Cloisite 30B in the PLA matrix. The TEM images of PLA containing different amounts of Cloisite 30B are presented in Figures 5.17 (a)-(d) where a representative region was chosen for each of the samples. As one can observe from pictures, there are more nanoplatelets available as barriers when the loading of Cloisite 30B is increased. Thus, the permeability decreased as expected. These pictures indicated that the clay platelets were pretty well dispersed in the PLA matrix for Cloisite 30B loading up to 2.6 vol%. The clay platelets formed both intercalated and exfoliated structures in the PLA matrix. However, as the loading of Cloisite 30B increased, there were more intercalated structures and even aggregated structures than exfoliated structures. This is not surprising since there was less space for nanoclay delamination in the PLA matrix [Thellen et al., 2005; Tenn et al., 2013]. The dispersion of Cloisite 30B was less accomplished at the highest concentration level. The TEM picture could be used to support the permeability result. The permeability decreased almost linearly for up to 2.6 vol% of Cloisite 30B but then the decrease was less than linear at 5.3 vol% because of nanoplatelet agglomeration in the PLA matrix.

Figure 5.16: Water vapor permeability through PLA nanocomposites ($x10^{14}$ kg/Pa/m/s).
Figure 5.17: TEM images of PLA containing Cloisite 30B (a) 0.5 vol%; (b) 1.5 vol%; (c) 2.6 vol%; (d) 5.3 vol%.

Figure 5.18 shows the water vapor diffusivity and solubility through PLA and PLA containing Cloisite 30B. The diffusivity was obtained from the permeation data by time-lag method as described in Section 2.1. Note that this method is correct for an unfilled material, but
it may not hold for a composite. The solubility was simply calculated by dividing the permeability by the calculated diffusivity. Gas diffusivity is expected to decrease as the loading of nanoclay increases because of the presence of barriers to gas diffusion [Ogasawara et al., 2006; Cerisuelo et al., 2012]. However, the water vapor diffusivity shown in Figure 5.18 increased at a loading of 0.5 vol% as compared to the neat PLA. Then it decreased for up to 5.3 vol%. But water vapor solubility is believed to increase when hydrophilic nanoclay is incorporated because hydrophilic clay surface can immobilize more water molecules [Abacha et al., 2009; Chung et al., 2010]. However, water vapor solubility values shown in Figure 5.18 did not change significantly after the incorporation of Cloisite 30B. Since the solubility was calculated from the diffusivity, uncertainties in the diffusivity would propagate to the solubility. There are at least two possible reasons behind the uncertainties: (1) obtaining diffusivity by the time-lag method involved human errors. Siegel and Coughlin (1970) reported that the error in the time-lag method came from the error in determining the slope. A small error in the slope could lead to several times larger error in the time-lag and thus the diffusivity; (2) there was an unusual behavior of diffusivity after the incorporation of Cloisite 30B. Therefore, solubility should be independently measured to eliminate these ambiguities.

![Figure 5.18: Water vapor diffusivity and solubility through PLA nanocomposites.](image-url)
Since the previous discussion stated that the measurement of diffusivity from the permeation data might involve errors, the solubility was independently measured. Because of the hydrophilicity of the Cloisite 30B, the water vapor solubility was believed to increase when the loading of clay increased. Figure 5.19 shows the water vapor solubility in PLA and PLA containing Cloisite 30B. The incorporation of Cloisite 30B increased the solubility because the nanoclay was relatively hydrophilic and could bond with more water molecules when exposed to humid environment. This kind of behavior, which the incorporation of nanoclay into the polymer matrix increased the solubility compared to the neat polymer, was also reported for epoxy resin containing Nanomer L30E organoclay [Abacha et al., 2009], native normal corn starch containing Cloisite Na⁺ [Chung et al., 2010], high-density polyethylene/thermoplastic starch containing Cloisite 20A [Sharif et al., 2011], ethylene-vinyl alcohol copolymer containing bentonite nanoclay [Cerisuelo et al., 2012], thermoplastic polyurethane containing Cloisite 30B [Benali et al., 2014], and poly(3-hydroxybutyrate-co-4-hydroxybutyrate) containing Cloisite 30B [Crétois et al., 2015]. Moreover, the solubility increased as the loading of Cloisite 30B increased. It was because more nanoclay surface was available for water sorption with the increased nanoclay loading. This phenomena was also reported for epoxy resin containing Nanomer L30E organoclay [Abacha et al., 2009], native normal corn starch containing Cloisite Na⁺ [Chung et al., 2010], high-density polyethylene/thermoplastic starch containing Cloisite 20A [Sharif et al., 2011], and poly(3-hydroxybutyrate-co-4-hydroxybutyrate) containing Cloisite 30B [Crétois et al., 2015].

For PLA and PLA containing 5.3 vol% of Cloisite 30B, the solubilities were 2.70±0.05 and 4.5±0.1 ×10⁻³ kg/(Paxm³) respectively. The moisture solubility in PLA containing 5.3 vol% of Cloisite 30B increased by 67% compared to neat PLA. The sample calculation can be found in Appendix 8. On the other hand, the solubility and the loading showed a linear relationship for up
to 2.6 vol% of Cloisite 30B. It was because the surface area increased proportionately to the amount of added clay. However, the solubility increased less than proportionately when the loading reached 5.3 vol% because there was agglomeration at high loading. This was also the conclusion for permeability measurements. The polymer weight gain in the solubility experiment can be found in Appendix 3.

![Graph](image)

Figure 5.19: Water vapor solubility in PLA nanocomposites ($\times 10^3$ kg/Pa/m$^3$).

## 5.5 Effect of Temperature on Water Vapor Transport through PLA and PLA Nanocomposites

In this section, the effect of temperature on the water vapor transport through PLA and PLA nanocomposites was studied based on the corresponding mixing conditions. Because food packaging material is subject to different temperature challenges, it is important to determine the water vapor permeation behavior under various conditions. At a relative humidity of 100%, the effect of temperature on water vapor permeability through PLA and PLA containing Cloisite 30B was investigated. Figure 5.20 shows the water vapor permeability through PLA and PLA
containing Cloisite 30B as a function of temperature. As the temperature increased, water vapor molecules gained more energy, and more water molecules could be transported through the polymer film. Thus the water vapor permeability increased as expected. Similar behavior was also observed in the literature for PLA [Shogren, 1997; Siparsky et al., 1997], poly(3-hydroxybutyrate-co-3-hydroxyvalerate) PHBV [Shogren, 1997], polypropylene PP and polyvinyl alcohol (PVA) [Chen et al., 2014]. On the other hand, the permeability through PLA nanocomposite was lower than that through unfilled PLA because of the tortuous effect. The dispersed Cloisite 30B particles forced the diffusing water molecules to travel a longer path and thus reduced the water vapor permeability. The percent reduction in permeability due to the presence of clay seems to be independent of the temperature of measurement. The results are shown in Table 5.5. The water vapor transmission rates of these samples can be found in Appendix 4.

![Figure 5.20: Effect of temperature on water vapor transport through PLA and PLA nanocomposites.](image_url)
Table 5.5: Percent reduction in water vapor permeability with the presence of clay at different temperatures.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Percent reduction in permeability (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>45</td>
</tr>
<tr>
<td>25</td>
<td>49</td>
</tr>
<tr>
<td>37</td>
<td>42</td>
</tr>
</tbody>
</table>

Since the water vapor permeability discussed above depended on the temperature, one could use the following equation to calculate an activation energy [Doty et al., 1946]:

\[
\ln P_1 - \ln P_2 = -\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{5.1}
\]

where \( P_1 \) is the permeability at temperature \( T_1 \), \( P_2 \) is the permeability at temperature \( T_2 \), \( E \) is the activation energy, and \( R \) is the universal the gas constant.

Figure 5.21: Semi-natural logarithm plot of permeability versus inverse of temperature.

Figure 5.21 shows the plot of natural logarithm of permeability versus the inverse of temperature. The two parameters exhibited a linear relationship as predicted by Eq. (5.1). By linear regression, the activation energies for PLA and PLA containing 2.6 vol% Cloisite 30B were found to be 3.7 kJ/mol and 5.5 kJ/mol respectively. Similar value (2.6 kJ.mol) was found for PLA in a temperature range of 20-50°C and 90% RH in the literature [Siparsky et al., 1997].
Compared to PLA, PLA nanocomposites had a higher activation energy because of the tortuous path. It was more difficult for water molecules to diffuse through PLA containing Cloisite 30B as compared to unfilled PLA. Thus the activation energy for the nanocomposite was higher.

5.6 Effect of Relative Humidity on Water Vapor Transport through PLA and PLA Nanocomposites

Following the discussion in Section 5.5, the effect of relative humidity difference on water vapor transport through PLA and PLA nanocomposites was studied. At a temperature of 25°C, the effect of relative humidity on water vapor permeability through PLA and PLA containing Cloisite 30B was investigated. Figure 5.2 shows the water vapor permeability through PLA and PLA containing Cloisite 30B as a function of relative humidity. The water vapor permeability increased with the increase in relative humidity. Similar behavior was also reported for PLA [Siparsky et al., 1997], PP [Chen et al., 2014], PVA [Chen et al., 2014], ethylene vinyl alcohol (EVOH) [Zhang et al., 2001], and chitosan [Aguirre-Loredo et al., 2016]. According to these studies, the reason was that PLA was relatively hydrophilic and absorbed water molecules. The polymer chain was plasticized to increasing extents with an increase in relative humidity. Thus the chain mobility was enhanced, and the water molecule diffusion became easier. On the other hand, the permeability through PLA nanocomposite was reduced compared to unfilled PLA because of the barrier effect created by the dispersed Cloisite 30B particles in the PLA matrix. Again, the percent reduction in moisture permeability upon clay addition is independent of the concentration driving force. The results are shown in Table 5.6. The water vapor transmission rates of these samples can be found in Appendix 4.
Figure 5.22: Effect of relative humidity on water vapor transport through PLA and PLA nanocomposites.

Table 5.6: Percent reduction in water vapor permeability with the presence of clay at different relative humidity difference.

<table>
<thead>
<tr>
<th>Relative humidity (%)</th>
<th>Percent reduction in permeability (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>51</td>
</tr>
<tr>
<td>75</td>
<td>49</td>
</tr>
<tr>
<td>100</td>
<td>49</td>
</tr>
</tbody>
</table>

5.7 Modeling of Diffusivity through PLA Nanocomposites

Since the results in Section 5.4.2 showed superior permeability values, the data were used to investigate the validity of the models described in Chapter 3 on predicting diffusivity through PLA containing Cloisite 30B.

To obtain diffusivity, the time-lag method can be used. However, drawing a straight line on the plot of permeation data is subjective. This results in errors in determining diffusivity. In
Section 5.4.2, the solubility was independently measured, which gave another way of getting diffusivity. By looking at Figure 5.19, one can see that the moisture solubility in the nanocomposite increased linearly as the loading of Cloisite 30B increased. It was because there was more surface areas of Cloisite 30B available for water sorption. When the water molecules were bonded on the clay surface, it was immobilized and became part of the clay. Thus, for PLA containing Cloisite 30B, the solubility in the main PLA matrix could be assumed as the same as the one of PLA without clay added. If we assume that there was a unit volume of PLA nanocomposite, the moisture immobilized on the Cloisite 30B surface could be calculated by the following equation:

\[ c_{\text{clay}} = c_N - c_{\text{PLA}}(1 - \phi) \]  \hspace{1cm} (5.2)

where \( c_{\text{clay}} \) is the moisture contained on the clay surface, \( c_N \) is the equilibrium water vapor concentration per unit volume of the PLA nanocomposite, \( c_{\text{PLA}} \) is the equilibrium water vapor concentration per unit volume of unfilled PLA, and \( \phi \) is the volume fraction of Cloisite 30B.

Using Eq. (5.2), the mass of water absorbed on the clay surface per unit volume of the nanocomposite as a function of clay volume percent was plotted in Figure 5.23. As the loading of nanoclay increased, the clay surface increased and so did the moisture content absorbed on the surface. It was because there was more surface available for bonding with the water vapor molecules. There was a linear relationship between the moisture absorbed by the clay and the amount of clay added except at 5.3 vol% of Cloisite 30B. At this concentration, there was some filler agglomeration and the lowered surface area results in less than expected absorption of moisture. This was confirmed by the TEM images Figure 5.17.
The diffusivity can be obtained by dividing permeability by solubility. Based on the above discussions, it could be concluded that the percent reduction in diffusivity was the same as the percent reduction in permeability since the solubility of the moisture in the polymer was the same for all PLA nanocomposites. Having established this, one can examine theoretical predictions. The barrier aspect ratio was obtained by analyzing TEM images Figures 5.17 and 5.24 using ImageJ software.

