Water vapour permeability of bio-based polymers

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Water Vapour Permeability of Bio-based Polymers

by

Zhouyang Duan

A doctoral thesis submitted in partial fulfilment of the requirements for the award of degree of Doctor of Philosophy of Loughborough University

Project Supervisor: Dr N. L. Thomas

Date: 20 September 2013
Abstract

This project investigates the moisture barrier properties of bio-based polymers and ways of improving them. The first section addresses the effect of crystallinity on the water permeability of poly(lactic acid) (PLA). The second section investigates PLA/talc composites and PLA/ montmorillonite nanocomposites. The third section is focused on a new polymer, polybutylene succinate (PBS), and its nanocomposites with montmorillonite.

In the first section, the water vapour transmission rates (WVTR) through samples of polylactic acid of different crystallinities have been measured. Three different grades of commercial PLA were used with different ratios of L-lactide and D-lactide to give a range of crystallinities from 0 to 50%. Sheets of PLA were prepared by melt compounding followed by compression moulding and annealing at different temperatures and for different times to give the range of crystallinities required. Crystallinity was measured by differential scanning calorimetry (DSC) and the morphology of the samples was observed under crossed polars in a transmitted light microscope. Water vapour transmission rates through the films were measured at 38°C and at a relative humidity of 90%. It was found that the measured values of WVTR decreased linearly with increasing crystallinity of the PLA from 0 to 50%. The results are discussed in terms of the effect of crystallinity on solubility and shown to fit the ‘tortuous path’ model. The model was also successfully used to explain published data on water permeability of polyethylene terephthalate.

In the second section, a series of PLA/talc composites and PLA/ montmorillonite nanocomposites were prepared by melt compounding followed by compression moulding. The morphologies of the composites were investigated using transmission electron microscopy (TEM) and wide-angle X-ray diffraction (WAXD) and it was found that the fillers were well dispersed in the polymer matrix. The average aspect ratio of the compounded talc was found to be 8, and that of the nanoclay was found to be 50. Water vapour transmission rates
(WVTR) through the films were measured at 38°C and at a relative humidity of 90%. It was found that the measured values of WVTR decreased with increasing filler content and the results gave good agreement with predictions from the Nielsen ‘tortuous path’ model.

In the third section, PBS/ montmorillonite nanocomposites were prepared by melt compounding followed by compression moulding. The melting and crystallisation behaviour of the pure PBS samples were investigated using differential scanning calorimetry (DSC) and cross polarised optical microscopy. A slight decrease of the degree of crystallinity was found in PBS containing 5% nanoclay. The morphology of the composites was investigated using transmission electron microscopy (TEM) and wide-angle X-ray diffraction (WAXD) and it was confirmed that that composite structures were intercalated. Water vapour transmission rates (WVTR) through the PBS sheets were measured using a MOCON Permatran-W®398. The measured values of WVTR decreased with increasing nanoclay content. However, the experimental values were all higher than the values predicted by the Nielsen tortuosity model. This result shows that in the case of PBS, which is a highly crystalline polymer, the nanoclay is not as well dispersed and is not as effective in reducing water vapour permeability as in the case of PLA.
Keywords

Poly(Lactic Acid), Polylactide, Polybutylene succinate, Talc, Montmorillonite, Crystallinity, Crystal morphology. Barrier Properties,
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<td>( \tau )</td>
<td>Tortuosity factor</td>
</tr>
<tr>
<td>( \Delta H )</td>
<td>Enthalpy</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
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<tr>
<td>GPC</td>
<td>Gel Permeation Chromatography</td>
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<tr>
<td>NW</td>
<td>NatureWorks</td>
</tr>
<tr>
<td>PBS</td>
<td>Polybutylene Succinate</td>
</tr>
<tr>
<td>PEO</td>
<td>Poly(ethylene oxide)</td>
</tr>
<tr>
<td>PDLA</td>
<td>Poly-D-lactic acid</td>
</tr>
<tr>
<td>PHA</td>
<td>Polyhydroxyalkanoates</td>
</tr>
<tr>
<td>PHB</td>
<td>Polyhydroxybutyrate</td>
</tr>
<tr>
<td>PLA</td>
<td>Poly(lactic acid)</td>
</tr>
<tr>
<td>PLLA</td>
<td>Poly-L-lactic acid</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>Tc</td>
<td>Crystallisation temperature</td>
</tr>
<tr>
<td>Tg</td>
<td>Glass transition temperature</td>
</tr>
<tr>
<td>Tm</td>
<td>Melting temperature</td>
</tr>
<tr>
<td>vol.%</td>
<td>Volume percentage</td>
</tr>
<tr>
<td>wt.%</td>
<td>Weight percentage</td>
</tr>
<tr>
<td>WVTR</td>
<td>Water vapour transmission rate</td>
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1 Introduction

1.1 Background

Plastic consumption in the world was more than 200 million tons in 2008, and is increasing at approximately 5% per annum\(^1\). In 2010 the global production of plastics increased to 270 million tons, and it rose to 280 million tonnes in 2011 according to first rough estimates published by PlasticsEurope\(^2\). Plastics are used in the packaging industry for their advantages of low cost, processability, good mechanical and optical properties. Most plastic materials, such as polyethylene terephthalate (PET), polyvinylchloride (PVC), polyethylene (PE) and polypropylene (PP), are based on petroleum and so the continuously rising price of oil is of concern. In addition, disposal of plastic packaging materials is becoming a world-wide environmental issue\(^1,3\). Therefore, it is increasingly important to develop bio-based polymers for packaging.

Bio-based polymers are polymers derived from renewable resources. A special category of bio-based polymers are biopolymers. Biopolymers are polymers that are produced by the metabolic processes of living cells. This group includes carbohydrates, such as cellulose and starch, and also proteins, such as keratin. Some biopolymers, such as cellulose, are functional or structural materials, while others, like starch and poly (alpha-D-glucose), are produced in nature for energy storage.

Bio-based polymers can be biodegradable, which means that they can undergo hydrolysis and bacterial breakdown in natural conditions, as shown in Figure 1. Some bio-based polymers are not biodegradable, such as polyethylene made from bio resources; while some polymers, such as polycaprolactone, are biodegradable, but they are not derived from renewable resources.
Biodegradation is a biological process that occurs after the plastics have started to degrade. A biodegradable plastic is a plastic in which degradation results in lower molecular weight fragments produced by the action of naturally occurring microorganisms such as bacteria, fungi and algae. Compostable plastic must pass ASTM D6400 or EN 13432, which specifies that it must biodegrade to carbon dioxide at 60% for a single polymer and 90% for a blend within 180 days, and leave less than 10% of its original weight after 84 days.

Some bio-based polymers that have been recently developed are shown in Figure 2. Kim et al. have reported the use of poly (lactic acid) (PLA) for applications such as bags and films for food packaging. PLA is produced by Naturework and Chronopol. Koch et al. suggested that the use of degradable plastics derived from starch could help to resolve the problem of waste plastics disposal, while Entwistle et al. reported development of starch based foam packaging materials.
Mayer and Kaplan\textsuperscript{9} have compared the physical, mechanical and barrier properties of several biopolymers, including starch, cellulose acetate and polyhydroxyalkanoates, giving suggestions of the use of these materials for various applications.

The global consumption of bioplastics is expected to reach 890,000 tonnes in 2013\textsuperscript{10}.

Of the various bio-based polymers, poly(lactic acid) has received the most attention. Its properties are similar to those of poly(ethylene terephthalate) (PET), making it a desirable substitute of this commonly-used plastic in food packaging applications.
Polybutylene succinate, also named as poly(tetramethylene succinate), is a synthetic aliphatic polyester. It has received much attention recently because of its excellent biodegradability, thermoplastic processability and balanced mechanical properties\textsuperscript{11}.

The water barrier properties of a material are very important in food packaging applications, since water vapour may transfer through the package and cause a change in food quality and affect its storage time\textsuperscript{1}. A material with good water barrier properties can protect food better and have a longer shelf-life. Yet according to studies by Ashley\textsuperscript{12}, Shogren\textsuperscript{13}, and Chandra\textsuperscript{14}, it is found that bio-based polymers have poorer water barrier properties compared with traditional commercial polymer due to their biodegradability and polarity, which becomes a difficulty in using them for food packaging. Polymer types and processing conditions can affect water barrier properties. Thus it is possible to improve the water barrier properties of a bio-based polymer by modifying its structure and processing method.
1.2 Aim of Project

Sponsored by PepsiCo International, the aim of this project is to prepare and test bio-based resins and blends capable of the highest possible moisture barrier property when converted into flexible films for food packaging.
1.3 Publications from the thesis

Some of the work presented in this thesis has already been published or submitted as follows:


2 Literature Survey

2.1 Biopolymers

As defined in the previous chapter, a bio-based polymer is a polymer derived from renewable resources. As shown in Figure 3, bio-based polymers are derived from various sources. Some, known as biopolymers, are directly produced by living cells. This group includes polysaccharides and proteins\textsuperscript{15,16}. Also in this group are polyhydroxy alkanoates (PHA) which are produced from bacteria.

![Figure 3 Classification of biopolymers](image)

PLA is rather different from the biopolymers mentioned above. It is chemically synthesized from a bio-based monomer, which is lactide derived from maize starch.

The vast majority of applications for biodegradable plastics are in short-life, disposable products. An important market is in food packaging.

PLA and cellulose are used for food packaging, due to their relatively cheap prices and relatively good mechanical properties and processabilities. Siracusaa et al.\textsuperscript{1} suggested Polyhydroxyalkanoates (PHA) have good barrier properties, but their price and processability could limit their commercial applications. Their
disadvantages have been discussed by Mayer et al. and Auras et al. Starch and cellulose degrade fast in a high humidity environment. Innovia® has developed a cellulose film with a water barrier coating of PVDC for packaging applications.

Biopolymers can degrade by enzyme actions of microorganisms such as bacteria, fungi, and algae. Abiotic hydrolysis is the initial step of biodegradation that breaks a polymer into fragments for some synthetic polymers such as PLA. Then these low molecular weight fragments are capable of being biodegraded.

2.1.1 Poly (Lactic Acid) (PLA)
Poly (lactic acid) is an aliphatic polyester. The monomer of PLA is lactic acid, which was first isolated from sour milk by Scheele in 1780 and commercially produced in 1881. Lactic acid is mainly derived by bacterial carbohydrate fermentation of corn, starch or sugar, using homolactic organisms such as Lactobacilli.

PLA is a desirable new material for food packaging with the following advantages: (1) it can be obtained from renewable agricultural sources; (2) it consumes carbon dioxide during production; (3) it is biodegradable and compostable; (4) it can be processed by various methods; (5) it can provide mechanical properties equivalent to polystyrene.