Figure 5.25 shows how to obtain the barrier aspect ratio and the platelet gap aspect ratio. For Nielsen’s model shown in Figure 3.1, $h/t$ was 29.6. On the other hand, for Cussler’s model shown in Figure 3.2, $h'/t$ was 32.8.
Figure 5.24: TEM images of (a)-(b) 0.5 vol% Cloisite 30B; (c)-(d) 1.5 vol% Cloisite 30B;
(e)-(f) 2.6 vol% Cloisite 30B; (g)-(h) 5.3 vol% Cloisite 30B.
Figure 5.25: Demonstration of determining barrier aspect ratio.

With the aspect ratios obtained above, the predictions from Nielsen’s model Eq. (3.13) and Cussler’s model Eq. (3.24) were compared with the experimental data. Figure 5.26 shows the comparisons of two theoretical models and the experimental results. The models underestimated the value of $D_0/D$ compared to the experimental data. First, as stated above, Nielsen’s model did not consider water vapor concentration gradient in the horizontal direction when molecules went around the nanoplatelets [Nielsen, 1967]. Second, both models assumed periodically arranged nanoplatelets and did not take into account geometrical complexities [Nielsen, 1967; Cussler et al., 1988]. In a real system of polymer nanocomposite, the particles are randomly dispersed in the polymer matrix. The horizontal concentration gradient and geometrical complexities lead to more complicated diffusion pathways and lowered gas diffusivity. Ignoring these factors possibly resulted in the overestimation of the diffusivity through the nanocomposite.
As discussed above, the existing theoretical models could not describe the experimental data, and a new model was proposed. The new model built on Nielsen’s model [Nielsen, 1967], and the details can be found in Section 3.3. The new model took into account both the change in the flux and the area of mass transfer after the nanoplatelets were incorporated into the polymer matrix. Figure 5.27 shows the comparison of the predictions from Eqs. (3.13), (3.24), (3.31) and the experimental data. Since more factors were involved, the estimation from the new model fitted the data far better than the existing theoretical models did.
Figure 5.27: Comparison of the proposed model and two existing models with experimental data of diffusivity through PLA nanocomposites.

5.8 Effect of Plasticizer on Properties of PLA Containing Cloisite 30B

5.8.1 Effect of Different Plasticizers on Water Vapor Permeability through plasticized PLA Containing Cloisite 30B

In the literature review, it was shown that the addition of plasticizer could enhance the dispersion state of nanoclay in the polymer matrix and thus improve the gas barrier properties of the polymer. However, one should be cautious while selecting the plasticizer for food packaging polymer. The plasticizer must be in the food-contact approval category. In this study, acetyl butyl citrate (ATBC), glycerol and palm oil were used as plasticizers. They were either food-contact approval or approved food additive. Also note that the presence of the plasticizer can increase the permeability through the polymer.
In this study, 5 wt% of Cloisite 30B and 5 wt% of various plasticizers were incorporated into PLA at 200°C and 80 rpm for 5 mins. In addition, the same amount of plasticizer only was mixed with PLA under the same conditions as reference. The water vapor permeability values through plasticized PLA and plasticized PLA nanocomposites are summarized in Table 5.7. Among the three different plasticizers tested, the use of ATBC showed the largest reduction in permeability in the presence of clay. This was because ATBC was the most compatible plasticizer with PLA and Cloisite 30B. Thus the dispersion state of Cloisite 30B was the best in ATBC-plasticized PLA and the permeability through this nanocomposite was the lowest. In addition, the sample with both glycerol and Cloisite 30B was so brittle that it broke into pieces before testing. It was because the addition of glycerol did not improve the mechanical properties of PLA [Martin and Avérous, 2001]. The incorporation of Cloisite 30B into the glycerol-plasticized PLA deteroriated the mechanical properties even more. Therefore, the compatibility of plasticizer with the polymer and the nanoclay played an important role in the final properties of the nanocomposites [Tang et al., 2008; Courgneau et al., 2011]. Tang et al. (2008) found that different plasticizers displayed different water vapor permeabilites even with the same amount of addition. It was because different plasticizers had different levels of interactions with the polymer and the nanoclay. Stronger interactions led to better properties of the nanocomposites. Couragneau et al. (2011) reported that ATBC had a better miscibility with PLA than polyethylene glycol did. This led to improvement in mechanical properties such as ductility and gas barrier properties for ATBC-plasticized PLA. In this study, ATBC had the best miscibility with PLA, and it showed the largest reduction in water vapor permeability compared to the reference. Therefore, ATBC was chosen for further investigation.
Table 5.7 Water vapor permeability through plasticized PLA and plasticized PLA nanocomposites ($\times 10^{14}$ kg/Pa/m/s).

<table>
<thead>
<tr>
<th></th>
<th>Without Cloisite 30B</th>
<th>With Cloisite 30B</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATBC</td>
<td>1.57±0.06</td>
<td>0.99±0.08</td>
</tr>
<tr>
<td>Glycerol</td>
<td>1.63±0.06</td>
<td>-</td>
</tr>
<tr>
<td>Palm oil</td>
<td>1.61±0.05</td>
<td>1.18±0.06</td>
</tr>
</tbody>
</table>

5.8.2 Effect of Mixing Method on Water Vapor Permeability through ATBC-plasticized PLA Containing Cloisite 30B

The effect of ATBC as plasticizer on the water vapor barrier properties through PLA containing Cloisite 30B was studied. Various mixing procedures were employed to obtain the best possible dispersion level of Cloisite 30B in PLA. All the samples were mixed at 200°C and 80 rpm. Three different methods were used:

M1: PLA, 5 wt% of ATBC and 5 wt% of Cloisite 30B were mixed together for 5 minutes;

M2: PLA was added to the mixer. 5 wt% of ATBC was added after 1 min and 5 wt% of Cloisite 30B after another min. The total mixing time was 5 minutes;

M3: PLA and 5 wt% of Cloisite 30B were added to the mixer. Then 5 wt% of ATBC was added after 2 min. The total mixing time was 5 minutes.

For all the above methods, samples without Cloisite 30B were processed under the same conditions for comparison.

Figure 5.28 shows the water vapor permeability through PLA nanocomposites processed with these methods. The reduction in permeability was in this order: No ATBC-M1 (49%) > M3 (42%) > M2 (38%) > 5 wt% ATBC-M1 (37%). This meant that the mixing sequence affected the final properties of the nanocomposites. Similar behavior was reported by Pandey and Singh (2005) and Scatto et al. (2013). According to their studies, there were two reasons that long
contact time between ATBC and PLA/Cloisite 30B would have negative impact on the properties of the nanocomposites. According to these authors, ATBC bonded with PLA chains and increased the chain mobility, and the polymer chains could not penetrate through the galleries of Cloisite 30B to force the stacks of nanoplatelets apart, resulting in the formation of intercalated structures. Second, ATBC competed with Cloisite 30B to bond with PLA. Therefore, there were less interactions between PLA and Cloisite 30B. This confirmed the results in our study. M3 had the least contact time for ATBC with PLA and Cloisite 30B. Thus this method showed the largest reduction in water vapor permeability compared to the other methods. However, the addition of plasticizer did not have a positive impact on the dispersion state of Cloisite 30B in PLA matrix. The dispersion was well accomplished without the use of plasticizer.

Figure 5.28: Water vapor permeability through ATBC-plastizied PLA-Cloisite 30B nanocomposites (×10^{14} \, \text{kg}/\text{Pa}/\text{m}/\text{s}).

Figure 5.29 shows the TEM images of non-plasticized PLA nanocomposite processed by M1 and plasticized PLA nanocomposite processed by M3. The images show that there was no significant difference in dispersion level after the addition of ATBC. Both samples exhibited
mostly intercalated and exfoliated structures. There were also minor agglomerations in the polymer matrix. Since the dispersion states of Cloisite 30B were similar between the unplasticized and plasticized nanocomposites, the reduction in permeability did not increase with the addition of plasticizer.

Figure 5.29: TEM images of PLA containing 5 wt% Cloisite 30B: (a) without ATBC-M1; (b) with 5 wt% ATBC-M3.

5.8.3 Effect of ATBC Concentration on Thermal Properties of ATBC-plasticized PLA Containing Cloisite 30B

In the previous section, M3 showed the largest reduction in permeability, so the effect of concentration of ATBC on the dispersion of Cloisite 30B in PLA was studied using M3. Figure 5.30 shows the first heating scan of ATBC-plasticized PLA films and PLA films containing 5 wt% Cloisite 30B using M3. The first transition was the glass transition. The step change after the glass transition was the polymer relaxation. The first exothermic peak in the region
represented the cold crystallization temperature. The last endothermic peaks were the melting peaks of the sample.

Figure 5.30: DSC 1st heating curve of ATBC-plasticized PLA and PLA containing 5 wt% Cloisite 30B.

Tables 5.8 and 5.9 shows the data for 1st heating scan and 2nd heating scan of PLA plasticized by ATBC. The sample designation is as follows: (a): PLA-M1; (b) PLA-2.5%ATBC-M3; (c): PLA-5%ATBC-M3; (d): PLA-5%Cloisite 30B-5%ATBC; (e): PLA-15%ATBC-M3.

The glass transition temperature, the cold crystallization temperature and the melting temperature decreased as the concentration of ATBC increased. It was because the addition of ATBC increased the free volume and polymer chain mobility [McHugh and Krochta, 1994; Coltelli et al., 2008; Courgneau et al., 2011]. The cold crystallization enthalpy and the melting enthalpy also decreased as the concentration of ATBC increased. It was because the polymer
content decreased. Furthermore, the addition of 15 wt% of ATBC made the crystals more uniform, so there was only one melting peak for that particular sample. On the other hand, the incorporation of Cloisite 30B had a minor effect on the thermal properties. Since the samples had similar cold crystallization enthalpy and melting enthalpy, they were considered as amorphous.

Table 5.8: Thermal properties of 1st heating scan of PLA nanocomposite films plasticized by ATBC.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T_g (°C)</th>
<th>T_cc (°C)</th>
<th>H_cc (J/g)</th>
<th>T_m1 (°C)</th>
<th>T_m2 (°C)</th>
<th>H_m (J/g)</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>59.6±0.5</td>
<td>110.2±0.1</td>
<td>27.8±0.5</td>
<td>147.4±0.2</td>
<td>154.7±0.1</td>
<td>28.4±0.7</td>
<td>~0%</td>
</tr>
<tr>
<td>(b)</td>
<td>56.1±0.8</td>
<td>108.3±0.1</td>
<td>26.8±0.5</td>
<td>146.2±0.2</td>
<td>153.9±0.1</td>
<td>27.1±0.6</td>
<td>~0%</td>
</tr>
<tr>
<td>(c)</td>
<td>52.1±0.9</td>
<td>102.8±0.2</td>
<td>26.2±0.7</td>
<td>143.4±0.4</td>
<td>152.7±0.1</td>
<td>25.6±0.7</td>
<td>~0%</td>
</tr>
<tr>
<td>(d)</td>
<td>50.9±0.1</td>
<td>103.8±0.7</td>
<td>25±1</td>
<td>143.5±0.2</td>
<td>152.3±0.1</td>
<td>25.4±0.7</td>
<td>~0%</td>
</tr>
<tr>
<td>(e)</td>
<td>34±1</td>
<td>86±2</td>
<td>22±2</td>
<td>-</td>
<td>148.7±0.5</td>
<td>23±2</td>
<td>~0%</td>
</tr>
</tbody>
</table>