2.1.1.1 Synthesis
Two optically active configurations of PLA exist because there is an asymmetric carbon atom in lactic acid(Figure 4). These two configurations can form three different lactides: L-lactide, D-lactide, and meso-lactide, as shown in Figure 5.
According to Auras et al.\textsuperscript{25}, the monomer of PLA, lactic acid, can be made by carbohydrate fermentation or chemical synthesis. Vink et al.\textsuperscript{27} have reported that lactic acid is produced by Cargill Dow\textsuperscript{®} as follows: starch in corn is separated and converted by enzymatic hydrolysis into dextrose, and then dextrose is fermented into lactic acid at near neutral PH, as shown in Figure 6. The resource is 100% renewable.
There are several methods of polymerisation to obtain high molecular weight PLA, including:

1. direct condensation polymerisation;
2. azeotropic dehydrative condensation;
3. and ring opening polymerisation. (Figure 7)
Among these three different PLA polymerisation methods, condensation polymerisation is the least expensive. However, as Auras et al. \(^{25}\) have discussed in their review, studies by Cotarca et al. \(^{29}\), Aharoni et al. \(^{30}\), Hyon et al. \(^{15}\) and Zhao et al. \(^{31}\) have shown that additional chain coupling agents are required to produce high molecular weight PLA due to the back-biting equilibrium reaction,
which increases cost and processing complexity. Hyon et al.\textsuperscript{15} also indicated that PLA with weight average molecular weights higher than 20000 were not obtained in condensation polymerisation without any chain coupling agents, and this PLA had very limited mechanical properties. Titanium (IV) butoxide (TNBT) was used as a chain coupling agent by Chen et al.\textsuperscript{32}, who obtained PLA with weight average molecular weights up to 120000 when the esterification reaction took up to 7 hours.

Azeotropic condensation polymerisation can produce high molecular weight PLA without the use of chain coupling agents, but catalysts are needed to achieve a high enough reaction rate, which introduces impurities in the final product\textsuperscript{25,33}. According to Auras et al.\textsuperscript{25}, the general procedure of PLA azeotropic condensation polymerisation starts by reducing the distillation pressure of lactic acid for 2-3 hours at 130\textdegree C, then the water generated in condensation is removed; catalyst is added along with diphenyl ester; after 30-40 hours of polymerisation in the reaction vessel at the same temperature, the PLA is isolated and purified. Ajioka et al.\textsuperscript{34} reported that the polymerisation time, solvent, catalysts, as well as the water content of the solution can affect the molecular weight of the final product. PLA with a weight average molecular weight of 33000 was obtained when 0.2 wt.% of SnCl\textsubscript{2}·2H\textsubscript{2}O was used as a catalyst in the polymerization reaction.

Ring-opening polymerisation is the method used by Cargill Dow LLC to produce high molecular weight PLA for commercial applications\textsuperscript{25}. PLA with a high optical purity can be obtained by ring-opening polymerisation by control of the isomer feedstock, temperature and catalysts\textsuperscript{25}. Garlotta\textsuperscript{28} used stannous octoate(tin[II] 2-ethylhexanoate) as a catalyst and produced PLLA with 96% L-lactide optical purity; Garlotta also found that the conversion rate of lactic acid became higher with increasing catalyst concentration, but the molecular weight of the final product decreased if the catalyst concentration was too high, as shown in Figure 8. In addition, it was also found that both the monomer conversion and the
molecular weight of poly-L-lactides increase with time in the initial stage of polymerization, followed by a slight decrease. As reaction temperature increased, the polymerisation rate rose and both molecular weight and conversion rate decreased.

Figure 8 Effect of catalyst concentration on the viscosity average molecular weight (Mv) of PLA and monomer conversion at 130°C for 72 hours. Upper curve: conversion; lower curve: Mv

PLA can be produced by both cationic and anionic polymerisation, with chain growth by the cleavage of alkyl-oxygen bonds. The cationic polymerisation was reported to be initiated by trifluoromethanesulphonic acid (triflic acid) and methyl trifluoromethanesulphonic acid(methyl acid)\textsuperscript{35}. Kricheldorf and Sumbel\textsuperscript{36} used SnCl\textsubscript{2}, SnBr\textsubscript{2}, SnCl\textsubscript{4} and SnBr\textsubscript{4} to polymerise PLLA and found no racemisation occurred after the reaction at 48 hours at the temperature range of 100-160°C. The anionic polymerisation was initiated by the nucleophilic reaction of an anion with carbonyl. One study showed that primary alkoxides such as potassium methoxide can work well with negligible racemisation, termination, or
transesterification\textsuperscript{37}.

2.1.1.2 Crystallinity
PLA containing 50-93\% of L-lactic acid is generally amorphous with a glass-transition temperature about 55\(^\circ\)C, since the presence of D-lactic acid introduces imperfections in the crystalline structure and thus decreases the degree of crystallinity. Amorphous PLA is transparent, glassy and stiff, similar to polystyrene. According to Garlotta\textsuperscript{28}, it is soluble in organic solvents such as THF, benzene and chloroform. Properties of amorphous PLA partly depend on the working temperature. Amorphous PLA may undergo physical aging and show ductile fracture at temperatures not far below its glass transition temperature. It decomposes above 215\(^\circ\)C\textsuperscript{17}.

Studies by Tsuji and Ikada\textsuperscript{38,39} showed that high molecular weight PLA containing more than 93\% of L-lactic acid is semi-crystalline. The glass-transition and melting temperatures are about 60\(^\circ\)C and 175\(^\circ\)C respectively. Poly(L-lactic acid) (PLLA) with a high crystallinity can be obtained by slow cooling or annealing above Tg, or if there is a stress applied during processing\textsuperscript{23}. Unzipping, chain scission reaction and thermal degradation can occur above the melting point\textsuperscript{40}. According to Tsuji and Ikada\textsuperscript{39}, the degree of crystallinity, crystal size, morphology and melting temperature depend on the processing procedure, annealing temperature and time. When the PLA melt was directly annealed, the morphology showed a strong dependence on the annealing temperature. Similar results were also found in research by Urbanovici et al.\textsuperscript{41}. In addition, crystallinity and melting temperature increased with increasing annealing temperature and time. Studies by Mazzullo et al.\textsuperscript{42} and Kolstad et al.\textsuperscript{43} showed that pure PLLA has a relatively fast crystallisation speed at a temperature between 110 and 130\(^\circ\)C. Auras et al.\textsuperscript{25} calculated that the peak crystallisation temperature was 125\(^\circ\)C. This was based on the nucleation parameters of PLLA from results obtained in isothermal and non-isothermal kinetic analysis by Vasanthakumari et al.\textsuperscript{44}, and Kishore et
al.\textsuperscript{45,46}, using the following equation:

$$K_g = \frac{4b\sigma\sigma_e T_m}{\Delta H_f k}$$

(1)

Where $K_g$ is the nucleation constant, $b$ is the layer thickness of the crystal, $\sigma$ is the lateral surface energy, $\sigma_e$ is the fold surface energy, $\Delta H_f$ is the heat of fusion, and $k$ is the Boltzmann constant, $T_m$ is the thermodynamic melting temperature.

In research by Yasuniwa et al.\textsuperscript{47}, they found that when the temperature increased above 113°C, there is a sudden decrease of crystallisation rate. In addition, the final dimension of the resulting crystals and the uniformity of the dimension increased when the annealing temperature was increased from 111 °C to 116°C, as shown in Figure 9.
Figure 9 Crossed polarised optical micrographs for PLLA isothermally crystallized at (a) 81 °C, (b) 91 °C, (c) 111 °C, (d) 116 °C, (e) 121 °C, and (f) 126 °C. Scale bar shows 50 μm.

Depending on the preparation conditions, PLA crystallizes in three forms (α, β and γ). The α form is stable. It exhibits a well-defined diffraction pattern. De Santis et al. and W. Hoogsteen et al. described the structure of the α form as a 10/3 helical conformation with a fibre repeat distance of 28.8 Å. Sasaki and
Asakura\textsuperscript{50} analysed the $\alpha$ form of PLA using linked-atom least squares refinements for X-ray diffraction data, and found that the $\alpha$ form has an orthorhombic $P2_12_12_1$ space group, with a unit cell containing two antiparallel chains. The lattice parameters are: $a = 10.66$ Å, $b = 6.16$ Å, and $c$ (chain axis) = 28.88 Å, with a crystal density of 1.26 g/cm\textsuperscript{3}\textsuperscript{50}. The schematic representation of the $\alpha$ form is shown in Figure 10.

![Figure 10 Schematic representation of the coordinate system used in the Monte Carlo simulation. The view is along the helix axis (c-axis). Only the eight parent-chain helices are represented. Open and dashed circles represent positions of parallel and antiparallel antiparallel chains, respectively\textsuperscript{51}.](image)

Pan et al.\textsuperscript{52} found that the disordered $\beta$ crystalline form (sometimes referred to the $\alpha'$ form), which is generally formed during processing or annealing at lower temperatures, transforms into the more ordered $\alpha$ form. The chain conformation of $\beta$ form is a left handed 3-fold helix\textsuperscript{48,50}. This form has an orthorhombic unit cell containing a $3/1(3$ Å rise/1 monomeric unit) polymeric helix. The unit cell dimensions are as follows: $a=10.31$ Å, $b=18.21$ Å, $c=9.0$ Å\textsuperscript{48}. The differences
between the β and α forms can be observed by wide angle X-ray diffraction (WAXD) spectrometry and DSC analysis. Pan et al.\textsuperscript{52,53} also found that the β-α phase transition in lower molecular weight PLA occurs at lower temperatures compared to higher molecular weight PLA. The crystal structure of α 10/3 and β 3/1 helical conformation is shown in Figure 11.

The γ form, found by epitaxial crystallization, contains two antiparallel s(3/2) helices in the pseudoorthorhombic unit cell. The parameters of γ form are: \(a=9.95\text{ Å}, b=6.25\text{ Å}, c=8.8\text{ Å} \).
2.1.1.3 Processing

Poly (lactic acid) can be processed by injection moulding, sheet extrusion, blow moulding, thermoforming and film forming.

Hartmann\textsuperscript{23} and Garlotta\textsuperscript{28} reported that the molecular weight of PLA was reduced after extrusion and injection moulding. This phenomenon was used by Perego et al.\textsuperscript{54} to prepare PLA samples of different molecular weight. They also reported that injection moulding results in PLA that is generally amorphous because PLA has a slow crystallisation rate.

Tabi et al.\textsuperscript{55} found that during injection moulding of amorphous PLA, more and more pellets stuck to the surface of the screw and remained there from cycle to cycle. The pellets stuck on the screw even in the feed zone. Finally the pellets that were stuck on the screw destabilised the injection moulding process and prevented further processing until the barrel was cleaned. Tabi et al.\textsuperscript{55} suggested that this is because the amorphous phase of the pellets softens locally due to the significant exothermic heat of crystallisation accumulated at the surface of the pellets and the low heat transfer capability of the material, as shown in Figure 12. This problem can be solved by re-crystallisation of the amorphous PLA before injection.

Figure 12 Welded surface of pellets at 80°C by SEM with a magnification of 20(left) and 2000(right)\textsuperscript{55}
PLA may also degrade by heat generated during injection moulding. Migliaresi et al.\textsuperscript{56} found that the reduction of molecular weight was due to thermal degradation caused by chain scission. There was no oxidation of PLA observed in their experiments. Auras et al.\textsuperscript{25} reported that residual monomers could also play an important role in inducing early degradation of the polymer.

### 2.1.1.4 Mechanical Properties

General mechanical properties of PLA are shown in Table 1. Perego et al.\textsuperscript{54} reported that PLA with a high viscosity-average molecular weight had high tensile strength and modulus. Impact strength and the Vicat softening temperature increased with an increase of crystallinity. According to their results, annealed PLLA, which was highly crystallised, had the highest tensile strength, elasticity modulus, flexural strength, impact strength and Vicat penetration temperature. On annealing, the impact resistance increased due to the crosslinking effects of the crystalline domains\textsuperscript{37,57}, while the tensile strength increased, presumably due to the stereoregularity of the chain\textsuperscript{28,54}.