Table 5.9: Thermal properties of 2nd heating scan of PLA nanocomposite films plasticized by ATBC.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T_g (°C)</th>
<th>T_cc (°C)</th>
<th>H_cc (J/g)</th>
<th>T_m1 (°C)</th>
<th>T_m2 (°C)</th>
<th>H_m (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>60.8±0.1</td>
<td>111.5±0.1</td>
<td>28.2±0.8</td>
<td>148.0±0.1</td>
<td>155.0±0.2</td>
<td>28.5±0.5</td>
</tr>
<tr>
<td>(b)</td>
<td>56.5±0.5</td>
<td>109.7±0.1</td>
<td>27.2±0.3</td>
<td>146.7±0.1</td>
<td>154.0±0.1</td>
<td>27.5±0.7</td>
</tr>
<tr>
<td>(c)</td>
<td>52.1±0.9</td>
<td>104.9±0.3</td>
<td>26.3±0.9</td>
<td>143.9±0.4</td>
<td>153.0±0.1</td>
<td>26.3±0.5</td>
</tr>
<tr>
<td>(d)</td>
<td>51.6±0.8</td>
<td>106.5±0.9</td>
<td>26.8±0.7</td>
<td>144.8±0.9</td>
<td>152.9±0.2</td>
<td>26.1±0.5</td>
</tr>
<tr>
<td>(e)</td>
<td>35±1</td>
<td>89±1</td>
<td>22±2</td>
<td>-</td>
<td>149.3±0.3</td>
<td>23±2</td>
</tr>
</tbody>
</table>

5.8.4 Effect of ATBC Concentration on Water Vapor Permeability through ATBC-plasticized PLA Containing Cloisite 30B

Figure 5.31 shows the effect of ATBC concentration on water vapor permeability through ATBC-plasticized PLA and PLA containing 5 wt% Cloisite 30B. The samples were processed using mixing method M3. When the concentration of ATBC increased from 2.5 to 5 wt%, there was a slight increase of percent reduction in water vapor permeability through plasticized PLA.
containing 5 wt% Cloisite 30B as compared to the reference in the absence of nanoclay. A further increase in ATBC concentration led to a decrease in the percent reduction in permeability. This implied that the dispersion state of Cloisite 30B into PLA was the optimum under the addition of 5 wt% ATBC. It is likely that a certain amount of plasticizer could promote the interactions between the polymer chains and the nanoclay surfaces by facilitating the penetration of polymer and plasticizer into the nanoclay galleries [Chiou et al., 2007; Tang et al., 2008]. Therefore, intercalated and exfoliated structures were obtained. However, excess plasticizer competed with the nanoclay on bonding with polymers and resulted in less interactions between the polymer and the nanoclay.

Figure 5.31: Effect of ATBC concentration on water vapor permeability through ATBC-plasticized PLA and PLA containing 5 wt% Cloisite 30B ($\times 10^{14}$ kg/Pa/m/s).

In addition, the incorporation of more than 5 wt% of ATBC led to a significant increase in permeability because the free volume increased and facilitated the movement of diffusing molecules. Similar behavior was also reported on poly(amide-b-ethylene oxide) copolymer plasticized by polyethylene glycol [Yave et al., 2009]. When the concentration of polyethylene glycol was below 20 wt%, the carbon dioxide permeability through the sample could be
considered as constant. However, the permeability significantly increased when the concentration exceeded 20 wt% because the plasticizer increased the polymer chain mobility and the free volume. Thus it led to an increase in both gas diffusivity and gas solubility. The water transmission rates of these samples can be found in Appendix 5.

Since the percent reduction in moisture permeability did not increase upon the addition of plasticizer, we conclude that dispersion of clay in the PLA matrix was quite good.

5.8.5 Effect of ATBC on Mechanical Properties ATBC-plasticized PLA Containing Cloisite 30B

Table 5.10 shows the mechanical properties of unplasticized and ATBC-plasticized PLA samples.

Table 5.10: Mechanical properties of unplasticized and ATBC-plasticized PLA samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Yield strength (GPa)</th>
<th>Elongation at yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA</td>
<td>4±1</td>
<td>0.9±0.1</td>
</tr>
<tr>
<td>PLA-5 wt% Cloisite 30B</td>
<td>0.80±0.07</td>
<td>0.79±0.08</td>
</tr>
<tr>
<td>PLA- 5 wt% ATBC</td>
<td>2.0±0.8</td>
<td>1.3±0.1</td>
</tr>
<tr>
<td>PLA-5 wt% ATBC- 5 wt% Cloisite 30B</td>
<td>0.72±0.09</td>
<td>1.0±0.1</td>
</tr>
</tbody>
</table>

As one can observe, yield strength and elongation at yield decreased when Cloisite 30B was added compared to its unfilled counterpart. It was because the clay-clay interaction led to weak adhesion between polymer chains and clay particles. This poor interaction resulted in local stress concentration and reduced mechanical properties. This kind of behavior was reported in other nanocomposite systems [Rhim et al., 2009; Singh et al., 2010; Fukushima et al., 2013]. On the other hand, as expected, the yield strength decreased with the addition of plasticizer ATBC [Courgneau et al., 2011; Wypych, 2012; Lim and Hoag, 2013]. In addition, the plasticization of the samples led to the increase in elongation at yield. It was because the fluidity of the sample
increased when ATBC was added. Similar results were reported by others [Courgneau et al., 2011; Lim and Hoag, 2013; Scatto et al., 2013]. These findings suggested that the employment of ATBC as plasticizer can reduce the brittleness of PLA nanocomposite.

5.9 Effect of Different Thermal Treatments on Properties of PLA

5.9.1 Effect of Different Thermal Treatments on Thermal Properties of PLA

The effect of different thermal treatments on PLA crystallinity was studied. PLA was subjected to different thermal treatments. The thermal treatments are summarized in Table 5.11.

Table 5.11: PLA samples under different thermal treatments.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Thermal Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>Unannealed</td>
</tr>
<tr>
<td>(b)</td>
<td>Annealed at 80°C for 40 hours</td>
</tr>
<tr>
<td>(c)</td>
<td>Annealed at 115°C for 40 hours</td>
</tr>
<tr>
<td>(d)</td>
<td>Annealed at 135°C for 40 hours</td>
</tr>
<tr>
<td>(e)</td>
<td>Slow cool down from 220°C to room temperature at a pressure of 10 tons</td>
</tr>
</tbody>
</table>

Figure 5.32 shows the first heating scan of unannealed and annealed PLA. The transition at around 60°C represents the glass transition. The peak following the step change is the polymer relaxation. The exothermic peak for the annealed sample at around 110°C (sample (a) and (e)) and 140°C (sample (b)) is due to cold crystallization. The endothermics peak at around 153°C is the melting peak of the sample.

Table 5.12 shows results of the 1st heating scan of PLA with different heat treatments. The glass transition temperatures were similar for both unannealed PLA and PLA samples with various heat treatments. However, compared to the unannealed sample which had a cold crystallization temperature of about 110°C, the samples with heat treatments had higher cold crystallization temperatures at 138°C and 115°C for sample (b) and sample (e) respectively.
Sample (c) and (d) did not exhibit any cold crystallization temperatures. Of the samples which had cold crystallization peaks, sample (b) and (e) had smaller cold crystallization enthalpy compared to the unannealed sample (a). The cold crystallization behavior of the samples with heat treatment was due to the fact that the heat treatment enhanced the crystallization process and led to higher crystallinity compared to the unannealed sample [Srithep et al., 2013]. Sample (a) and (e) had two melting peaks corresponding to two types of crystals with different size and perfection. The samples (b)-(d) showed only one melting peak except for sample (e) because they formed just one type of crystals after the heat treatment. On the other hand, among samples (b)-(d), the crystallinity increased as the annealing temperature increased. It was because the high temperature facilitated the movement of the polymer chains and the formation of crystals.

Figure 5.32: DSC 1st heating curve of unannealed and annealed PLA.
This behavior was also reported by the others on PLA [Tsuji and Ikada, 1995; Srithep et al., 2013].

Table 5.12: Thermal properties of 1st heating scan of PLA with different heat treatments.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( T_g ) (°C)</th>
<th>( T_{cc} ) (°C)</th>
<th>( H_{cc} ) (J/g)</th>
<th>( T_{m1} ) (°C)</th>
<th>( T_{m2} ) (°C)</th>
<th>( H_m ) (J/g)</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>59.6±0.5</td>
<td>110.2±0.1</td>
<td>27.8±0.5</td>
<td>147.4±0.2</td>
<td>154.7±0.1</td>
<td>28.4±0.7</td>
<td>~0%</td>
</tr>
<tr>
<td>(b)</td>
<td>59.4±0.3</td>
<td>138.4±0.9</td>
<td>1.0±0.1</td>
<td>-</td>
<td>153.1±0.1</td>
<td>23.9±0.4</td>
<td>24.4±0.5</td>
</tr>
<tr>
<td>(c)</td>
<td>58.7±0.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>154.7±0.1</td>
<td>37.8±0.9</td>
<td>40±1</td>
</tr>
<tr>
<td>(d)</td>
<td>58.3±0.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>154±2</td>
<td>44±1</td>
<td>47±2</td>
</tr>
<tr>
<td>(e)</td>
<td>59.5±0.2</td>
<td>114.8±0.5</td>
<td>3.8±0.4</td>
<td>148.2±0.3</td>
<td>154.1±0.1</td>
<td>30.7±0.4</td>
<td>28.7±0.3</td>
</tr>
</tbody>
</table>

Table 5.13 shows results of the 2nd heating scan of PLA with different heat treatments. The glass transition temperature, cold crystallization temperature and melting temperatures were similar for both unannealed PLA and PLA samples with various heat treatments. There were two melting peaks because there were two types of crystals of different sizes and perfections. On the other hand, the melting enthalpy was similar to the cold crystallization enthalpy. This implied that the samples were amorphous.

Table 5.13: Thermal properties of 2nd heating scan of PLA with different heat treatments.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( T_g ) (°C)</th>
<th>( T_{cc} ) (°C)</th>
<th>( H_{cc} ) (J/g)</th>
<th>( T_{m1} ) (°C)</th>
<th>( T_{m2} ) (°C)</th>
<th>( H_m ) (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>60.8±0.1</td>
<td>111.5±0.1</td>
<td>28.2±0.8</td>
<td>148.0±0.1</td>
<td>155.0±0.2</td>
<td>28.5±0.5</td>
</tr>
<tr>
<td>(b)</td>
<td>59.3±0.1</td>
<td>110.6±0.8</td>
<td>29.6±0.4</td>
<td>147.9±0.1</td>
<td>155.2±0.1</td>
<td>28.6±0.8</td>
</tr>
<tr>
<td>(c)</td>
<td>58.2±0.9</td>
<td>109.2±0.1</td>
<td>33.2±0.1</td>
<td>147.8±0.1</td>
<td>156.0±0.1</td>
<td>32.3±0.7</td>
</tr>
<tr>
<td>(d)</td>
<td>58.3±0.4</td>
<td>111.5±0.2</td>
<td>36±1</td>
<td>148.6±0.2</td>
<td>156.4±0.2</td>
<td>35±1</td>
</tr>
<tr>
<td>(e)</td>
<td>59.6±0.3</td>
<td>111.3±0.3</td>
<td>29.0±0.5</td>
<td>147.9±0.4</td>
<td>155.1±0.1</td>
<td>28.6±0.3</td>
</tr>
</tbody>
</table>

5.9.2 Effect of Different Thermal Treatments on Crystal Structure of PLA

Figure 5.33 shows the WAXS profile of PLA with different thermal treatments.
For unannealed PLA, no peaks could be seen since there were no crystal structures in the sample. This matched the result from the DSC data. For PLA samples (c) and (d), for which the annealing temperatures were above 115°C, there were two major peaks at $2\theta = 16.8^\circ$ and $19.1^\circ$, which corresponded to the more ordered $\alpha$ crystalline form and the less ordered $\alpha'$ crystalline form of PLA [Kawai et al., 2007; Bouapao et al., 2009; Tsuji and Tsuruno, 2010]. For the other two thermal treatments (b) and (e), the $2\theta$ shifted to the left. It was because the crystal structures of treatments (b) and (e) were different from the $\alpha$ form of (c) and (d) [Kawai et al., 2007]. In addition, the very small peak at $2\theta = 15.1^\circ$ was specific to the $\alpha$ form [Kawai et al., 2007; Bouapao et al., 2009; Tsuji and Tsuruno, 2010]. The crystal structure of those samples was a combination of $\alpha$ form and $\alpha'$ form. This explained why the melting temperature of those samples in the 1$\text{st}$ heating scan was lower than the second melting temperature in the 2$\text{nd}$ heating scan. Although the DSC shows one melting peak in the 1$\text{st}$ heating scan, not all the crystals were in the more ordered $\alpha$ form. Thus the melting temperature of those samples was lower than that of $\alpha$ form. In addition, as expected, the peak intensity increased as the crystallinity increased.
5.9.3 Effect of Different Thermal Treatments on Water Vapor Permeability through PLA