<table>
<thead>
<tr>
<th></th>
<th>PLLA</th>
<th>Annealed PLLA</th>
<th>Amorphous PLA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strength at break (MPa)</td>
<td>59</td>
<td>66</td>
<td>44</td>
</tr>
<tr>
<td>Strain at break (%)</td>
<td>7.0</td>
<td>4.0</td>
<td>5.4</td>
</tr>
<tr>
<td>Young’s modulus (MPa)</td>
<td>3750</td>
<td>4150</td>
<td>3900</td>
</tr>
<tr>
<td>Yield strength (MPa)</td>
<td>70</td>
<td>70</td>
<td>53</td>
</tr>
<tr>
<td>Flexural strength (MPa)</td>
<td>106</td>
<td>119</td>
<td>88</td>
</tr>
<tr>
<td>Unnotched izod impact (J/m)</td>
<td>195</td>
<td>350</td>
<td>150</td>
</tr>
<tr>
<td>Notched izod impact (J/m)</td>
<td>26</td>
<td>66</td>
<td>18</td>
</tr>
<tr>
<td>Rockwell hardness</td>
<td>88</td>
<td>88</td>
<td>76</td>
</tr>
<tr>
<td>Heat deflection temperature (°C)</td>
<td>55</td>
<td>61</td>
<td>50</td>
</tr>
<tr>
<td>Vicat penetration (°C)</td>
<td>59</td>
<td>165</td>
<td>52</td>
</tr>
</tbody>
</table>

Table 1 Mechanical Properties of PLA by injection moulding at 195°C\textsuperscript{28,54}

Tsuji and Ikada\textsuperscript{39} found similar results, showing that Young’s modulus increased
with increasing crystallinity. However, they found that tensile strength decreased when large spherulites were formed.

2.1.1.5 Degradation
PLA degrades by hydrolysis when the polymer is exposed to moisture over a period of time depending on the temperature. Polymer chains are shortened by random non-enzymatic chain scission of the ester groups, as shown in Figure 13. After this, biodegradation can occur, and PLA fragments with low molecular weight are converted to carbon dioxide, water and humus by microorganisms\textsuperscript{17}.

PLA degradability is driven by the hydrolysis and breakage of the ester linkage. It is auto-catalysed by carboxylic acid end groups and follows first order kinetics\textsuperscript{58}. Since the polymer degradation rate is determined by the polymer reactivity with water and catalysts, many factors such as particle size and shape, temperature, humidity, crystallinity, residual lactic acid concentration, molecular weight and
molecular weight distribution, water diffusion coefficient, acids and bases existing in the system, and metal impurities from catalysts, may affect the polymer degradation rate\textsuperscript{25}.

Tsuji et al.\textsuperscript{59, 60} investigated hydrolysis of PLLA film under different conditions. From a study of the hydrolysis of PLLA films in alkaline solution at 37°C, it appeared that hydrolysis of PLLA chains mainly occurred in the amorphous region. The rate of weight loss per unit surface area decreased linearly with an increase in the initial crystallinity, but the size of spherulite had no significant effect on the hydrolysis of the PLLA film\textsuperscript{60}. Tsuji et al.\textsuperscript{59} also found that on hydrolysis of the PLLA films at high temperature (97°C), the hydrolysis mechanism does not change when temperature is increased, but the hydrolysis mainly takes place in the chains in the amorphous region. The initial degradation occurring in the amorphous region was also observed in the work of Ohya et al.\textsuperscript{61}.

In addition, Tsuji et al.\textsuperscript{62} found different hydrolysis mechanisms appeared in different hydrolysis media, as shown in Table 2. In the system with proteinase K, PLA surface starts to lose weight at the beginning, indicating that exothermic chain scission occurs.

<table>
<thead>
<tr>
<th>Hydrolysis media</th>
<th>Hydrolysis mechanisms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkaline solution (pH 11.9±0.1)</td>
<td>Chain scission</td>
</tr>
<tr>
<td></td>
<td>Endothermic</td>
</tr>
<tr>
<td></td>
<td>Bulk</td>
</tr>
<tr>
<td>Phosphate-buffered solution (pH 7.4±0.1)</td>
<td>Endothermic</td>
</tr>
<tr>
<td></td>
<td>Surface</td>
</tr>
<tr>
<td>With proteinase K (1mg/5mL. pH 8.6±0.1)</td>
<td>Endothermic and exothermic</td>
</tr>
<tr>
<td></td>
<td>Surface</td>
</tr>
</tbody>
</table>

Table 2 Mechanisms of PLLA film in different hydrolysis media\textsuperscript{62}
In another research on hydrolysis of PLLA, Tsuji et al.\textsuperscript{63} found that the hydrolysis of the PLLA films proceeds homogeneously along the film cross section mainly by a bulk erosion mechanism. The durability of PLLA films in the acid solution is very similar to that in a neutral medium but higher than that in an alkaline medium. The ions and lactic acid oligomers and monomers present in the lactic acid monomer solution appear to have no significant catalytic effects on the hydrolysis of the PLLA chains.

According to Drumright et al.\textsuperscript{64}, hydrolysis of PLA can be accelerated by acids or bases and is affected by both temperature and moisture levels. In the research by Hoyn et al.\textsuperscript{65}, it was found that the residual monomer existing in PLA obviously increases degradation rate, leaves holes within the film during degradation and causes the polymer matrix to lose its mechanical strength, as shown in Figure 14.

![Figure 14 Tensile strength remaining after hydrolytic degradation of PLA containing different contents of monomer](image)
2.1.2 PLA Composites

PLA can be compounded with fillers such as talc and nanoclay to improve properties and reduce cost.

2.1.2.1 PLA composite with Talc

Talc is a trioctahedral layered phyllosilicate mineral with the chemical formula \([\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2]\)\(^{66}\). It is a secondary mineral formed through the hydrothermal degradation of magnesium-rich metamorphic rocks\(^{66, 67}\). Dolomite, calcite, chlorite and quartz are the most common impurities in talc\(^{68}\).

The structure of talc leads to a neutrally charged system with all vacancies satisfied and no net surface charge. The lamellar platelets are only held together by Van der Waals forces, thus talc is quite soft\(^{66}\). Douillard et al. \(^{69}\) also reported that the main places for chemical attack or amphiphilic reactions on talc surface are mineralogical defects and platelet edges. The crystal structure of talc is shown as Figure 15.

![Crystal structure of talc](image)

**Figure 15** Crystal structure of talc\(^{70}\)

Harris and Lee\(^{71}\) reported that the addition of talc not only results in an increased level of crystallinity, but also makes crystallisation faster; the isothermal crystallisation halftimes of PLA decreased nearly 65-fold by the
addition of 2% talc as shown in Figure 16. Yu et al.\textsuperscript{72} confirmed that talc has a significant nucleation effect and the cold crystallization decreased with increasing talc content. According to their result, the injection-moulded specimens of PLA/talc composites were still amorphous as the cooling process of all specimens was fast in injection moulding.

Figure 16 Isothermal crystallization half-times for PLA, PLA with 1% talc, with 1% talc +5% acetyl triethyl citrate (ATC), and with 1% talc +5% Polyethylene glycol (PEG)\textsuperscript{71}.

Talc can improve thermal stability and reduce flammability of PLA\textsuperscript{73}. Yu et al.\textsuperscript{72} reported that the thermal degradation temperature of PLA/talc composites were slightly higher than neat PLA. The increase of thermal degradation temperature was mainly attributed to the fact that talc filler dispersed in the PLA matrix and
obstructed diffusion of degradation products by creating a maze or tortuous path\textsuperscript{73}.

Talc has a significant reinforcing effect and toughening effect, as shown in Figure 17. Neat PLA exhibited the characteristics of brittle fracture behaviour and fractured with low elongation at break, meanwhile a few crazes were observed in the direction perpendicular to the tensile stress without necking. At the talc content range of 0–2.0\%, the strength increased significantly with increasing talc content. For PLA composites with 3-5 weight\% talc, samples failed with noted stress-whitening and necking phenomenon, which resulted in a higher elongation at break; however, the tensile strength is slightly lower\textsuperscript{72}.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure17.png}
\caption{Tensile Stress-strain curves of neat PLA (1) and PLA composites with 1 to 6\% talc(2-7)\textsuperscript{72}.}
\end{figure}

According to the SEM micrographs of the fracture surfaces of PLA composite specimens shown in Figure 18, the reinforcing effect of talc particles could be mainly attributed to the good interfacial adhesion between the PLA matrix and the orientated talc layers during processing\textsuperscript{72}. Interfacial debonding of PLA/talc
composite can induce massive crazing. Meanwhile talc particles in the PLA matrix can prevent void coalescence and propagation of the crazes\textsuperscript{72,74,75}. Thicker talc particles appeared in composites with higher talc content. They act as a stress concentration points or weak points and resulted in poor toughness of PLA/talc composites\textsuperscript{72}. 
Figure 18 SEM micrographs of the fracture surfaces of tensile specimens: (a) PLA, (b)-(g) PLA+1-6%talc at magnification of 600, (h) PLA+6%talc at magnification of 5000.\textsuperscript{72}
Layered silicates that are used to make nanocomposites generally have two particular characteristics: the ability of the silicate particles to disperse into individual layers; and the ability to fine-tune their surface chemistry through ion exchange reactions with organic and inorganic cations. The hydrophilic silicate surface needs to be converted to an organophilic one to increase the miscibility of the polymer matrix and layered silicate. This can be done by ion-exchange reactions with cationic surfactants including primary, secondary, tertiary, and quaternary alkylammonium or alkylphosphonium cations. Alkylammonium or alkylphosphonium cations in the organosilicates lower the surface energy of the inorganic host and improve the wetting characteristics of the polymer matrix, and result in a larger interlayer spacing. The alkylammonium or alkylphosphonium cations can also provide functional groups that can react with the polymer matrix, or in some cases initiate the polymerization of monomers to improve the strength of the interface between the inorganic and the polymer matrix.

The layered phyllosilicate structure is two tetrahedrally coordinated silicon atoms fused to an edge-shared octahedral sheet of either aluminium or magnesium hydroxide, as shown in Figure 19.
Layered silicates have layer thickness on the order of 1 nm and a very high aspect ratio between 10 and 1000. A few weight percentages of layered silicates that are properly dispersed throughout the polymer matrix thus create much higher surface area for polymer/filler interaction. Depending on the strength of interfacial interactions between the polymer matrix and layered silicate (modified or not), three different types of polymer layered silicates nanocomposites are thermodynamically achievable, as shown in Figure 20:

a. Intercalated nanocomposites: in intercalated nanocomposites, the insertion of a polymer matrix into the layered silicate structure occurs in a crystallographically regular fashion, regardless of the clay to polymer ratio. In intercalated nanocomposites the interlayer is normally a few molecular layers of polymer; 

b. Flocculated nanocomposites: conceptually this is same as intercalated nanocomposites. However, silicate layers are sometimes flocculated due to hydroxylated edge – edge interaction of the silicate layers;
c. Exfoliated nanocomposites: in an exfoliated nanocomposite, the individual clay layers are separated in a continuous polymer matrix by an average distances that depends on clay loading. Usually, the clay content of an exfoliated nanocomposite is much lower than that of an intercalated nanocomposite\textsuperscript{79}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{nanocomposites.png}
\caption{Schematic representation of three types of polymer/clay nanocomposites\textsuperscript{79,80}}
\end{figure}

According to Gao et al.\textsuperscript{81}, it is possible to expand interlayer distance of either a hydrophilic layered-silicate or an organophilic clay in a polymer simply by blending and compression of their solid mixture.