Figure 5.34 shows the effect of different thermal treatments on water vapor permeability through PLA. As shown above, all of the thermal treatments increased the crystallinity of PLA. The water vapor permeability was reduced as the crystallinity increased. It was because the impermeable crystalline phase replaced some of the permeable amorphous phase in the PLA. The crystals acted as barriers against gas diffusion and forced the water vapor molecules to travel a tortuous path. The crystalline region also had lower water vapor solubility than the amorphous region did. Thus the water vapor permeability decreased as reported in the literature [Shogren, 1997; Siparsky et al., 1997]. On the other hand, compared to the unannealed sample (a), there were reductions of 11%, 45% and 21% in permeability for samples (b), (c) and (e) respectively. It was because of differences in the crystallinity among these samples: amorphous for sample (a), 24% for sample (b), 40% for sample (c) and 29% for sample (e). The increase in crystallinity replaced more permeable amorphous phases and more crystals acted as barrier against gas diffusion. Therefore, it led to a reduction in water vapor permeability. Similar results were reported by others [Duan and Thomas, 2014]. On the other hand, sample (d) showed the highest crystallinity, but the sample was so brittle that it broke into small pieces before testing. The water vapor permeability could not be determined. It was because the elongation at break decreased with the increase in annealing temperature [Tsuji and Ikada, 1995]. Among all the heat treatments, method (c) showed the most promising result and was further investigated.
Figure 5.34: Effect of thermal treatment on water vapor permeability through PLA ($\times 10^{14}$ kg/Pa/m/s).

5.10 Effect of Annealing Time on Properties of PLA

5.10.1 Effect of Annealing Time on Thermal Properties of PLA

Table 5.14 shows results of the 1st heating scan of PLA annealed at 115°C with different amounts of annealing time.

Table 5.14: Thermal properties of 1st heating scan of PLA with different amounts of annealing time.

<table>
<thead>
<tr>
<th>Annealing time (hr)</th>
<th>$T_g$ (°C)</th>
<th>$T_m$ (°C)</th>
<th>$H_m$ (J/g)</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>59.1±0.4</td>
<td>153.1±0.1</td>
<td>26±1</td>
<td>27±1</td>
</tr>
<tr>
<td>4</td>
<td>59.3±0.1</td>
<td>153.4±0.1</td>
<td>33.1±0.8</td>
<td>35.4±0.9</td>
</tr>
<tr>
<td>8</td>
<td>59.1±0.5</td>
<td>154.1±0.1</td>
<td>35.6±0.8</td>
<td>38.1±0.7</td>
</tr>
<tr>
<td>20</td>
<td>59.0±0.5</td>
<td>154.5±0.4</td>
<td>36±1</td>
<td>39±1</td>
</tr>
<tr>
<td>40</td>
<td>58.7±0.6</td>
<td>154.7±0.1</td>
<td>37.8±0.9</td>
<td>40±1</td>
</tr>
<tr>
<td>60</td>
<td>59.1±0.1</td>
<td>155.3±0.2</td>
<td>41.4±0.5</td>
<td>44.2±0.5</td>
</tr>
</tbody>
</table>
The glass transition temperature was similar for all the samples. The melting temperature increased as the annealing time increased. It was because the crystals became more ordered as the annealing time increased [Yeh et al., 1976]. On the other hand, the melting enthalpy and the crystallinity increased as the annealing time increased. Similar behavior was reported by the others on PLA [Tsuji and Ikada, 1995; Srithep et al., 2013].

Table 5.15 shows results of the 2nd heating scan of PLA annealed at 115°C with different annealing time. The glass transition temperature, cold crystallization temperature and melting temperatures were similar for PLA annealed for different amounts of time. There were two melting peaks because there were two types of crystals of different sizes and perfections. On the other hand, the melting enthalpy was similar to the cold crystallization enthalpy. This implied that the samples were amorphous.

Table 5.15: Thermal properties of 2nd heating scan of PLA with different amounts of annealing time.

<table>
<thead>
<tr>
<th>Annealing time (hr)</th>
<th>T_g (°C)</th>
<th>T_cc (°C)</th>
<th>H_cc (J/g)</th>
<th>T_m1 (°C)</th>
<th>T_m2 (°C)</th>
<th>H_m (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>59.9±0.4</td>
<td>111.4±0.1</td>
<td>28.3±0.4</td>
<td>148.0±0.1</td>
<td>155.0±0.1</td>
<td>27.6±0.6</td>
</tr>
<tr>
<td>4</td>
<td>59.4±0.9</td>
<td>111.5±0.1</td>
<td>29±1</td>
<td>148.1±0.2</td>
<td>155.1±0.1</td>
<td>30.6±0.6</td>
</tr>
<tr>
<td>8</td>
<td>59.6±0.5</td>
<td>110.5±0.1</td>
<td>30.9±0.1</td>
<td>148.5±0.2</td>
<td>155.8±0.2</td>
<td>31.4±0.6</td>
</tr>
<tr>
<td>20</td>
<td>59.7±0.4</td>
<td>109.9±0.1</td>
<td>31.1±0.5</td>
<td>147.9±0.2</td>
<td>155.6±0.3</td>
<td>31.8±0.4</td>
</tr>
<tr>
<td>40</td>
<td>58.2±0.9</td>
<td>109.2±0.1</td>
<td>33.2±0.1</td>
<td>147.8±0.1</td>
<td>156.0±0.1</td>
<td>32.3±0.7</td>
</tr>
<tr>
<td>60</td>
<td>58.5±0.1</td>
<td>110.3±0.1</td>
<td>35.0±0.4</td>
<td>148.2±0.3</td>
<td>156.5±0.1</td>
<td>34.4±0.4</td>
</tr>
</tbody>
</table>

5.10.2 Effect of Annealing Time on Crystal Structure of PLA

Figure 5.35 shows the WAXS profile of PLA annealed at 115°C for different amounts of time. For the samples annealed more than 40 hours, there were two major peaks at 2θ = 16.8° and 19.1°, which corresponded to the more ordered α form and the less ordered α’ form of PLA [Kawai et al., 2007; Bouapao et al., 2009; Tsuji and Tsuruno, 2010]. For the samples annealed
less than 40 hours, the $2\theta$ shifted to the left because the crystal structures of the samples annealed for less than 40 hours were different from those annealed for more than 40 hours [Kawai et al., 2007]. In addition, the very small peak at $2\theta = 15.1^\circ$ was specific to the $\alpha$ form [Kawai et al., 2007; Bouapao et al., 2009; Tsuji and Tsuruno, 2010]. The crystal structure of those samples was a combination of $\alpha$ form and $\alpha'$ form. Although the DSC shows one melting peak in the 1$^{\text{st}}$ heating scan, not all the crystals were in the more ordered $\alpha$ form. The diffraction data explained why the melting temperature of those samples in the 1$^{\text{st}}$ heating scan was lower than the second melting temperature in the 2$^{\text{nd}}$ heating scan. In addition, as expected, the peak intensity increased as the crystallinity increased.

![Figure 5.35: WAXS profiles of PLA annealed at 115°C for different amount of time.](image)

### 5.10.3 Effect of Annealing Time on Water Vapor Permeability through PLA

Figure 5.36 shows the effect of annealing time on water vapor permeability through PLA.
Figure 5.36: Effect of annealing time on water vapor permeability through PLA (×10^{14} kg/Pa/m/s).

As the sample was annealed for 4 hours, the crystallinity increased to 35% and the permeability was reduced by 22% compared to the amorphous sample. It was because the impermeable crystals acted as barriers against gas diffusion and forced the diffusing molecules to travel a tortuous path when the crystallinity increased. In addition, the crystalline region had lower water vapor solubility than the amorphous region did. Similar behavior was reported for PLA by the others [Duan and Thomas, 2014]. In addition, when the annealing time increased from 4 to 40 hours, the crystallinity increased merely from 35 to 40% but the permeability through the 40-hour sample was reduced by 30% compared to the 4-hour sample. The result showed that a small change in the crystallinity led to a significant decrease in the permeability. It was because the crystals repacked and realigned to form more stable crystals when held at sufficient long annealing time [Yeh et al., 1976]. This could be proved by the slight increase in melting temperature observed in Table 5.11. On the other hand, when the sample was annealed for 60 hours, the sample showed the highest crystallinity. However, the sample was so brittle that it could not withstand the testing process, and the water vapor permeability could not be...
determined. It was because the elongation at break decreased with the increase in crystallinity [Tsuji and Ikada, 1995]. From the discussion in Sections 5.9 and 5.10, it could be seen that annealing at 115°C for 40 hours led to the lowest water vapor permeability. This experimental condition was applied for further investigation.

5.11 Effect of Cloisite 30B and Crystallinity on Properties of PLA

5.11.1 Effect of Cloisite 30B and Crystallinity on Thermal Properties of PLA

Table 5.16 shows results of the 1st heating scan of PLA containing Cloisite 30B annealed at 115°C for 40 hours.

<table>
<thead>
<tr>
<th>Clay vol%</th>
<th>$T_g$ (°C)</th>
<th>$T_m$ (°C)</th>
<th>$H_m$ (J/g)</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>58.7±0.6</td>
<td>154.7±0.1</td>
<td>37.8±0.9</td>
<td>40±1</td>
</tr>
<tr>
<td>2.6</td>
<td>57.5±0.7</td>
<td>154.7±0.2</td>
<td>40±1</td>
<td>45±1</td>
</tr>
</tbody>
</table>

The glass transition temperature $T_g$ of PLA containing Cloisite 30B decreased as the loading of Cloisite 30B increased. Similar behavior was reported on PLA containing Cloisite 30B [Pluta et al., 2007; Fukushima et al., 2009]. It was because the surfactant of Cloisite 30B (20 wt% in Cloisite 30B) plasticized the polymer. Therefore, the polymer chain mobility was enhanced and the glass transition temperature decreased. Another possible reason was that the degradation reaction occurred in the melt-processing and resulted in the loss of molecular weight of PLA [Gamez-Perez et al., 2011]. Thus, the glass transition temperature of sample containing Cloisite 30B was reduced. The melting temperature was similar for all the samples. Both the melting enthalpy and the crystallinity increased as Cloisite 30B was incorporated into PLA. It was because the effect of nucleating agent Cloisite 30B helped the crystal growth and led to the
increase in crystallinity. In addition, there was only one melting peak because only one type of crystal existed.

Table 5.17 shows results of the 2nd heating scan of PLA containing Cloisite 30B annealed at 115°C for 40 hours. The glass transition temperature, cold crystallization temperature and melting behavior were similar for all the samples. The cold crystallinity and the melting enthalpy decreased as the loading of Cloisite 30B increased because the amount of organic content decreased. There were two melting peaks because there were two types of crystals of different sizes and perfections. On the other hand, the melting enthalpy was similar to the cold crystallization enthalpy. This implied that the samples were amorphous.

Table 5.17: Thermal properties of 2nd heating scan of PLA containing Cloisite 30B annealed at 115°C for 40 hours.

<table>
<thead>
<tr>
<th>Clay vol%</th>
<th>T_g (°C)</th>
<th>T_cc (°C)</th>
<th>H_cc (J/g)</th>
<th>T_m1 (°C)</th>
<th>T_m2 (°C)</th>
<th>H_m (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>58.2±0.9</td>
<td>109.2±0.1</td>
<td>33.2±0.1</td>
<td>147.8±0.1</td>
<td>156.0±0.1</td>
<td>32.3±0.7</td>
</tr>
<tr>
<td>2.6</td>
<td>57.9±0.5</td>
<td>108.0±0.3</td>
<td>32±1</td>
<td>147.5±0.3</td>
<td>155.5±0.1</td>
<td>31±1</td>
</tr>
</tbody>
</table>

5.11.2 Effect of Cloisite 30B and Crystallinity on Water Vapor Permeability through PLA

Based on the study in Section 5.10, annealing at 115°C for 40 hours was found to be the optimized thermal treatment for PLA. Therefore, this processing condition was applied to PLA containing Cloisite 30B. Figure 5.37 shows how the incorporation of Cloisite 30B and crystallinity affect the water vapor permeability through PLA. Compared to the amorphous PLA, PLA with thermal treatment had a crystallinity of 40% and the permeability was reduced by 43%. It was because the crystalline regions led to a tortuous path for the diffusing molecules and lowered the water vapor solubility. The reduction in permeability through semi-crystalline polymer can be described as a function of crystallinity by the Maxwell law [Peterlin, 1975]:
where $P_{SC}$ is the permeability through the semi-crystalline polymer, $P_A$ is the permeability through the amorphous polymer, $X_c$ is the crystallinity. The crystallinity of PLA annealed at 115°C for 40 hours had a crystallinity of 40%. When this value of the crystallinity was introduced in Eq. (5.3), the ratio of $P_{SC}/P_A$ was 0.5 while the experimental data shows a ratio of 0.55. When the experimental error (5%) was taken into account, the experimental result was in good agreement with the theoretical model. On the other hand, the permeability was further reduced when both Cloisite 30B and thermal treatment were applied to PLA. Similar behavior was reported on PLA containing Nanofil 804 by others [Picard et al., 2011]. In their study, the oxygen permeability through PLA containing 3.8 wt% of nanoclay and 46% crystallinity was reduced by 60% compared to neat PLA. In the present study, PLA containing 2.6 vol% of Cloisite 30B with thermal treatment had a reduction of 41% in water vapor permeability compared to the counterpart without thermal treatment. This reduction was caused by the increase in crystallinity. The impermeable crystalline region led to a tortuous path for diffusing water molecules and lowered the water vapor solubility. Thus the permeability decreased. In addition, the water vapor permeability through PLA containing 2.6 vol% of Cloisite 30B with thermal treatment was 0.53±0.05 ×10^{-14} \text{kg/(m×Pa×s)}. The permeability through this sample was reduced by 66% compared to neat PLA. The result was similar to that through PLA containing 5.3 vol% of Cloisite 30B. This implied that the improvement of gas barrier properties could be accomplished by the mere addition of nanoclay or the incorporation of both nanoclay and crystallinity [Tan and Thomas, 2017]. The water transmission rates of the annealed samples can be found in Appendix 6.
Figure 5.37: Effect of Cloisite 30B and crystallinity on water vapor permeability through PLA ($\times 10^{14}$ kg/Pa/m/s).

5.12 Effect of ATBC and Crystallinity on Properties of PLA

5.12.1 Effect of ATBC and Crystallinity on Thermal Properties of PLA

Based on the study in Section 5.8, ATBC was the most compatible plasticizer for PLA. Table 5.18 shows results of the 1st heating scan of neat PLA and PLA with 5 wt% of ATBC processed according to M3 in Section 5.8.2 and annealed at 115°C for 40 hours. The glass transition temperature and the melting temperature were reduced after the addition of ATBC because the plasticizer increased the free volume and the polymer chain mobility. Reductions in glass transition temperature and melting temperature were also observed on PLA containing polyethylene glycol as plasticizer [Li et al., 2010]. There was only one melting peak because there was only single type of crystal existing. In addition, the crystallinity slightly increased with the use of plasticizer.
Table 5.18: Thermal properties of 1st heating scan of PLA and PLA containing 5 wt% ATBC annealed at 115°C for 40 hours.

<table>
<thead>
<tr>
<th>ATBC wt%</th>
<th>T_g (°C)</th>
<th>T_m (°C)</th>
<th>H_m (J/g)</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>58.7±0.6</td>
<td>154.7±0.1</td>
<td>37.8±0.9</td>
<td>40±1</td>
</tr>
<tr>
<td>5</td>
<td>53.2±0.3</td>
<td>153.5±0.1</td>
<td>37.5±0.1</td>
<td>42.2±0.1</td>
</tr>
</tbody>
</table>

Table 5.19 shows results of the 2nd heating scan of neat PLA and PLA with 5 wt% of ATBC. The glass transition temperature, cold crystallization temperature and melting temperatures increased after the incorporation of ATBC. It was because the plasticizer increased the free volume of the polymer and enhanced the polymer chain mobility. The cold crystallization enthalpy and the melting enthalpies decreased when ATBC was added because there was less polymer content in the samples. On the other hand, there were two melting peaks because there were two types of crystals of different size and perfection. In addition, the samples were amorphous since the cold crystallization enthalpy was similar to the melting enthalpy.

Table 5.19: Thermal properties of 2nd heating scan of PLA and PLA containing 5 wt% ATBC annealed at 115°C for 40 hours.

<table>
<thead>
<tr>
<th>ATBC wt%</th>
<th>T_g (°C)</th>
<th>T_cc (°C)</th>
<th>H_cc (J/g)</th>
<th>T_m1 (°C)</th>
<th>T_m2 (°C)</th>
<th>H_m (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>58.2±0.9</td>
<td>109.2±0.1</td>
<td>33.2±0.1</td>
<td>147.5±0.1</td>
<td>156.0±0.1</td>
<td>32.3±0.7</td>
</tr>
<tr>
<td>5</td>
<td>53.4±0.9</td>
<td>104.5±0.5</td>
<td>31.1±0.2</td>
<td>144.8±0.7</td>
<td>154.5±0.1</td>
<td>30±1</td>
</tr>
</tbody>
</table>

5.12.2 Effect of ATBC and Crystallinity on Water Vapor Permeability through PLA

In this study, samples containing ATBC were processed according to M3 in Section 5.8.2 and annealed at 115°C for 40 hours to increase the crystallinity. Figure 5.38 shows the synergistic effect of ATBC and crystallinity on water vapor permeability through PLA. With thermal treatment, the crystallinity increased and the permeability decreased. It was because the
impermeable crystals acted as barriers and forced the diffusing molecules to travel a longer path. Moreover, the addition of 5 wt% of ATBC did not have a significant change in water vapor permeability. Similar behavior was reported by others when adding a low concentration of plasticizer in that this did not lead to a significant increase in gas permeability [Yave et al., 2009]. When PLA containing 5 wt% of ATBC was annealed at 115°C for 40 hours, the crystallinity increased to 42% and the permeability was reduced by 48% compared to neat PLA. However, the use of plasticizer could enhance the processibility of the polymer and these results are shown in the next section.

Figure 5.38: Effect of ATBC and crystallinity on water vapor permeability through PLA ($\times 10^{14}$ kg/Pa/m/s).

5.13 Effect of Cloisite 30B, ATBC and Crystallinity on Properties of PLA

5.13.1 Effect of Cloisite 30B, ATBC and Crystallinity on Thermal Properties of PLA

Based on the studies above, Cloisite 30B and ATBC were the most compatible nanofiller and plasticizer for PLA respectively. PLA containing ATBC and Cloisite 30B was processed
according to M3 in Section 5.8.2. In this study, samples containing Cloisite 30B and ATBC were annealed at 115°C for 40 hours to increase the crystallinity. Table 5.20 shows results of the 1st heating scan of PLA containing 5 wt% of ATBC and Cloisite 30B with thermal treatment. The glass transition temperature decreased as the loading of Cloisite 30B increased. This kind of behavior was also reported by others [Pluta et al., 2007; Fukushima et al., 2009]. It was because the surfactant of Cloisite 30B (20 wt% in Cloisite 30B) plasticized PLA and enhanced the polymer chain mobility. Thus, the glass transition temperature was reduced. Another possible reason was due to the loss of molecular weight of PLA during melt-processing [Gamez-Perez et al., 2011]. Therefore, the glass transition temperature of sample containing Cloisite 30B was reduced. The melting temperature was similar because all the samples possessed crystals of similar size and perfection. There was only one melting peak because there was only a single type of crystal. On the other hand, the crystallinity increased when Cloisite 30B was incorporated because of the nucleating effect.

Table 5.20: Thermal properties of 1st heating scan of PLA and PLA containing 5 wt% ATBC with Cloisite 30B annealed at 115°C for 40 hours.

<table>
<thead>
<tr>
<th>Clay vol%</th>
<th>T_g (°C)</th>
<th>T_m (°C)</th>
<th>H_m (J/g)</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>53.2±0.3</td>
<td>153.5±0.1</td>
<td>37.5±0.1</td>
<td>42.2±0.1</td>
</tr>
<tr>
<td>2.6</td>
<td>52±1</td>
<td>153.5±0.2</td>
<td>38.5±0.2</td>
<td>45.7±0.2</td>
</tr>
<tr>
<td>5.3</td>
<td>50.3±0.2</td>
<td>153.2±0.1</td>
<td>37±1</td>
<td>46±1</td>
</tr>
</tbody>
</table>

Table 5.21 shows results of the 2nd heating scan of PLA containing 5 wt% of ATBC and Cloisite 30B with thermal treatment. The glass transition temperature decreased as the loading of Cloisite 30B increased. It was because of the plasticization effect by the surfactant of Cloisite 30B [Pluta et al., 2007; Fukushima et al., 2009] and the loss of molecular weight during melt-processing [Gamez-Perez et al., 2011]. Both effects resulted in the enhancement of polymer
chain mobility and the reduction in glass transition temperature. The cold crystallization temperature decreased as the loading of Cloisite 30B increased because of the nucleating effect by the Cloisite 30B nanoplatelets. The melting temperatures were similar since the samples possessed crystal structures of similar sizes and perfection states. There were two melting peaks because there were two different types of crystals. The cold crystallization enthalpy and the melting enthalpy decreased as the loading of nanoclay increased because the polymer content decreased. On the other hand, the polymer was amorphous since the cold crystallization enthalpy and the melting enthalpy were similar.

Table 5.21: Thermal properties of 2nd heating scan of PLA and PLA containing 5 wt% ATBC with Cloisite 30B annealed at 115°C for 40 hours.

<table>
<thead>
<tr>
<th>Clay vol%</th>
<th>$T_g$ (°C)</th>
<th>$T_{cc}$ (°C)</th>
<th>$H_{cc}$ (J/g)</th>
<th>$T_{m1}$ (°C)</th>
<th>$T_{m2}$ (°C)</th>
<th>$H_m$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>53.4±0.9</td>
<td>104.5±0.5</td>
<td>31.1±0.2</td>
<td>144.8±0.7</td>
<td>154.5±0.1</td>
<td>30±1</td>
</tr>
<tr>
<td>2.6</td>
<td>52±1</td>
<td>102.5±0.8</td>
<td>30.3±0.1</td>
<td>143.9±0.8</td>
<td>153.9±0.2</td>
<td>31.5±0.1</td>
</tr>
<tr>
<td>5.3</td>
<td>49.9±0.2</td>
<td>100.4±0.4</td>
<td>29.3±0.6</td>
<td>143.8±0.6</td>
<td>153.7±0.1</td>
<td>29.1±0.7</td>
</tr>
</tbody>
</table>

5.13.2 Effect of Cloisite 30B, ATBC and Crystallinity on Water Vapor Permeability through PLA

The water vapor permeabilities through the samples described in Section 5.13.1 were investigated. Figure 5.39 shows the combined effects of Cloisite 30B, ATBC and crystallinity on water vapor permeability through PLA. As expected, the permeability decreased when Cloisite 30B was incorporated into PLA because the impermeable nanoplatelets acted as barrier against gas diffusion and forced the water vapor molecules to travel a longer path. In addition, the permeability was further reduced when the crystallinity increased via thermal treatment. It was
because the impermeable crystals led to a tortuous path for the diffusing molecules and lower water vapor solubility.