PLA nanocomposites can be solvent-cast blended as well. Ogata et al.\textsuperscript{82} mixed PLLA pellets with distearyldimethylammonium-exchanged organomontmorillonite and blended together in hot chloroform. After the chloroform was fully vaporized, 100 µm thick films remained. PLLA did not intercalate into the organoclay and tactoids of pure clay were detected parallel to the surface of the films. The clay platelets further aligned themselves to the film surface as the films were drawn out.

The effect of clay on crystallisation behaviour of PLA is not as obvious as talc. Boesel et al.\textsuperscript{83} prepared PLA 4032D composites with a high content of clay (Dellite 43B, montmorillonite modified with dimethylbenzylltallow ammonium ions) up to 80% in chloroform. They found that 50% of clay did not dramatically change the crystallisation behaviour of PLA, whereas 80% of clay severely
hindered crystallisation of the polymer, specially melt crystallisation, as shown in Table 3. They also found WVTR of PLA with 80% clay decreased from $15 \pm 7.0 \times 10^{-15}$ kg.m/m$^2$.s.pa without clay to about $1.4 \times 10^{-15}$ kg.m/m$^2$.s.pa$^{83}$.

<table>
<thead>
<tr>
<th>PLA (%)</th>
<th>$T_g$ (ºC)</th>
<th>$T_m$ (ºC)</th>
<th>$\chi_C$ (%)$^a$</th>
<th>$T_g$ (ºC)</th>
<th>$T_m$ (ºC)</th>
<th>$\chi_C$ (%)</th>
</tr>
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<tbody>
<tr>
<td>100</td>
<td>53</td>
<td>167</td>
<td>44</td>
<td>65</td>
<td>168</td>
<td>45</td>
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<td>20</td>
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<td>164</td>
<td>-</td>
<td>65</td>
<td>164</td>
<td>16</td>
</tr>
</tbody>
</table>

$^a$Calculated from the second heating curve.

Table 3 Thermal properties of composites before and after annealing, obtained during the first heating, except where Indicated Otherwise $^{83}$

Pluta et al. $^{84}$ developed PLA/clay nanocomposites loaded with 3 wt% organomodified montmorillonite and PLA/clay microcomposites containing 3 wt% sodium montmorillonite using melt blending. By investigating the morphological and thermal properties of the nanocomposites and microcomposites and comparing them with the unfilled PLA, they found that the unmodified clay-filled PLA formed a microcomposite with a phase-separated microstructure. They also reported that PLA is a polymer that readily interacts during melt blending with a montmorillonite organomodified with dimethyl 2-ethylhexyl (hydrogenated tallow alkyl) ammonium cations, leading to the formation of at least an intercalated structure, which led to the formation of a nanocomposite. Thermal investigations showed an improvement in the nanocomposite thermal stability under oxidative conditions in comparison to those for the microcomposite and unfilled PLA, as shown in Figure 21.
Figure 21 TGA and DTG traces recorded at 20°C/min under (a) air flow and (b) helium flow for (1) unfilled PLA, (2) PLA/clay microcomposite, and (3) PLA/clay nanocomposite.

Earlier PLA nanocomposites have been reported to give improvements in mechanical properties, barrier properties and biodegradability. The complete dispersion of clay nanolayers in a polymer optimises the number of available reinforcing elements that carry an applied load and deflect evolving cracks. The coupling between the large surface area of the clay and the polymer matrix
facilitates the stress transfer to the reinforcing phase allowing for the improvement of the tensile stress and toughness\textsuperscript{80,87,88,89}. Thellen et al.\textsuperscript{90} found that the Young’s modulus for the PLA nanocomposite samples was about 30–40\% greater than that of the neat polymer; however, incorporation of nanoclay into the PLA matrix produced no significant change in the tensile strength of the resulting films; elongation was about 16–40\% greater for the nanocomposite films than for the neat films.

Ogata et al.\textsuperscript{82} solvent-cast blended PLLA with organophilic montmorillonite using chloroform and found the loss tangent $\tan \sigma = E'/E''$ increased with increasing of clay content. The Young’s modulus of the PLLA/clay annealed blend and as-cast blend increased with increasing of clay content as well(Figure 22).

Figure 22 Effect of clay content on Young’s modulus of PLLA/clay blends\textsuperscript{82}
Nieddu et al.\textsuperscript{91} found PLA nanocomposites compounded with various types of nanoclay had improved properties of Young’s modulus, but the peak stress and strain at break slightly decreased in most cases, as shown in Figure 23.

Figure 23 Tensile test performed on nanocomposite samples. A: Young Modulus, B: peak stress, C: strain at break. M1-M11 are pure PLA 4042D; PLA+5\%Bentone SD2; PLA+10\%Bentone SD2; PLA+5\%Cloisite 30B; PLA+5\%Cloisite 30B; PLA+5\%Nanofil 804; PLA+10\%Nanofil 804; PLA+5\%Sepiolite CD1; PLA+10\%Sepiolite CD1; PLA+5\%Somasif MEE; PLA+10\%Somasif MEE \textsuperscript{91}.

Another advantage of nanocomposites is their enhanced barrier properties. The impermeable clay layers cause a tortuous pathway for a penetrant passing through the nanocomposite. The ‘tortuous path’ model is discussed in section 2.2.3. It is reported that gas permeability through polymer films can be significantly reduced even with small loadings of nanoclay. The relevant research on polymer–clay nanocomposite concerns mostly oxygen, carbon
dioxide and nitrogen barrier films for packaging food and carbonated drinks. Other applications include gas tanks and coatings.

The effect of nanoclay on barrier properties of PLA composite films depends on the type and amount of nanoclay added, as well as its dispersion and aspect ratio. Ray et al.\textsuperscript{92} reported that oxygen permeability of PLA was reduced from 200 ml.mm/m\(^2\).day.Mpa to about 150 ml.mm/m\(^2\).day.Mpa after 7 wt.% of nanoclay was added. Thellen et al.\textsuperscript{90} found that PLA nanocomposite blown films with 5 wt.% of nanoclay had better oxygen barriers than the pure PLA films, with a reduction up to 48% in oxygen permeation rate and a reduction of about 50% in water vapour permeation. Zenkiewicz and Richert\textsuperscript{93} reported that with 5 wt.% of Cloisite\textsuperscript{®} 30B added, the water vapour permeability decreased from about 120g/m\(^2\).day to about 68g/m\(^2\).day, with a reduction of 57% by value. They also found a reduction of 39% in oxygen transmission rate of PLA/nanoclay composite film compared with pure PLA\textsuperscript{93}.

Nanoclay can also improve biodegradability of PLA. Rhim et al.\textsuperscript{94} found that PLA composite films compounded with Cloisite\textsuperscript{®} 30B showed bacteriostatic activity against L. monocytogenes.

Ray et al.\textsuperscript{95} studied the biodegradability of PLA nanocomposites with clay organically modified by various types of surfactants (Table 4). They found the incorporation of various types of organically modified layered silicate in the PLA matrix resulted in a different mode of attack on the PLA component of the test samples which was possible due to the presence of each kind of modified salts and layered silicates. Since PLA is an aliphatic polyester, it is conceivable that incorporation of various types of organically modified layered silicate resulted in a different mode of disruption of some of the ester linkages, as shown in Figure 24.
Table 4 Characteristic parameters and designation of various organically modified layered silicate

<table>
<thead>
<tr>
<th>OMLS code</th>
<th>Pristine layered silicates</th>
<th>Surfactants used for the modification of pristine layered silicates</th>
<th>Particle length nm</th>
<th>CEC meq/100 g</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{15}MMT</td>
<td>montmorillonite</td>
<td>octadecylammonium cation</td>
<td>~150</td>
<td>110</td>
</tr>
<tr>
<td>qC_{18}-MMT</td>
<td>montmorillonite</td>
<td>dioctadecyldimethylammonium cation</td>
<td>~100</td>
<td>90</td>
</tr>
<tr>
<td>qC_{16}-MMT</td>
<td>montmorillonite</td>
<td>octadecyltrimethylammonium cation</td>
<td>~100</td>
<td>90</td>
</tr>
<tr>
<td>qC_{16}-SAP</td>
<td>saponite</td>
<td>hexadecyltributylphosphonium cation</td>
<td>~50</td>
<td>86.6</td>
</tr>
<tr>
<td>qC_{13}(OH)-mica</td>
<td>synthetic fluorine mica</td>
<td>N-(cocoalkyl)-N,N-[bis(2-hydroxyethyl)]-N-methylammonium cation</td>
<td>200–300</td>
<td>120</td>
</tr>
</tbody>
</table>

CEC is the cation exchange capacity and generally expressed as meq/v100 g.

Figure 24 Time dependence of (a) degree of biodegradation (i.e. CO2 evolution); (b) change of matrix Mw of PLA and PLA nanocomposites in compost.
Nieddu et al.\textsuperscript{91} reported PLA/nanoclay composites have higher lactic acid release rate and rate of weight loss that pure PLA (Figure 25); the effect of nanoclay on degradation rate of PLA depends on:

a. interaction between clays and matrix;

b. the percentage of clay;

c. the quality of clay.
Figure 25 Weight loss of PLA nanocomposites with respect to pure PLA at increasing times of plasma incubation M1-M11 are pure PLA 4042D; PLA+5%Bentone SD2; PLA+10%Bentone SD2; PLA+5%Cloisite 30B; PLA+5%Cloisite 30B; PLA+10% Nanofil 804; PLA+10% Nanofil 804; PLA+5% Sepiolite CD1; PLA+10% Sepiolite CD1; PLA+5% Somasif MEE; PLA+10% Somasif MEE.
Fukushima et al.\textsuperscript{96} prepared amorphous PLA nanocomposites with 4 wt.% organic modified kaolinite and montmorillonite and then biodegraded these in compost. They found the addition of nanoclays increases the PLA degradation rate, especially for kaolinite, due to the presence of hydroxyl groups belonging to the silicate layers of these clays. Addition of montmorillonite to PLA also has a catalytic effect on polymer degradation in compost, but only in the last stages of degradation. In the early stages, montmorillonite tends to delay the degradation of PLA probably due to its higher dispersion level into the polymer matrix as compared to kaolinite, creating a barrier effect of montmorillonite layers towards water hydrolysis at PLA ester groups.

Figure 26 Remaining mass of PLA, PLA/kaolinite and PLA/montmorillonite as a function of degradation time in compost\textsuperscript{96}

### 2.1.3 Polybutylene succinate

Polybutylene succinate (PBS), also named as poly(tetramethylene succinate), is a synthetic aliphatic polyester. It has received much attention recently because of its excellent biodegradability, thermoplastic processability and balanced mechanical properties\textsuperscript{11}. The molecular structure of PBS is shown in Figure 27.
Succinic acid and 1,4-butanediol are the two monomers used in PBS synthesis.

![Molecular structure of polybutylene succinate](image)

Figure 27 Molecular structure of polybutylene succinate

2.1.3.1 Monomers

Succinic acid is synthesized through a petro chemical process that requires high temperature and pressure. A new method is being developed to produce succinic acid by bacterial fermentation of agricultural carbohydrates. H. Song and S. Y. Lee found the best candidates for succinic acid production are A. succinogenes, M. succiniciproducens and A. succiniciproducens by PEP carboxylation pathway to form succinic acid. The pathways are shown in Figure 28. The enzymes that catalyse the reactions competing with the succinic acid pathway, such as pyruvate kinase, phosphotransacetylase/acetate kinase, lactate dehydrogenase, pyruvate formate lyase and alcohol dehydrogenase are responsible for the formation of by-products. The production strains, fermentation process, fermentation media, operating conditions and filtration have been improved to increase the yield of succinic acid.
1,4-butanediol can be obtained by the reduction of succinic acid. Deshpande et al. developed a method to hydrogenate succinic acid to γ-butyrolactone and 1,4-butanediol using ruthenium–cobalt bimetallic catalysts, as shown in Figure 29. Minh et al. found bio-succinic acid from a fermentation process is efficiently hydrogenated on 4 wt%Re – 2 wt% Pd/Co to 1,4-butanediol without significant loss of selectivity.
2.1.3.2 Synthesis of PBS

PBS is synthesized by a two-step melt polycondensation reaction of succinic acid and 1,4-butanediol, as shown in Figure 30. PBS synthesis can be carried out with titanium (IV) isopropoxide\textsuperscript{106,107,108}, titanium (IV) isobutoxide\textsuperscript{109}, titanium (IV) n-butoxide\textsuperscript{110,111,112,113}, zirconium (IV) n-butoxide\textsuperscript{110}, tin 2-ethylhexanoate\textsuperscript{110}, antinomy (III) n-butoxide\textsuperscript{110}, hafnium (IV) n-butoxide\textsuperscript{110}, bismuth neodecanoate\textsuperscript{110}, scandium(III) triflate [Sc(OTf)\textsubscript{3}] or scandium(III) trifluoromethanesulfonimide [Sc(NTf\textsubscript{2})\textsubscript{3}]\textsuperscript{115,116}, and Stannic components, such as...
Pranamuda et al.\textsuperscript{106} removed 1,4-butenediol in polycondensation of PBS at 200 °C in a vacuum with isopropyl titanate(IV) as a catalyst, then the polymer was purified by precipitation in methanol after being dissolved in chloroform. By using this method they produced PBS with a number average molar mass of 5.74x10\textsuperscript{4} g/mol. Takasu et al.\textsuperscript{115,116} used Sc(OTf)\textsubscript{3} or Sc(NTf\textsubscript{2})\textsubscript{3} as catalysts in bulk polycondensation of SA with BDO at 35 °C for over 50 hours, and produced PBS with a number average molar mass of 0.5-1.2 x10\textsuperscript{4} g/mol. M. Ishii et al.\textsuperscript{117} developed distannoxane-catalyzed polycondensation of aliphatic dicarboxylic acids and aliphatic diols in a two-phase system of solvent and molten polymer in the presence of 0.001 mol. % of 1-chloro-3-hydroxy-1,1,3,3-tetrahydrodistannoxane for 24-80 hours, and produced PBS with a weight average molar mass of 2.77x10\textsuperscript{5} g/mol. Buzin et al.\textsuperscript{114} used bismuth based compounds for the synthesis of aliphatic polyesters from direct polycondensation of dicarboxylic acid at 80 °C for over 48 hours, and obtained the final product with a number average molar mass of 3 x10\textsuperscript{4} g/mol. By using various types of catalysts in polycondensation of PBS, Jacquel et al.\textsuperscript{110} found that with regard to the reduced viscosity variation during the transesterification step, the efficiency of catalysts is: Ti > Ge > Zr- Sn > Hf > Sb > Bi, as shown in Table 5; however, although Ti-based catalysts are highly efficient, they should be
used with caution due to the degradation reaction that they induce.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>ppm</th>
<th>η_{red} (mL g⁻¹)</th>
<th>η_{red} variation (mL g⁻¹ min⁻¹)</th>
<th>Mn (g mol⁻¹)</th>
<th>PDI</th>
<th>CC (l mol⁻¹)</th>
<th>Yellowness index</th>
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<td>99</td>
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<td>Sb(OBu)₃</td>
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<tr>
<td>Bi(ODec)₂</td>
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<td>65</td>
<td>0.18</td>
<td>–</td>
<td>–</td>
<td>18</td>
<td>1.4</td>
</tr>
</tbody>
</table>

* ppm of metal present in the final polymer.
* Reduced viscosity of the final polymer reported on the transesterification time.
* Measured by SEC in HFP with PMMA standards.
* Polydispersity index.
* Carboxylic acid end-groups content.

Table 5 Characterization of PBS prepared with various organometal catalysts (transesterification temperature = 230 °C, butanediol excess = 5 mol %) 110

2.1.3.3 Properties

PBS is a white semi-crystalline thermoplastic. By differential scanning calorimeter at a scanning rate of 20 °C/min, the glass transition temperatures of PBS is reported to be about −32 °C, and melting point is 114 °C 108,119,120. However, the glass transition temperature of PBS is about −36 °C, and the melting point is 116 °C at a scanning rate of 10 °C/min 121. Miyata and Masuko 122 calculated the exothermic enthalpy of crystallization for a large crystal of infinite size to be 200 J/g⁻¹, according to the linear relationship between exothermic enthalpy change and density for the PBS film and considering the density of the PTMS crystal (α-form) to be 1.34 g/cm³. By comparing the thermal properties of PBS prepared by using different catalysts, Jacquel et al. 110 found that PBS synthesized with Ti, Zr and Sn based catalysts has similar glass transition temperatures, crystallization temperatures, melting temperatures and degree of crystallinity. Copolymers synthesized with GeO₂/lactic acid based catalysts are random copolyesters which exhibit decreasing of both melting temperature (from
110 °C for 2.4 mol. % of lactic acid to 102 °C for 6.9 mol. % of lactic acid), crystallization temperatures (from 56 °C for 2.4 mol. % of lactic acid to 29 °C for 6.9 mol. % of lactic acid) and degree of crystallinity (from 31% for 2.4 mol. % of lactic acid to 26% for 6.9 mol. % of lactic acid). The glass transition temperature remains unchanged (approximately −30°C), as shown in Table 6.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>ppm</th>
<th>LA/PBS (mol %)</th>
<th>η&lt;sub&gt;red&lt;/sub&gt; (mL g&lt;sup&gt;−1&lt;/sup&gt;)</th>
<th>T&lt;sub&gt;g&lt;/sub&gt; (°C)</th>
<th>T&lt;sub&gt;c&lt;/sub&gt; (°C)</th>
<th>T&lt;sub&gt;m&lt;/sub&gt; (°C)</th>
<th>x&lt;sub&gt;c&lt;/sub&gt; (%)</th>
<th>T&lt;sub&gt;d10&lt;/sub&gt; (°C)&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti(OCMe)&lt;sub&gt;3&lt;/sub&gt;</td>
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<td>0</td>
<td>209</td>
<td>−31</td>
<td>66</td>
<td>114</td>
<td>32</td>
<td>355</td>
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<tr>
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<td>115</td>
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<td>351</td>
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<td>343</td>
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<td>−</td>
<td>116</td>
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<td>205</td>
<td>−31</td>
<td>69</td>
<td>114</td>
<td>32</td>
<td>351</td>
</tr>
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<td>Sn(OCT)&lt;sub&gt;2&lt;/sub&gt;</td>
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<td>0</td>
<td>126</td>
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<td>117</td>
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<td>114</td>
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<td>340</td>
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<td>LA/GeO&lt;sub&gt;2&lt;/sub&gt;a</td>
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<td>−29</td>
<td>29</td>
<td>102</td>
<td>26</td>
<td>365</td>
</tr>
</tbody>
</table>

<sup>a</sup> For a lactic acid/Ge molar ratio of 105.
<sup>b</sup> ppm of metal present in the final polymer.
<sup>c</sup> Degree of crystallinity calculated with ΔH<sub>PES</sub> = 210 J g<sup>−1</sup>
<sup>d</sup> Temperature recorded at 10 wt % loss in N<sub>2</sub> atmosphere.

Table 6 Thermal properties of PBS prepared by using various organometal catalysts at 230 °C with a butanediol excess of 5 mol. %. η<sub>red</sub> is the reduced viscosity.<sup>110</sup>

There are two forms of crystal structures in PBS. The β form appears with the application of stress. These two modifications belonged to the monoclinic system with the space group of P2₁/n. For the α form, the cell dimensions were a = 0.523 nm; b = 0.912 nm; c (fibre axis) = 1.090 nm; and β = 123.9°; for the β form, a = 0.584 nm; b = 0.832 nm; c (fibre axis) = 1.86 nm; and β = 131.6°, as shown in Figure 31. The difference in the fibre periods of the two crystalline forms is attributed mainly to the conformational difference in the tetramethylene unit.<sup>123</sup>
Figure 31 Crystal structures of PBS (a) for the α form; (b) for the β form. All hydrogen atoms are omitted.\textsuperscript{\textsuperscript{123}}
PBS is a soft polymer. According to the material datasheet of EnPol® G4560 produced by IRE Chemicals Ltd., that grade of PBS has a tensile strength of 40MPa and Elongation at break of 150%. Cao et al.\textsuperscript{121} measured mechanical properties of PBS, poly caprolactone(PCL) and their co-polymer film samples at a drawing rate of 10mm/min, the results shows PBS has a modulus of elasticity of 286 MPa, yield stress of 26.5 MPa, fracture stress of 28.8 MPa, and fracture strain of 278%. By comparing mechanical properties of poly(ethylene succinate) (PES), poly(propylene succinate) (PPS) and PBS, Bikiaris and Achilias\textsuperscript{113} found that the mechanical properties are both synthesis temperature and polyester type dependent; an increase in temperature leads to higher tensile strengths and Young's modulus which is a result of the higher average molecular weight of the samples produced, as shown in Figure 32.
Figure 32 Young's modulus, tensile strength, and elongation at break versus polycondensation temperature of PES, PPS and PBS.
2.1.3.4 Biodegradation

PBS can biodegrade in a liquid culture\textsuperscript{106,124}, in compost\textsuperscript{125,126}, and in soil\textsuperscript{127}.

Pranamuda et al.\textsuperscript{106} found that in liquid cultures with PBS powder, strain HT-6, an actinomycete, showed the highest degrading activity. It assimilated about 60\% of the ground PBS powder after 8 days of cultivation. They also found that degradation of PBS film by the strain occurred in two steps: fragmentation, and then the formation of hemispherical holes on the surface of the film.

In composting test, Zhao et al.\textsuperscript{126} found there are three phases during the degradation process, as shown in Figure 33. At the beginning, the degradation of PBS is slow; a small amount of random hydrolytic cleavage of ester linkages takes place within the polymer bulk in this phase, and this cleavage is nonenzymatic. But most of the fragments formed in this stage were large and remained relatively immune to microbial attack. Then there is a rapid increase in the biodegradation rate. It is possible that the molecular weight of the polymer decreases to a point where the scission produces fragments small enough to diffuse from the polymer bulk and be attacked by microorganisms. At a certain level of degradation rate, the biodegradation rate reduces.