![Figure 5.39: Effect of Cloisite 30B, ATBC and crystallinity on water vapor permeability through PLA (×10^{14} \text{ kg/Pa/m/s}).](image)

As discussed above in Section 5.12.2, the addition of 5 wt% of ATBC did not lead to a significant increase in permeability. PLA and PLA containing 2.6 vol% of Cloisite 30B with thermal treatment had similar permeabilities with their counterparts without thermal treatment. However, the addition of ATBC enhanced the processibility of PLA containing Cloisite 30B. When PLA containing 5.3 vol% of Cloisite 30B was annealed at 115°C for 40 hours, the sample was so brittle that it could not withstand the testing process. Thus the water vapor permeability could not be determined. When 5 wt% of ATBC was added, the sample was less brittle so that the permeation experiment could be conducted. With the incorporation of 5.3 vol% of Cloisite 30B and thermal treatment of being annealed at 115°C for 40 hours, the sample had a permeability of 0.41±0.04 \times10^{-14} \text{ kg/(m×Pa×s)}. Compared to the counterpart without thermal treatment, the permeability through this sample was further reduced by 16%. The reduction was
smaller than expected. Since the sample was brittle, it is possible that there might be microcracks inside that created a preferred path for diffusing gas molecules. In addition, this sample had a significant reduction of 74% in permeability compared to PLA. This value is lower than that of polystyrene (PS) given in Table 1.1. The water transmission rates of the annealed samples can be found in Appendix 7.
6 CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The research focus of this work was to (i) synthesize polymer nanocomposites employing biodegradable polylactic acid (PLA) and having excellent water vapor barrier properties and (ii) use the experimental data to fit to theoretical models to investigate the validity of these models. To accomplish these goals, several techniques were employed: adding nanoclays to increase the path for diffusing molecules, crystallizing the polymer to increase the impermeable region in the polymer, and combining these two factors to further improve the barrier properties of PLA. Moreover, a new model was developed to explain the experimental data and the result was compared with predictions of existing mathematical models. After these studies, the conclusions are:

1. In general, the addition of nanoclay regardless of its surface character has little effect on the glass transition temperature, cold crystallization temperature and melting temperature. The cold crystallization enthalpy and the melting enthalpy decrease after the incorporation of nanoclay. In addition, the thermal data show that compression molded samples without thermal treatment are amorphous.
2. The addition of nanoclay reduces the water vapor permeability through the PLA nanocomposite. However, the nanoclay surface character affects the nanoclay dispersion in the PLA matrix. The untreated nanoclay Cloisite Na⁺ has no effect on permeability. Among all the nanoclays tested, Cloisite 30B causes the largest reduction in permeability.
3. For PLA containing Cloisite 30B, mixing screw speed in the internal mixer has no effect on water vapor permeability beyond a certain speed, while increase in mixing temperature and mixing time both lead to reductions in permeability. However, rheology measurements show that
high mixing temperatures and long mixing times result in polymer degradation. The optimized processing conditions are 200°C and 80 rpm for 5 mins.

4. Water vapor permeability decreases as the loading of Cloisite 30B increases. With the addition of 5.3 vol% (10 wt%) of Cloisite 30B, the water vapor permeability is reduced by 69% compared to neat PLA. This value is comparable to that through polystyrene. The clay platelets are well dispersed in the PLA matrix for up to addition of 2.6 vol% of Cloisite 30B. There is some agglomeration at the loading of 5.3 vol%.

5. As the temperature increases, the water vapor permeability increases for both PLA and PLA containing Cloisite 30B. On the other hand, as the relative humidity increases, the permeability increases as well. However, the percent reduction in permeability is independent of the temperature and the relative humidity. This validates the tortuous path concept.

6. The time-lag method does not provide accurate measurement of water vapor diffusivity, so the water vapor solubility should be independently measured. The water vapor solubility in the nanocomposite increases as the clay loading increases because the clay surface sequesters moisture. With the incorporation of 5.3 vol% of Cloisite 30B, the solubility increases by 67%.

7. Although water vapor solubility in the nanocomposite increases linearly as the loading of Cloisite 30B increases, solubility in the PLA matrix does not change after the clay is added. Therefore, the reduction in diffusivity can be taken to be the same as the reduction in permeability.

8. The selection of plasticizer is critical because the properties depend on the miscibility between the polymer and the plasticizer. Among all the plasticizers tested, Acetyl butyl citrate (ATBC) is the most compatible with PLA. On the other hand, the mixing sequence affects the final properties of the nanocomposite.
9. The glass transition temperature, the cold crystallization temperature and the melting temperature decreases when ATBC concentration increases. On the other hand, the reduction in water vapor permeability is the largest when 5 wt% of ATBC is added. There is no effect on permeability for up to the addition of 5 wt% of ATBC. Further increase in ATBC concentration leads to an increase in permeability.

10. When the annealing temperature or the annealing time is increased, the crystallinity increases and more ordered crystals are formed for PLA. The optimized thermal treatment is annealing at 115°C for 40 hours. Under these conditions, the crystallinity of PLA increased to 40% and the water vapor permeability was reduced by 45% compared to unannealed PLA.

11. When 2.6 vol% of Cloisite 30B is added to PLA along with annealing treatment (115°C for 40 hours), the crystallinity of the annealed sample is increased to 45% because Cloisite 30B acts as nucleating agent. In addition, the water vapor permeability through this sample is reduced by 66% compared to neat PLA. This is similar to that through an unannealed PLA sample containing 5.3 vol% of Cloisite 30B.

12. When 5 wt% of ATBC is added to PLA along with annealing treatment (115°C for 40 hours), the glass transition temperature and the melting temperature are reduced because the chain mobility increases. The crystallinity slightly increases to 42% with the addition of 5 wt% ATBC. In addition, for the annealed samples, the addition of 5 wt% ATBC has no effect on the water vapor permeability.

13. The glass transition temperature decreases as the loading of Cloisite 30B increases in the ATBC-plasticized PLA samples. The crystallinity increases with the incorporation of Cloisite 30B, while the melting temperature is not affected.
14. When 10 wt% of Cloisite 30B is added to PLA along with annealing treatment (115°C for 40 hours), the sample is brittle. The sample becomes more ductile when 5 wt% of ATBC is added, so it can be used in permeation experiments. This sample has a crystallinity of 46% and the water vapor permeability through this sample is reduced by 74% compared to neat PLA. This value is lower than that of PS.

15. A new model is proposed to explain permeability data taking into account the reduction in flux and area of mass transfer. This simple model fits experimental data better than the existing theoretical models.

6.2 Recommendations

The following topics may be of interest for future workers:

1. Mechanical properties are important for a food packaging material. When the loading of nanoclay is high and the particles agglomerate, the material loses its ductility. The water vapor permeability through polylactic acid (PLA) containing 5.3 vol% Cloisite 30B is comparable to that through polystyrene when there is agglomeration at this loading. Therefore, it is worth measuring the mechanical properties of this material to see if it matches the industrial standards.

2. The model developed in this work is based on the reduction in flux and area of mass transfer when nanoplatelets are added to polymer. This model can be applied to fit the gas diffusion data in other polymer nanocomposites.

3. Food, like heart-healthy unsaturated fat, is sensitive to other gases such as oxygen. Measuring oxygen permeability can give information about the further application of PLA containing Cloisite 30B.

4. PLA is subjected to hydrolysis. It is worth testing the role of Cloisite 30B in PLA hydrolysis. This information is important for determining the degradability of this material.
REFERENCES


APPENDICES

Appendix 1 Water Vapor Transmission Rates through PLA Containing Various Nanoclays

Figure A 1: Water vapor transmission rate through PLA mixed at 180°C and 80 rpm for 5 mins.

Figure A 2: Water vapor transmission rate through PLA containing 2.6 vol% of Cloisite 15A mixed at 180°C and 80 rpm for 5 mins.
Figure A 3: Water vapor transmission rate through PLA containing 2.6 vol% of Cloisite 20A mixed at 180°C and 80 rpm for 5 mins.

Figure A 4: Water vapor transmission rate through PLA containing 2.6 vol% of Cloisite 93A mixed at 180°C and 80 rpm for 5 mins.
Figure A 5: Water vapor transmission rate through PLA containing 2.6 vol% of Cloisite 25A mixed at 180°C and 80 rpm for 5 mins.

Figure A 6: Water vapor transmission rate through PLA containing 2.6 vol% of Cloisite 30B mixed at 180°C and 80 rpm for 5 mins.
Figure A 7: Water vapor transmission rate through PLA containing 2.6 vol% of Cloisite 10A mixed at 180°C and 80 rpm for 5 mins.

Figure A 8: Water vapor transmission rate through PLA containing 2.6 vol% of Cloisite Na⁺ mixed at 180°C and 80 rpm for 5 mins.
Table A 1: Summary of water vapor transmission rate through PLA containing different nanoclays mixed at 180°C and 80 rpm for 5 mins (measured at 25°C and 100% RH).

<table>
<thead>
<tr>
<th>Nanoclay</th>
<th>Thickness $l$ (mm)</th>
<th>Water vapor transmission rate (g/(m²·d))</th>
</tr>
</thead>
<tbody>
<tr>
<td>No (1ˢᵗ run)</td>
<td>0.484</td>
<td>9.44</td>
</tr>
<tr>
<td>No (2ⁿᵈ run)</td>
<td>0.447</td>
<td>10.4</td>
</tr>
<tr>
<td>No (3ʳᵈ run)</td>
<td>0.442</td>
<td>10.2</td>
</tr>
<tr>
<td>Cloisite 15A (1ˢᵗ run)</td>
<td>0.483</td>
<td>7.32</td>
</tr>
<tr>
<td>Cloisite 15A (2ⁿᵈ run)</td>
<td>0.452</td>
<td>7.32</td>
</tr>
<tr>
<td>Cloisite 15A (3ʳᵈ run)</td>
<td>0.458</td>
<td>7.93</td>
</tr>
<tr>
<td>Cloisite 20A (1ˢᵗ run)</td>
<td>0.451</td>
<td>7.03</td>
</tr>
<tr>
<td>Cloisite 20A (2ⁿᵈ run)</td>
<td>0.438</td>
<td>6.79</td>
</tr>
<tr>
<td>Cloisite 20A (3ʳᵈ run)</td>
<td>0.475</td>
<td>6.81</td>
</tr>
<tr>
<td>Cloisite 93A (1ˢᵗ run)</td>
<td>0.459</td>
<td>7.04</td>
</tr>
<tr>
<td>Cloisite 93A (2ⁿᵈ run)</td>
<td>0.477</td>
<td>7.16</td>
</tr>
<tr>
<td>Cloisite 93A (3ʳᵈ run)</td>
<td>0.470</td>
<td>6.15</td>
</tr>
<tr>
<td>Cloisite 25A (1ˢᵗ run)</td>
<td>0.473</td>
<td>6.69</td>
</tr>
<tr>
<td>Cloisite 25A (2ⁿᵈ run)</td>
<td>0.455</td>
<td>6.77</td>
</tr>
<tr>
<td>Cloisite 25A (3ʳᵈ run)</td>
<td>0.466</td>
<td>6.60</td>
</tr>
<tr>
<td>Cloisite 30B (1ˢᵗ run)</td>
<td>0.494</td>
<td>6.01</td>
</tr>
<tr>
<td>Cloisite 30B (2ⁿᵈ run)</td>
<td>0.452</td>
<td>6.42</td>
</tr>
<tr>
<td>Cloisite 30B (3ʳᵈ run)</td>
<td>0.484</td>
<td>6.36</td>
</tr>
<tr>
<td>Cloisite 10A (1ˢᵗ run)</td>
<td>0.478</td>
<td>6.99</td>
</tr>
<tr>
<td>Cloisite 10A (2ⁿᵈ run)</td>
<td>0.453</td>
<td>6.83</td>
</tr>
<tr>
<td>Cloisite 10A (3ʳᵈ run)</td>
<td>0.457</td>
<td>7.80</td>
</tr>
<tr>
<td>Cloisite Na⁺ (1ˢᵗ run)</td>
<td>0.461</td>
<td>10.3</td>
</tr>
<tr>
<td>Cloisite Na⁺ (2ⁿᵈ run)</td>
<td>0.448</td>
<td>10.3</td>
</tr>
<tr>
<td>Cloisite Na⁺ (3ʳᵈ run)</td>
<td>0.474</td>
<td>10.6</td>
</tr>
</tbody>
</table>
Appendix 2 Water Vapor Transmission Rates through PLA Containing Cloisite 30B

Figure A 9: Water vapor transmission rate through PLA mixed at 200°C and 80 rpm for 5 mins.

Figure A 10: Water vapor transmission rate through PLA containing 0.5 vol% of Cloisite 30B mixed at 200°C and 80 rpm for 5 mins.
Figure A 11: Water vapor transmission rate through PLA containing 1.5 vol% of Cloisite 30B mixed at 200°C and 80 rpm for 5 mins.