![Figure 33 Biodegradation of PBS samples in compost\textsuperscript{126}](image-url)
Abe et al.\textsuperscript{127} found fungal strain WF-6, belonging to \textit{Fusarium solani}, could degrade PBS in soil environments. As shown in Figure 34, Strain WF-6 degraded 2.8% of the PBS in a 14-day experimental run in a sterile soil environment. The degradability of strain WF-6 is enhanced by co-culturing with bacterial strain \textit{Stenotrophomonas maltophilia} YB-6. However, YB-6 cannot degrade PBS by itself.

![Figure 34](image)

Figure 34 Degradation of PBS in soil environments, A-2: soil with strains WF-6; B-2: soil with strains YB-6, and C-2: soil with strains WF-6 + YB-6\textsuperscript{127}.

### 2.1.4 Cellulose

Cellulose, with the formula $\left(C_6H_{10}O_5\right)_n$, is a very common organic compound which forms the primary cell wall of green plants. A study shows more than 40% of a tree is cellulose\textsuperscript{128}. Cellulose is a type of polysaccharide consisting of a regular linear chain of $1\rightarrow4$ linked $\beta$-D-glucose units\textsuperscript{16,129}. The structure of cellulose is shown in Figure 35.
The name “cellulose” was first given by Payen in the 19\textsuperscript{th} century. However, the study of cellulose in chemistry really started around 1940s by Phillips\textsuperscript{131} and Reid et al.\textsuperscript{132}.

Each cellulose chain may consist of a D-glucose unit with a C\textsubscript{4}-OH group and another with an C\textsubscript{1}-OH group at each end. Additional carbonyl and carboxyl groups exist in industrial cellulose after the isolation and purification processes. According to the experimental results obtained by Röhrling et al.\textsuperscript{133} these carbonyl groups can affect the molecular weight distribution of cellulose.

Cellulose can be produced in different ways, as shown in Figure 36. Since plants contain a lot of cellulose, they are also the main resource of cellulose production. Cotton is a good resource, as its seed hairs are almost pure cellulose, with small amounts of waxes and pectin. Chemical pulping of wood is another way to produce cellulose. This is a process in which the fibre cementing material is dissolved and separated\textsuperscript{134}.  

Figure 35 Structure of cellulose\textsuperscript{130}
Some bacteria (such as Acetobacter and Acanthamoeba), algae (such as Valonia) and fungi can produce cellulose as well\(^1\)\(^{135,136}\). By selecting the substrates, cultivation conditions, additives and bacteria, the molecular weight and supramolecular structure of cellulose can be controlled. The cellulose produced by bacteria has a high degree of polymerisation (DP), with the value of 2000-8000. This is higher than cellulose produced from wood pulps, in which the value is typically 300-1700\(^1\)\(^{135}\). The degree of crystallinity can reach up to 90%.

In addition, synthesis of cellulose in vitro has been achieved by Nakatsubo et al.\(^1\)\(^{137}\). They used a cationic ring-opening polymerisation of 3,6-di-O-benzyl-α-D-glucose 1,2,4-orthopivalate and removal of the proactive groups. The final product was identical to cellulose triacetate.

Cellulose can be transformed into many derivatives, such as cellulose esters, giving them different characteristics for various applications. Cellulose esters are cellulose with hydroxyl groups reacted with acids, for example, acetic acid (cellulose acetate). By reducing the number of hydroxyl groups, the hydrogen
bonding between polymer chains is decreased. As a result, cellulose acetate is amorphous and transparent. However, it has limited resistance to heat and water vapour permeation. Cellulose acetate can be coated with poly(vinylidene chloride) to improve its barrier properties\textsuperscript{138}.

The Mechanical properties of cellulosic plastics and films are shown in Table 7. It can be seen that cellulose acetate butyrate has the highest flexibility, but is weak in compression compared with other cellulosics; cellophane film has the highest tensile strength; ethyl cellulose film has the best resistance to tearing and folding. Due to the high crystallinity and structure, cellulose produced by bacteria has high tensile strength and Young’s modulus. It is currently used by Sony Corp. for headphone and loudspeaker membranes because of its good mechanical properties\textsuperscript{135}.

As Walker and Wilcon cited in their review\textsuperscript{139}, enzymatic hydrolysis of cellulose occurs by reactions involving five steps:

(1) transfer of enzymes from the bulk aqueous phase to the surface;
(2) adsorption of enzymes and formation of enzyme-substrate complexes;
(3) hydrolysis of cellulose;
(4) transfer of the celloextrins, glucose and cellobiose from the surface to the bulk aqueous phase, and
(5) hydrolysis of celloextrins and cellobiose into glucose in the aqueous phase.
Fan and Lee\textsuperscript{140} found that adsorption of enzymes and the formation of enzyme-substrate complexes are critical steps in the enzymatic hydrolysis of cellulose and are influenced by the structural features of cellulose, the mode of interaction between the celluloses and the cellulose fibre, the nature of the celluloses employed and susceptibility of the enzymes to product inhibition. In addition, degree of crystallinity also obviously affects the hydrolysis rate since the crystalline region is more difficult for enzymes to attack\textsuperscript{141}.

Although cellulose is biodegradable, its derivatives, affected by constituents along the chain, may not undergo biodegradation.

\textbf{2.1.5 Polyhydroxyalkanoates (PHA)}

Polyhydroxyalkanoates are a family of biological polyesters containing (R)-3HA monomer units\textsuperscript{142}. PHA is optically active with asymmetric carbon atoms existing

<table>
<thead>
<tr>
<th></th>
<th>Cellophane</th>
<th>Cellulose acetate</th>
<th>Cellulose acetate(high-acetyl)</th>
<th>Cellulose acetate-butyrate</th>
<th>Cellulose nitrate</th>
<th>Ethyl cellulose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young's modulus (x10^3MPa)</td>
<td>0.59-2.8</td>
<td>0.69-2.4</td>
<td>0.48-1.4</td>
<td>1.3-1.5</td>
<td>0.69-2.1</td>
<td></td>
</tr>
<tr>
<td>Strain at break for plastic [%]</td>
<td>6-70</td>
<td>4-55</td>
<td>40-88</td>
<td>40-45</td>
<td>5-40</td>
<td></td>
</tr>
<tr>
<td>Strain at break for plastic [%]</td>
<td>15-45</td>
<td>15-45</td>
<td>60-70</td>
<td>30-40</td>
<td>30-65</td>
<td></td>
</tr>
<tr>
<td>Tensile strength for plastic (MPa)</td>
<td>13-59</td>
<td>21-55</td>
<td>18-48</td>
<td>48-55</td>
<td>14-55</td>
<td></td>
</tr>
<tr>
<td>Tensile strength for film (MPa)</td>
<td>124-193</td>
<td>34-83</td>
<td>41-62</td>
<td>69-76</td>
<td>48-69</td>
<td></td>
</tr>
<tr>
<td>Flexural strength (MPa)</td>
<td>14-110</td>
<td>24-90</td>
<td>12-64</td>
<td>62-76</td>
<td>28-83</td>
<td></td>
</tr>
<tr>
<td>Compressive strength (MPa)</td>
<td>90-248</td>
<td>96-248</td>
<td>52-152</td>
<td>152-241</td>
<td>69-241</td>
<td></td>
</tr>
<tr>
<td>Notched izod impact strength (J/m)</td>
<td>21-277</td>
<td>21-277</td>
<td>43-336</td>
<td>267-373</td>
<td>107-427</td>
<td></td>
</tr>
<tr>
<td>Tearing strength (g)</td>
<td>2-10</td>
<td>2-25</td>
<td>4</td>
<td></td>
<td>7-36</td>
<td></td>
</tr>
</tbody>
</table>

Table 7 Mechanical properties of cellulosic plastics and films\textsuperscript{139}
According to Steinbüchel and Valentin\textsuperscript{143}, biosynthesis of PHA in bacteria can be divided into three metabolic phases, as shown in Figure 37. At the beginning, a suitable carbon source for biosynthesis enters the cell from the environment. This is achieved either by a specific transport system located in the cytoplasmic membrane or just by diffusion of the compound into the cell. After that, the compound is converted by abolic and/or catabolic reactions. Finally, PHA synthase uses these thioesters as substrates and catalyses the formation of the ester bond.

![Figure 37 An illustration of PHA biosynthesis\textsuperscript{143}](image)

PHA can be synthesised by many bacteria. However, PHA synthase is the key enzyme which determines the types of PHA synthesised by the micro-organism\textsuperscript{143,144}. The synthase is only active with hydroxyalkanoate (HA) monomers with an R configuration.

Steinbüchel et al.\textsuperscript{145} categorised PHA synthase into three general types according to their primary structures and substrate specificities. The first type of PHA synthase is represented by \textit{R. eutropha}. It includes those which are active to HA monomers of short chain length, such as 3-, 4- and 5-HA monomers containing 3 to 5 carbon atoms. The second type of PHA synthase is
represented by *P. oleovorans*. The PHA synthase is active to (R)-3HA monomers with 6-14 carbon atoms. The third type of PHA synthase is represented by *C. vinosum*. Unlike the other two types, the third type of PHA synthase consists of two subunits named as C- and E- subunits. Both of the subunits are necessary for PHA synthesis, and generally prefer to act with HA monomers of short chain length\textsuperscript{143}.

As shown in Figure 38, the biosynthesised 3-hydroxyalkanoic acids are in the R-configuration because of the stereo-specificity of the polymerising enzyme, PHA synthase. It may be clearly observed with a phase contrast light microscope because of high refractivity\textsuperscript{144}.

![Figure 38 General molecular structure of PHA\textsuperscript{146}](image)

When the R group is CH\textsubscript{3}, it is poly-3-hydroxybutyrate (PHB), the most common member of the PHA family, which belongs to the category of short chain length PHA. Its glass-transition and melting temperatures are about 4°C and 180°C respectively\textsuperscript{144,147}. According to research by Barham et al.\textsuperscript{147}, the spherulite growth rate of PHB reaches a maximum in the temperature range of 70 to 80°C, as shown in Figure 39. PHB was reported to be 55-80% crystalline when it was isolated from bacteria\textsuperscript{148}, and to be about 90% crystalline after storage at room temperature\textsuperscript{147}.
Physical properties of PHB are shown in Table 8. It is notable that PHB is very brittle and stiff. PHB can be toughened by annealing because of its good crystallisability, and smaller spherulites are formed\textsuperscript{144}. A more common way to improve physical properties of PHB is to have poly-3-hydroxybutyrate copolymerised with other hydroxyalkanoates such as hydroxyvalerate. The copolymer, poly (hydroxybutyrate-co-hydroxyvalerate) (PHBV), has a lower crystallinity compared to PHB, thus it becomes more ductile, the strength and melting temperature decrease as well. An increase of hydroxyvalerate content can further weaken forces between PHB chains and decrease the order of polymer chains, resulting in a reduction in crystallinity, glass-transition temperature, melting temperature, and strength\textsuperscript{144,149}.

Figure 39 Variation in crystal growth rates with temperature\textsuperscript{147}
PHB shows rapid thermal degradation above 190°C, giving it a very narrow processing window and limiting its applications. The chain scission during thermal degradation results in a decrease in molecular weight and strength. This thermal degradation can be reduced by introducing plasticizers which can reduce melting temperature.

PHA is capable of being completely degraded by microorganisms including bacteria and fungi in various environments such as soil, sea water and lake water. Mergaert et al. studied the degradation of PHB and P(3HB-co-10\%3HV) in soil at constant temperatures. They found the weight loss rate of polymer depends on the polymer and the soil. In addition, the copolymer loses weight faster than the homopolymer in the same conditions.

Doi et al. tested degradation of PHB and its copolymers in sea water. Their results showed that the rate of surface erosion was almost independent of the copolymer composition, but strongly dependent on temperature of the sea water.

Kumagai et al. found that for the enzymatic degradation of PHB films at 37°C, the rate of enzymatic degradation of PHB films decreases with an increase in

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_w$ (g/mol)</td>
<td>$1 \times 10^4 - 3 \times 10^6$</td>
</tr>
<tr>
<td>Density (crystal) (g/cm$^3$)</td>
<td>1.26</td>
</tr>
<tr>
<td>Density (amorphous) (g/cm$^3$)</td>
<td>1.18</td>
</tr>
<tr>
<td>Young's modulus (GPa)</td>
<td>3.5</td>
</tr>
<tr>
<td>Tensile Strength (MPa)</td>
<td>43</td>
</tr>
<tr>
<td>Extension to break</td>
<td>5%</td>
</tr>
<tr>
<td>Notched izod impact strength (J/m)</td>
<td>50</td>
</tr>
</tbody>
</table>

Table 8 Physical properties of PHB
degree of crystallinity, but it is not affected by the size of spherulite. They suggested that hydrolysis of the PHB chains would firstly start in the amorphous region on the surface of the films, and then extend to the crystalline region.

2.2 Barrier properties

Barrier properties are important for packaging materials to control the permeation of water, gases, etc.\textsuperscript{156}. According to Crank and Park\textsuperscript{157}, transport of gases in and through polymers can be divided into five stages, as shown in Figure 40.

The five stages are:
1. Diffusion through the surface layer of the side of higher penetrant concentration (upstream side);
2. Absorption of gas by the polymer (by chemical affinity or/and by solubility);
3. Diffusion of gas inside the polymer membrane;
4. Desorption of gas at the side of lower penetrant concentration;
5. Diffusion of gas through surface layer of the downstream side.
For a single-layer homogeneous polymer, steps 1 and 5 are negligible. Therefore, the process can be simplified to three steps: condensation and solution of the penetrant at the upstream side of the polymer; then diffusion driven by the concentration gradient; finally, evaporation at the downstream side. In the permeation of non-condensable gases in polymeric membranes in a short period of time, little gas is absorbed by the polymer because interactions between the penetrant and the polymer are weak. Permeation of soluble liquid vapours, such as water in cellulose, shows a concentration dependence of both diffusivity and solubility because the interactions between the penetrant and the polymer are strong.

2.2.1 Theories of Diffusion

2.2.1.1 Fick’s Laws of Diffusion and Film Permeation

The flux (J) is the amount of substance diffusing across unit area in unit time,
given by:

\[ J = \frac{Q}{At} \]  \hspace{1cm} (2)

Where \( Q \) is the amount of penetrant which has passed through the membrane during the time \( t \), and \( A \) is the surface area of the membrane.

Fick’s first law\(^{163} \) is the fundamental law of diffusion. It states that in the steady state where concentration \( c \) is independent of time, the flux in the x-direction (\( J_x \)) is proportional to the concentration gradient (\( \frac{\partial c}{\partial x} \)):

\[ J_x = -D \left( \frac{\partial c}{\partial x} \right) \]  \hspace{1cm} (3)

Where \( D \) is the diffusion coefficient.

When diffusion is limited to one direction and diffusion coefficient is dependent on absorbed penetrant concentration, Fick’s second law can be simplified to\(^{159} \):

\[ \frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left[ D(c) \frac{\partial c}{\partial x} \right] \]  \hspace{1cm} (4)

For a film of thickness (\( l \)) and area (\( A \)) separating two chambers of permeable gas or vapour at different pressures, the gas will then permeate through the film. Assume that there is no permeation at zero time and the gas pressure in both chambers are steady at \( p_1 \) and \( p_2 \). The amount of gas to permeate the membrane \( Q \) is given by\(^{159} \):

\[ \frac{Q}{lC_1} = \frac{Dt}{l^2} - \frac{1}{6} - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp \left( -\frac{Dt}{l^2} \pi^2 n^2 \right) \]  \hspace{1cm} (5)

Where \( C_1 \) is the concentration of penetrant at surface of the film and chamber 1. As shown in Figure 41, when \( t \rightarrow \infty \), \( Q \) and \( t \) show a linear relationship, and equation (5) can be simplified to:

\[ Q = \frac{DC_1}{l} \left( t - \frac{l^2}{6D} \right) \]  \hspace{1cm} (6)
The intercept on the time axis is known as the time lag $\tau$. Assume the penetrant concentration gradient within membrane is constant, the diffusion coefficient $D$ can be determined by:

$$D = \frac{l^2}{6\tau}$$

(7)

This it called the time lag method developed by Barrer$^{160}$. 

In the linear region of Figure 41, penetrant concentration in the film tends to be constant, ($\frac{\partial c}{\partial t} = 0$). Therefore, this is steady state diffusion, and Fick’s first law can be applied. The flux is given by Equation (2) and (3) i.e.

$$J = \frac{Q}{At} = -\frac{D(C_2 - C_1)}{l}$$

(8)

Where $C_1$ and $C_2$ are the concentrations of penetrant at the surface of the film and chamber 1 and 2.

Assuming that Henry’s law applies at the interfaces, then the solubility coefficient, $S$, is given by:
\[ S = \frac{C_1}{p_1} = \frac{C_2}{p_2} \]  \hspace{1cm} (9)

By combining equation (8) and (9), the total amount of gas or vapour that has passed through the film is:

\[ Q = -DAf(C_2 - C_1)/l = -DSf(p_2 - p_1)/l \]  \hspace{1cm} (10)

Based on this equation, the gas permeability coefficient \( P \), which equals to \( D \) time \( S \), can be determined\textsuperscript{159}:

\[ P = DS = \frac{Ql}{At\Delta p} \]  \hspace{1cm} (11)

2.2.1.2 Diffusion Mechanisms\textsuperscript{156,157,162,164,165}

Diffusion of gas in a polymer membrane can be classified into three categories depending on the interactions and relative mobility of penetrant and polymer:

(1) Case I (Fickian): diffusion rate is much smaller than the relaxation rate of the polymer matrix, the system attains sorption equilibrium quickly, and the boundary conditions are independent of time and swelling kinetics.

(2) Case II (non-Fickian): diffusion rate is much higher than the relaxation rate of polymer and sorption has a strong dependence on swelling kinetics. A sharp boundary of penetrant moving inwards from surface with constant velocity can be observed in this case.

(3) Anomalous: diffusion and polymer relaxation rates are comparable. The penetrant motion is affected by chemical structure of the polymer.

The mechanism of diffusion can be ascertained by fitting the sorption results to the following equation\textsuperscript{164}:

\[ \frac{M_l}{M_\infty} = kt^n \]  \hspace{1cm} (12)
Where $M_t$ is the mass uptake at time $t$, $M_\infty$ is the mass uptake at equilibrium, and $k$ is a constant. The value of $n$ indicates the type of diffusion mechanism that occurs. For Fickian diffusion, $n = 0.5$; for non-Fickian diffusion (Case II), $n = 1$; and for anomalous diffusion $n$ shows an intermediate value, i.e. $0.5 < n < 1^{162}$.

The diffusion mechanism may change with changes in temperature (compared with $T_g$) and penetrant activity.

### 2.2.2 Factors affecting permeability

According to Thomas$^{162}$, temperature and the concentration of gas within the polymer are the two major factors affecting gas permeability. Other factors, such as the nature of the polymer and the gas, crystallinity, orientation, crosslinking and plasticizers also affect permeability$^{162}$.

#### 2.2.2.1 Temperature

Temperature can affect gas permeability by changing the segmental motions of polymer chains and interactions between polymer chains$^{166}$. According to Rogers$^{165}$, an increase in temperature increases polymer chain segment motion and this provides more free volume in a rubbery polymer and allow more small gas molecules to pass through. Koros and Paul$^{167}$ tested permeation of carbon dioxide through PET at different temperatures between 25 -115°C. They found that the diffusion coefficient was more sensitive to temperature than to solubility, and the permeability coefficient increased with increasing temperature.

#### 2.2.2.2 Concentration and Pressure

As the polymer matrix “swells” because of absorbed gases, the free volume of the polymer increases if there is no strong interaction between the polymer and the gas molecules. The effect of gas concentration is then similar to that of temperature. However, since interactions of polymer chains and the polymer with the gas penetrant are various, the relationships of concentration and permeability are determined by different modes of sorption. According to Klopffer
et al.\textsuperscript{156}, there are five classic sorption modes, as shown in Figure 42.

Figure 42 Isotherm plots of absorbed concentration versus vapour pressure of sorption modes\textsuperscript{156}
The Henry's Law sorption works when the gas in considered as ideal and the penetrant concentration in the membrane shows a linear relationship with its partial pressure:

\[ C = Sp \quad (13) \]

Where \( S \), the solubility coefficient of the gas in the polymer, is independent of the concentration at a given temperature. This mode is often observed for inactive gas at low pressure where polymer-gas and gas-gas interactions are very weak compared to polymer-polymer interaction.

The Langmuir sorption mode corresponds to a predominance of penetrant-polymer interactions. Gas molecules occupy specific sites in the polymer, for example, pre-existing microvoids or concentrate in the area of inorganic fillers. When all the sites are occupied, the rest of the diffusing molecules cannot be absorbed. The penetrant concentration is then given by:

\[ C'_H = \frac{C'_H bp}{1 + bp} \quad (14) \]

Where \( C'_H \) is the maximum penetrant concentration, and \( b \) is a constant.

The Flory-Huggins Mode works when interactions between the diffusing molecules are stronger than the penetrant-polymer interactions and the solubility coefficient increases continuously with pressure. This behaviour can be found when the polymer is plasticized by the penetrant or in water-hydrophobic polymer sorption when penetrant clusters.

The BET Mode corresponds to a combination of the Langmuir and Flory-Huggins modes. Hernandez and Gavara\textsuperscript{168} found this mode works in the sorption of water in Nylon-6 films. Initially, the water molecules are strongly absorbed in specific sites corresponding to polar groups, then at higher pressures, the clustering process may occur.
The dual-mode sorption corresponds to the combination of Henry's Law and Langmuir sorption. It can be found in sorption of low-activity gases in polymers if no swelling or plasticization of polymer occurs during the sorption.

Stern et al.\textsuperscript{169} found that with increasing pressure, the permeation coefficient of organic or soluble gases increases in PE above the glass transition temperature, while the permeation coefficient of insoluble gases, such as He and N\textsubscript{2}, decreases. This is because an increase in the penetrant pressure can either increase the concentration of the penetrant absorbed in the polymer and increase the free volume, or increase hydrostatic pressure on the polymer matrix and decrease the free volume. The permeability increases with an increase of free volume, and vice versa.