Figure A 12: Water vapor transmission rate through PLA containing 2.6 vol% of Cloisite 30B mixed at 200°C and 80 rpm for 5 mins.
Figure A 13: Water vapor transmission rate through PLA containing 5.3 vol% of Cloisite 30B mixed at 200°C and 80 rpm for 5 mins.

Table A 2: Summary of water vapor transmission rate through PLA containing Cloisite 30B mixed at 200°C and 80 rpm for 5 mins (measured at 25°C and 100% RH).

<table>
<thead>
<tr>
<th>Vol% Cloisite 30B</th>
<th>Thickness ( l ) (mm)</th>
<th>Water vapor transmission rate (g/(m²•day))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (1st run)</td>
<td>0.490</td>
<td>8.91</td>
</tr>
<tr>
<td>0 (2nd run)</td>
<td>0.509</td>
<td>8.65</td>
</tr>
<tr>
<td>0 (3rd run)</td>
<td>0.434</td>
<td>9.78</td>
</tr>
<tr>
<td>0.5 (1st run)</td>
<td>0.515</td>
<td>6.98</td>
</tr>
<tr>
<td>0.5 (2nd run)</td>
<td>0.428</td>
<td>8.90</td>
</tr>
<tr>
<td>0.5 (3rd run)</td>
<td>0.478</td>
<td>7.39</td>
</tr>
<tr>
<td>1.5 (1st run)</td>
<td>0.473</td>
<td>6.48</td>
</tr>
<tr>
<td>1.5 (2nd run)</td>
<td>0.490</td>
<td>6.56</td>
</tr>
<tr>
<td>1.5 (3rd run)</td>
<td>0.486</td>
<td>6.01</td>
</tr>
<tr>
<td>2.6 (1st run)</td>
<td>0.499</td>
<td>4.63</td>
</tr>
<tr>
<td>2.6 (2nd run)</td>
<td>0.482</td>
<td>4.43</td>
</tr>
<tr>
<td>2.6 (3rd run)</td>
<td>0.469</td>
<td>4.91</td>
</tr>
<tr>
<td>5.3 (1st run)</td>
<td>0.575</td>
<td>2.30</td>
</tr>
<tr>
<td>5.3 (2nd run)</td>
<td>0.556</td>
<td>2.50</td>
</tr>
<tr>
<td>5.3 (3rd run)</td>
<td>0.525</td>
<td>2.45</td>
</tr>
</tbody>
</table>
Appendix 3 Polymer Weight Gain in Solubility Experiment

Figure A 14: PLA weight gain in solubility experiment.

Figure A 15: PLA containing 0.5 vol% of Cloisite 30B weight gain in solubility experiment.
Figure A 16: PLA containing 1.5 vol% of Cloisite 30B weight gain in solubility experiment.

Figure A 17: PLA containing 2.6 vol% of Cloisite 30B weight gain in solubility experiment.
Figure A 18: PLA containing 5.3 vol% of Cloisite 30B weight gain in solubility experiment.
Table A 3: Summary of weight change of PLA containing Cloisite 30B mixed at 200°C and 80 rpm for 5 mins in solubility experiment (measured at 25°C and 99% RH).

<table>
<thead>
<tr>
<th>Vol% Cloisite 30B</th>
<th>Initial weight $W_0$ (mg)</th>
<th>Final weight $W$ (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (1\textsuperscript{st} run)</td>
<td>170.273</td>
<td>171.509</td>
</tr>
<tr>
<td>0 (2\textsuperscript{nd} run)</td>
<td>170.045</td>
<td>171.277</td>
</tr>
<tr>
<td>0 (3\textsuperscript{rd} run)</td>
<td>148.872</td>
<td>149.933</td>
</tr>
<tr>
<td>0 (4\textsuperscript{th} run)</td>
<td>163.798</td>
<td>164.946</td>
</tr>
<tr>
<td>0 (5\textsuperscript{th} run)</td>
<td>134.379</td>
<td>135.321</td>
</tr>
<tr>
<td>0.5 (1\textsuperscript{st} run)</td>
<td>94.104</td>
<td>94.835</td>
</tr>
<tr>
<td>0.5 (2\textsuperscript{nd} run)</td>
<td>87.214</td>
<td>87.878</td>
</tr>
<tr>
<td>0.5 (3\textsuperscript{rd} run)</td>
<td>76.422</td>
<td>76.995</td>
</tr>
<tr>
<td>0.5 (4\textsuperscript{th} run)</td>
<td>80.375</td>
<td>80.971</td>
</tr>
<tr>
<td>0.5 (5\textsuperscript{th} run)</td>
<td>66.444</td>
<td>66.929</td>
</tr>
<tr>
<td>1.5 (1\textsuperscript{st} run)</td>
<td>123.349</td>
<td>124.517</td>
</tr>
<tr>
<td>1.5 (2\textsuperscript{nd} run)</td>
<td>140.692</td>
<td>142.018</td>
</tr>
<tr>
<td>1.5 (3\textsuperscript{rd} run)</td>
<td>118.141</td>
<td>119.216</td>
</tr>
<tr>
<td>1.5 (4\textsuperscript{th} run)</td>
<td>159.579</td>
<td>161.036</td>
</tr>
<tr>
<td>1.5 (5\textsuperscript{th} run)</td>
<td>133.368</td>
<td>134.592</td>
</tr>
<tr>
<td>2.6 (1\textsuperscript{st} run)</td>
<td>111.191</td>
<td>112.399</td>
</tr>
<tr>
<td>2.6 (2\textsuperscript{nd} run)</td>
<td>113.066</td>
<td>114.259</td>
</tr>
<tr>
<td>2.6 (3\textsuperscript{rd} run)</td>
<td>111.704</td>
<td>112.864</td>
</tr>
<tr>
<td>2.6 (4\textsuperscript{th} run)</td>
<td>128.033</td>
<td>129.366</td>
</tr>
<tr>
<td>2.6 (5\textsuperscript{th} run)</td>
<td>93.567</td>
<td>94.560</td>
</tr>
<tr>
<td>5.3 (1\textsuperscript{st} run)</td>
<td>72.719</td>
<td>73.556</td>
</tr>
<tr>
<td>5.3 (2\textsuperscript{nd} run)</td>
<td>112.499</td>
<td>113.877</td>
</tr>
<tr>
<td>5.3 (3\textsuperscript{rd} run)</td>
<td>60.159</td>
<td>60.893</td>
</tr>
<tr>
<td>5.3 (4\textsuperscript{th} run)</td>
<td>71.090</td>
<td>71.910</td>
</tr>
<tr>
<td>5.3 (5\textsuperscript{th} run)</td>
<td>96.393</td>
<td>97.562</td>
</tr>
</tbody>
</table>
Appendix 4 Water Vapor Transmission Rates through PLA Containing Cloisite 30B

Measured at Different Conditions

Figure A 19: Water vapor transmission rate through PLA measured at 13°C and 100% RH.

Figure A 20: Water vapor transmission rate through PLA containing 2.6 vol% of Cloisite 30B measured at 13°C and 100% RH.
Figure A 21: Water vapor transmission rate through PLA measured at 25°C and 100% RH.

Figure A 22: Water vapor transmission rate through PLA containing 2.6 vol% of Cloisite 30B measured at 25°C and 100% RH.
Figure A 23: Water vapor transmission rate through PLA measured at 37°C and 100% RH.

Figure A 24: Water vapor transmission rate through PLA containing 2.6 vol% of Cloisite 30B measured at 37°C and 100% RH.
Figure A 25: Water vapor transmission rate through PLA measured at 25°C and 50% RH.

Figure A 26: Water vapor transmission rate through PLA containing 2.6 vol% of Cloisite 30B measured at 25°C and 50% RH.
Figure A 27: Water vapor transmission rate through PLA measured at 25°C and 75% RH.  

Figure A 28: Water vapor transmission rate through PLA containing 2.6 vol% of Cloisite 30B measured at 25°C and 75% RH.
Table A 4: Summary of water vapor transmission rate through PLA and PLA containing 2.6 vol% of Cloisite 30B mixed at 200°C and 80 rpm for 5 mins (measured at various temperatures and 100% RH).

<table>
<thead>
<tr>
<th>Vol% Cloisite 30B</th>
<th>Temperature (°C)</th>
<th>Thickness ( l ) (mm)</th>
<th>Water vapor transmission rate ( \frac{g}{(m^2 \times d)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (1\textsuperscript{st} run)</td>
<td>13</td>
<td>0.478</td>
<td>3.74</td>
</tr>
<tr>
<td>0 (2\textsuperscript{nd} run)</td>
<td>13</td>
<td>0.477</td>
<td>5.37</td>
</tr>
<tr>
<td>0 (3\textsuperscript{rd} run)</td>
<td>13</td>
<td>0.526</td>
<td>3.88</td>
</tr>
<tr>
<td>2.6 (1\textsuperscript{st} run)</td>
<td>13</td>
<td>0.492</td>
<td>2.13</td>
</tr>
<tr>
<td>2.6 (2\textsuperscript{nd} run)</td>
<td>13</td>
<td>0.516</td>
<td>2.59</td>
</tr>
<tr>
<td>2.6 (3\textsuperscript{rd} run)</td>
<td>13</td>
<td>0.499</td>
<td>2.39</td>
</tr>
<tr>
<td>0 (1\textsuperscript{st} run)</td>
<td>25</td>
<td>0.490</td>
<td>8.91</td>
</tr>
<tr>
<td>0 (2\textsuperscript{nd} run)</td>
<td>25</td>
<td>0.509</td>
<td>8.65</td>
</tr>
<tr>
<td>0 (3\textsuperscript{rd} run)</td>
<td>25</td>
<td>0.434</td>
<td>9.78</td>
</tr>
<tr>
<td>2.6 (1\textsuperscript{st} run)</td>
<td>25</td>
<td>0.499</td>
<td>4.63</td>
</tr>
<tr>
<td>2.6 (2\textsuperscript{nd} run)</td>
<td>25</td>
<td>0.482</td>
<td>4.43</td>
</tr>
<tr>
<td>2.6 (3\textsuperscript{rd} run)</td>
<td>25</td>
<td>0.469</td>
<td>4.91</td>
</tr>
<tr>
<td>0 (1\textsuperscript{st} run)</td>
<td>37</td>
<td>0.519</td>
<td>17.5</td>
</tr>
<tr>
<td>0 (2\textsuperscript{nd} run)</td>
<td>37</td>
<td>0.497</td>
<td>16.1</td>
</tr>
<tr>
<td>0 (3\textsuperscript{rd} run)</td>
<td>37</td>
<td>0.492</td>
<td>18.1</td>
</tr>
<tr>
<td>2.6 (1\textsuperscript{st} run)</td>
<td>37</td>
<td>0.524</td>
<td>10.1</td>
</tr>
<tr>
<td>2.6 (2\textsuperscript{nd} run)</td>
<td>37</td>
<td>0.560</td>
<td>9.30</td>
</tr>
<tr>
<td>2.6 (3\textsuperscript{rd} run)</td>
<td>37</td>
<td>0.513</td>
<td>7.74</td>
</tr>
</tbody>
</table>
Table A 5: Summary of water vapor transmission rate through PLA and PLA containing 2.6 vol% of Cloisite 30B mixed at 200°C and 80 rpm for 5 mins (measured at 25°C and various RHs).

<table>
<thead>
<tr>
<th>Vol% Cloisite 30B</th>
<th>RH (%)</th>
<th>Thickness $l$ (mm)</th>
<th>Water vapor transmission rate (g/(m²×d))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (1ˢᵗ run)</td>
<td>50</td>
<td>0.485</td>
<td>3.09</td>
</tr>
<tr>
<td>0 (2ⁿᵈ run)</td>
<td>50</td>
<td>0.483</td>
<td>3.81</td>
</tr>
<tr>
<td>0 (3ʳᵈ run)</td>
<td>50</td>
<td>0.492</td>
<td>2.79</td>
</tr>
<tr>
<td>2.6 (1ˢᵗ run)</td>
<td>50</td>
<td>0.488</td>
<td>1.24</td>
</tr>
<tr>
<td>2.6 (2ⁿᵈ run)</td>
<td>50</td>
<td>0.529</td>
<td>1.46</td>
</tr>
<tr>
<td>2.6 (3ʳᵈ run)</td>
<td>50</td>
<td>0.498</td>
<td>1.42</td>
</tr>
<tr>
<td>0 (1ˢᵗ run)</td>
<td>75</td>
<td>0.516</td>
<td>4.57</td>
</tr>
<tr>
<td>0 (2ⁿᵈ run)</td>
<td>75</td>
<td>0.475</td>
<td>5.07</td>
</tr>
<tr>
<td>0 (3ʳᵈ run)</td>
<td>75</td>
<td>0.468</td>
<td>5.31</td>
</tr>
<tr>
<td>2.6 (1ˢᵗ run)</td>
<td>75</td>
<td>0.478</td>
<td>2.39</td>
</tr>
<tr>
<td>2.6 (2ⁿᵈ run)</td>
<td>75</td>
<td>0.528</td>
<td>3.03</td>
</tr>
<tr>
<td>2.6 (3ʳᵈ run)</td>
<td>75</td>
<td>0.539</td>
<td>2.42</td>
</tr>
<tr>
<td>0 (1ˢᵗ run)</td>
<td>100</td>
<td>0.490</td>
<td>8.91</td>
</tr>
<tr>
<td>0 (2ⁿᵈ run)</td>
<td>100</td>
<td>0.509</td>
<td>8.65</td>
</tr>
<tr>
<td>0 (3ʳᵈ run)</td>
<td>100</td>
<td>0.434</td>
<td>9.78</td>
</tr>
<tr>
<td>2.6 (1ˢᵗ run)</td>
<td>100</td>
<td>0.499</td>
<td>4.63</td>
</tr>
<tr>
<td>2.6 (2ⁿᵈ run)</td>
<td>100</td>
<td>0.482</td>
<td>4.43</td>
</tr>
<tr>
<td>2.6 (3ʳᵈ run)</td>
<td>100</td>
<td>0.469</td>
<td>4.91</td>
</tr>
</tbody>
</table>
Appendix 5 Water Vapor Transmission Rates through ATBC-Plasticized PLA Containing Cloisite 30B

Figure A 29: Water vapor transmission rate through PLA containing 2.5 wt% of ATBC.

Figure A 30: Water vapor transmission rate through PLA containing 2.5 wt% of ATBC and 5 wt% (2.6 vol%) of Cloisite 30B.
Figure A 31: Water vapor transmission rate through PLA containing 5 wt% of ATBC.

Figure A 32: Water vapor transmission rate through PLA containing 5 wt% of ATBC and 5 wt% (2.6 vol%) of Cloisite 30B.
Figure A 33: Water vapor transmission rate through PLA containing 15 wt% of ATBC.

Figure A 34: Water vapor transmission rate through PLA containing 15 wt% of ATBC and 5 wt% (2.6 vol%) of Cloisite 30B.
Table A 6: Summary of water vapor transmission rate through ATBC-plasticized PLA nanocomposites mixed at 200°C and 80 rpm for 5 mins (measured at 25°C and 100% RH).

<table>
<thead>
<tr>
<th>wt% Cloisite 30B</th>
<th>wt% ATBC</th>
<th>Thickness $l$ (mm)</th>
<th>Water vapor transmission rate (g/(m²·d))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (1st run)</td>
<td>2.5</td>
<td>0.498</td>
<td>8.52</td>
</tr>
<tr>
<td>0 (2nd run)</td>
<td>2.5</td>
<td>0.535</td>
<td>8.05</td>
</tr>
<tr>
<td>0 (3rd run)</td>
<td>2.5</td>
<td>0.511</td>
<td>8.25</td>
</tr>
<tr>
<td>5 (1st run)</td>
<td>2.5</td>
<td>0.544</td>
<td>4.76</td>
</tr>
<tr>
<td>5 (2nd run)</td>
<td>2.5</td>
<td>0.529</td>
<td>4.63</td>
</tr>
<tr>
<td>5 (3rd run)</td>
<td>2.5</td>
<td>0.495</td>
<td>5.45</td>
</tr>
<tr>
<td>0 (1st run)</td>
<td>5</td>
<td>0.513</td>
<td>8.02</td>
</tr>
<tr>
<td>0 (2nd run)</td>
<td>5</td>
<td>0.509</td>
<td>9.43</td>
</tr>
<tr>
<td>0 (3rd run)</td>
<td>5</td>
<td>0.504</td>
<td>8.41</td>
</tr>
<tr>
<td>5 (1st run)</td>
<td>5</td>
<td>0.573</td>
<td>4.47</td>
</tr>
<tr>
<td>5 (2nd run)</td>
<td>5</td>
<td>0.504</td>
<td>5.04</td>
</tr>
<tr>
<td>5 (3rd run)</td>
<td>5</td>
<td>0.514</td>
<td>5.00</td>
</tr>
<tr>
<td>0 (1st run)</td>
<td>15</td>
<td>0.505</td>
<td>11.0</td>
</tr>
<tr>
<td>0 (2nd run)</td>
<td>15</td>
<td>0.511</td>
<td>10.9</td>
</tr>
<tr>
<td>0 (3rd run)</td>
<td>15</td>
<td>0.493</td>
<td>11.4</td>
</tr>
<tr>
<td>5 (1st run)</td>
<td>15</td>
<td>0.490</td>
<td>9.02</td>
</tr>
<tr>
<td>5 (2nd run)</td>
<td>15</td>
<td>0.525</td>
<td>8.52</td>
</tr>
<tr>
<td>5 (3rd run)</td>
<td>15</td>
<td>0.505</td>
<td>8.99</td>
</tr>
</tbody>
</table>
Appendix 6 Water Vapor Transmission Rates through Annealed PLA and PLA Containing Cloisite 30B

Figure A 35: Water vapor transmission rate through PLA annealed at 115°C for 40 hours.

Figure A 36: Water vapor transmission rate through PLA containing 2.6 vol% of Cloisite 30B annealed at 115°C for 40 hours.
Table A 7: Summary of water vapor transmission rate through annealed PLA and PLA containing Cloisite 30B mixed at 200°C and 80 rpm for 5 mins (measured at 25°C and 100% RH).

<table>
<thead>
<tr>
<th>Vol% Cloisite 30B</th>
<th>Thickness (l) (mm)</th>
<th>Water vapor transmission rate (g/(m²×d))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (1\textsuperscript{st} run)</td>
<td>0.499</td>
<td>4.75</td>
</tr>
<tr>
<td>0 (2\textsuperscript{nd} run)</td>
<td>0.509</td>
<td>4.91</td>
</tr>
<tr>
<td>0 (3\textsuperscript{rd} run)</td>
<td>0.492</td>
<td>4.56</td>
</tr>
<tr>
<td>2.6 (1\textsuperscript{st} run)</td>
<td>0.511</td>
<td>2.85</td>
</tr>
<tr>
<td>2.6 (2\textsuperscript{nd} run)</td>
<td>0.495</td>
<td>3.21</td>
</tr>
<tr>
<td>2.6 (3\textsuperscript{rd} run)</td>
<td>0.485</td>
<td>2.71</td>
</tr>
</tbody>
</table>
Appendix 7 Water Vapor Transmission Rates through Annealed ATBC-Plasticized PLA Containing Cloisite 30B

Figure A 37: Water vapor transmission rate through PLA containing 5 wt% of ATBC annealed at 115°C for 40 hours.

Figure A 38: Water vapor transmission rate through PLA containing 5 wt% of ATBC and 5 wt% (2.6 vol%) of Cloisite 30B annealed at 115°C for 40 hours.
Figure A 39: Water vapor transmission rate through PLA containing 5 wt% of ATBC and 10 wt% (5.3 vol%) of Cloisite 30B annealed at 115°C for 40 hours.

Table A 8: Summary of water vapor transmission rate through annealed ATBC-plasticized PLA nanocomposites (measured at 25°C and 100% RH).

<table>
<thead>
<tr>
<th>wt% Cloisite 30B</th>
<th>wt% ATBC</th>
<th>Thickness $l$ (mm)</th>
<th>Water vapor transmission rate (g/(m²×d))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (1&lt;sup&gt;st&lt;/sup&gt; run)</td>
<td>5</td>
<td>0.471</td>
<td>4.44</td>
</tr>
<tr>
<td>0 (2&lt;sup&gt;nd&lt;/sup&gt; run)</td>
<td>5</td>
<td>0.526</td>
<td>4.81</td>
</tr>
<tr>
<td>0 (3&lt;sup&gt;rd&lt;/sup&gt; run)</td>
<td>5</td>
<td>0.469</td>
<td>4.41</td>
</tr>
<tr>
<td>5 (1&lt;sup&gt;st&lt;/sup&gt; run)</td>
<td>5</td>
<td>0.527</td>
<td>2.99</td>
</tr>
<tr>
<td>5 (2&lt;sup&gt;nd&lt;/sup&gt; run)</td>
<td>5</td>
<td>0.537</td>
<td>3.10</td>
</tr>
<tr>
<td>5 (3&lt;sup&gt;rd&lt;/sup&gt; run)</td>
<td>5</td>
<td>0.564</td>
<td>2.72</td>
</tr>
<tr>
<td>10 (1&lt;sup&gt;st&lt;/sup&gt; run)</td>
<td>5</td>
<td>0.529</td>
<td>2.34</td>
</tr>
<tr>
<td>10 (2&lt;sup&gt;nd&lt;/sup&gt; run)</td>
<td>5</td>
<td>0.523</td>
<td>2.17</td>
</tr>
<tr>
<td>10 (3&lt;sup&gt;rd&lt;/sup&gt; run)</td>
<td>5</td>
<td>0.515</td>
<td>2.19</td>
</tr>
</tbody>
</table>
Appendix 8 Sample Calculations

Here is a demonstration of obtaining water vapor permeability from the plot of water transmission rate of a PLA sample. By looking at Figure A 1, one can see that the steady-state water vapor transmission rate is \( J = 9.44 \, g/(m^2 \times d) \). Since the sample is \( l = 0.484 \, mm \) in thickness and the water vapor pressure is \( p = 3167 \, Pa \) at 25°C and 100% RH, the permeability can be obtained from Eq. (2.7):

\[
P = \frac{J \times l}{(\Delta p)}
\]

\[
P = \frac{9.44 \, g}{m^2 \times d} \times \frac{0.484 \times 10^{-3} m}{-(0 - 3167 \, Pa)} \times \frac{kg}{1000 \, g} \times \frac{d}{86400 \, s}
\]

\[
P = 1.67 \times 10^{-14} \frac{kg}{Pa \times m \times s}
\]

Here is a demonstration of obtaining water vapor solubility from the plot of polymer weight change in the solubility experiment. By looking at Figure A 14, one can see that the weight of dried PLA is \( W_0 = 170.273 \, mg \), and the weight of water-saturated PLA \( W = 171.509 \, mg \). By using Eq. (4.2), the equilibrium water vapor concentration \( c_{eq} \) is:

\[
c_{eq} = \frac{(W - W_0)22414\rho}{18W_0}
\]

\[
c_{eq} = \frac{(171.509 - 170.273)mg}{18 \frac{g}{mol} \times 170.273mg} \times 22414 \frac{cm^3 \, STP}{mol} \times \frac{1.2 \, g}{cm^3}
\]

\[
c_{eq} = 10.85 \frac{cm^3 \, STP}{cm^3}
\]

The conversion factor in Eq. (4.3), which is 0.803, is calculated as follows is equal to the ratio of molecular weight of water to the molar volume of water vapor at STP conditions:

\[
\frac{18 \frac{g}{mol}}{22414 \frac{cm^3 \, STP}{mol}} \times \frac{kg}{1000 \, g} \times \frac{10^6 \, cm^3}{m^3} = 0.803 \frac{kg \times cm^3}{cm^3 \, STP \times m^3}
\]
By using Eq. (4.3) and saturated water vapor pressure \( p = 3167 \text{ Pa} \) at 25°C and 100% RH, one can obtain solubility \( S \):

\[
S = \frac{0.803c_{eq}}{p}
\]

\[
S = 10.85 \frac{cm^3 \text{ STP}}{cm^3} \times \frac{0.803 \text{ kg} \times cm^3}{cm^3 \text{ STP} \times m^3} \times \frac{1}{3167 \text{ Pa}}
\]

\[
S = 2.67 \times 10^{-3} \frac{kg}{m^3 \times Pa}
\]