2.2.2.3 Penetrant Size
Large penetrant molecules have a low diffusion coefficient but a high sorption coefficient. According to Klopffer et al.\textsuperscript{156}, Berens et al.\textsuperscript{170} and Tikhomirov et al.\textsuperscript{171}, large gas molecules require more activation energy to separate polymer chains for diffusion, as shown in Figure 43.
The solubility of gases in polymer depends on the boiling temperature or the Lennard-Jones parameters. Large gas molecules require more energy for vaporization. As a result, large gas molecules usually have a high sorption coefficient.\textsuperscript{156,165}

2.2.2.4 Polarity

Polarity of a polymer is determined by its skeletal structure and functional groups. According to Table 9, it can be found that with increasing polymer polarity, the permeability of oxygen and carbon dioxide decreases, but the permeability of
water vapour increases. It is difficult for non-polar gases to permeate through polymers with low structural symmetry and high polarity, as the diffusion is slow due to high cohesive energy and strong molecular interaction. Polymers with high polarity have poor water barrier properties, since absorption rates of water in the polar polymers are high. Take poly(vinyl alcohol) for example, it contains many hydroxyl groups and has excellent gas barrier properties but poor resistance to water vapour. However, polystyrene shows poor gas barrier properties but a low water permeation rate because of its non-polarity provided by its carbon chain and benzene ring.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Oxygen [cm$^3$ 100 μm (m$^2$ d atm)$^{-1}$]</th>
<th>Carbon dioxide [cm$^3$ 100 μm (m$^2$ d atm)$^{-1}$]</th>
<th>Water vapour [cm$^3$ 10 μm (m$^2$ d atm)$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly(vinyl alcohol) dry</td>
<td>0.04</td>
<td>0.12</td>
<td>79000</td>
</tr>
<tr>
<td>poly(vinylidene chloride)*</td>
<td>0.4</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>cellophane (dry)</td>
<td>0.5</td>
<td>1.2</td>
<td>14000</td>
</tr>
<tr>
<td>epoxy (bisphenol A/amine)*</td>
<td>12</td>
<td>35</td>
<td>160</td>
</tr>
<tr>
<td>nylon 6*</td>
<td>20</td>
<td>35</td>
<td>700</td>
</tr>
<tr>
<td>poly(ethylene terephthalate)*</td>
<td>20–39</td>
<td>47–79</td>
<td>80–160</td>
</tr>
<tr>
<td>poly(vinyl chloride)*</td>
<td>31–59</td>
<td>79–157</td>
<td>80–120</td>
</tr>
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<td>poly(vinyl fluoride)*</td>
<td>59</td>
<td>118</td>
<td>70</td>
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<tr>
<td>poly(methyl methacrylate)*</td>
<td>67</td>
<td>157</td>
<td>470</td>
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<td>poly(vinyl acetate)</td>
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<td>4920</td>
<td>510</td>
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<tr>
<td>low-density polyethylene (LDPE)</td>
<td>1890</td>
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<td>60</td>
</tr>
<tr>
<td>polybutadiene</td>
<td>15000</td>
<td>31000</td>
<td>670</td>
</tr>
</tbody>
</table>

*Oxygen and carbon dioxide permeabilities measured at 100% RH.

Table 9 Permeation rate of polymers.
2.2.2.5 Crystallinity

Crystallisability of a polymer is affected by its symmetry. Crystalline polymers have better barrier properties than amorphous polymers. Poly(vinylidene chloride) (PVDC), has double the chlorine content of poly(vinyl chloride). The structure of PVDC, i.e. \((\text{CH}_2\text{-CCl}_2)_n\), has greater symmetry along the chain than PVC. Thus PVDC is easier to crystallise, which provides higher resistance for gas and water permeation, as shown in Table 9.

According to the results obtained by Guinault et al.\textsuperscript{173}, the permeability of helium and oxygen generally decreases with increasing crystallinity of PLLA. As shown in Figure 44, when the degree of crystallinity of PLLA film rises from 2.5% to 58%, the helium permeability decreased from \(98 \times 10^{18} \text{ m}^3/\text{m}^2\cdot\text{s}\cdot\text{Pa}\) to \(38 \times 10^{18} \text{ m}^3/\text{m}^2\cdot\text{s}\cdot\text{Pa}\) at room temperature and 0% RH. Oxygen permeability decreased from \(2.1 \times 10^{18} \text{ m}^3/\text{m}^2\cdot\text{s}\cdot\text{Pa}\) to \(1.2 \times 10^{18} \text{ m}^3/\text{m}^2\cdot\text{s}\cdot\text{Pa}\) at 23°C and 0% RH.
The effect of crystallinity is explained by the two-phase model, developed by Michaels et al.\textsuperscript{174,175,176}. They tested both solubilities and diffusivities of helium, oxygen, nitrogen, argon, carbon dioxide and methane in poly(ethylene terephthalate) below and above the glass transition temperature. According to their results, below glass the transition temperature, diffusion is impeded purely geometrically by the presence of the crystallites, and the impedance factor is equal to the reciprocal of the amorphous volume fraction. In the rubbery state,
diffusion is Fickian and apparent activation energies for diffusion are higher than those in the glassy crystalline polymer. They suggested that the crystalline phase both increases the effective path length of diffusion and reduces the polymer chain mobility in the amorphous phase. This lead to a higher activation energy of diffusion.

The two-phase model works in the case of water permeation through PLA according to Tsuji et al.\textsuperscript{177,178}. However, Budzien et al.\textsuperscript{179} have reported that gas solubilities predicted by using the Flory-Huggins mode for data for amorphous PE are higher than those predicted by extrapolation of the two phase model of Michaels et al.\textsuperscript{176}. They suggest the difference is due to the oversimplification of the two-phase model. Factors, such as size and morphology of crystallites, and their distribution, may also affect barrier properties.

Drieskens et al.\textsuperscript{180} have investigated the effect of crystallinity on the oxygen permeability of poly(lactic acid). Crystallisation of PLA caused a reduction in oxygen permeability but this was not in linear proportion with the decrease in amorphous volume. Diffusivity decreased with increasing crystallinity but solubility of oxygen in PLA showed an increase instead. The results were discussed in terms of the presence of a constrained or rigid amorphous fraction with lower density that gave rise to the observed effects on the solubility coefficient.
2.2.2.6 Orientation

Weinkauf et al.\textsuperscript{181} suggested that orientation improves the barrier properties of a polymer, as drawing can condense the amorphous phase and reduce the free volume. For semi-crystalline polymers, orientation may modify the distribution and directions of crystallities. This can lead to a change of the path length for diffusion of gases, and affect gas permeation. However, the effect of orientation may depend on the type of penetrant and matrix, as well as the processing conditions, since reports showed different results by using different gases and polymers with different draw ratios and directions\textsuperscript{156}.

Sha and Harrison\textsuperscript{182} stretched HDPE in the presence of CO\textsubscript{2} at a sufficiently high draw ratio to modify the morphology and obtained the transformation of the spherulitic structure to a microfibrillar one. As shown in Figure 45, with increasing draw ratio, the solubility coefficient $S$ increases slightly at draw ratios below 5, and then decreases monotonically; variations in $P$ and $D$ with draw ratio are more dramatic but follow a similar pattern: both parameters show a slight initial increase when $\lambda < 2.2$, and then drop steadily as $\lambda$ increases. They concluded that that the change in $D$ is the dominant factor that results in the large drop in permeability, which is because of the variations of the fractional free volume of the amorphous phase, $f_a$, defined as:

$$f_a = \frac{v-v_0}{v}$$  \hspace{1cm} (15)

Where $v$ and $v_0$ are the specific volume and specific occupied volume of the amorphous phase.

McGonigle \textit{et al.}\textsuperscript{183} performed permeation experiments of various gases including N\textsubscript{2}, Ar, He, CO\textsubscript{2}, O\textsubscript{2} in bi-axially drawn films of PET and PEN, and observed a decrease of $S$ and $D$ with the draw ratio. They concluded that the effect of orientation on permeability is based on the morphology modification such as variation of the crystallinity degree, reorientation effect, disentanglement and alignment of the chains, higher degree of packing, and the reduction of segmental mobility.
Figure 45 Variation of solubility coefficient (upper left), diffusivity coefficient (upper right) and permeability coefficient (lower) as a function of draw ratio

2.2.2.7 Crosslinking and Plasticizer

According to free volume theory, crosslinking reduces polymer chain mobility as well as the free volume. Therefore, when the degree of crosslinking increases, the diffusion coefficient of gas decreases. In addition, Michaels et al. have found the activation energy of diffusion increases with increasing branching.

Addition of plasticisers to a polymer increases chain segmental mobility and lowers the glass transition temperature, resulting in a reduction of the barrier
properties. Highly polar polymers are susceptible to plasticisation by moisture. Oxygen permeability in dry cellophane is \(0.5 \text{ cm}^3 \text{ 100} \mu\text{m} \text{ (m}^2\text{d atm})^{-1}\), but can increase to \(787\text{ cm}^3 \text{ 100} \mu\text{m} \text{ (m}^2\text{d atm})^{-1}\) at 100% RH\(^{172}\).

2.2.3 Nielsen Tortuosity Model\(^{184}\)

Nielsen tortuosity model is a simple permeability model to predict the minimum permeability of a polymer filled with plate-like particles.

When the filler particles in a polymer matrix are impenetrable to diffusing gas or liquid molecules, the diffusing molecules need to go around the filler particles. This leads to a tortuous path. In addition, the presence of filler particles reduces the area of polymer matrix in cross section. Assuming the fractional area of polymer in any cross section is equal to its volume fraction, the equation is given as:

\[
\frac{P}{P_u} = \frac{1 - \Phi}{\tau}
\]  

(16)

Where \(P\) and \(P_u\) are the permeabilities of the filled and pure polymer, \(\Phi\) is the volume fraction of the filler, and \(\tau\) is the tortuosity factor. The tortuosity factor \(\tau\) is defined by:

\[
\tau = \text{distance a molecule travels through the film / thickness of the film}
\]
Assuming the filler particles are all circular or rectangular plates; they are uniformly and completely dispersed in the polymer, and oriented parallel to the polymer film surface, as shown in Figure 46. Then diffusing molecules has the maximum tortuosity factor for permeation, given by:

$$\tau = 1 + \frac{\alpha}{2} \Phi$$  \hspace{1cm} (17)

Where $\alpha = L/W$ is the aspect ratio of the filler.

Combining Equation (16) and (17), the permeability equation is given as:
\[
\frac{P}{P_u} = \frac{1-\Phi}{1+\frac{\alpha}{2}\Phi}
\]  

(18)

Figure 47 shows predicted permeability of gases through a polymer filled with plates with different aspect ratios. When the aspect ratio of filler equals to 1, the line looks quite straight. When the aspect ratio of filler is high, the permeability drops very fast at the beginning to a certain region, then the permeability continuously decreases slowly until the end.
For polymers filler plates with non-uniform orientation in the polymer, the order parameter $S'$ is given by:

$$S' = \frac{1}{2}(3\cos^2\theta - 1) \quad (19)$$

Where $\theta$ is the angle between the diffusion direction and the unit vector normal to the surface of a platelet.

As shown in Figure 48, when all platelets are parallel to the direction of diffusion ($\theta = 0$), then the order parameter is $S' = -1/2$; when $\theta = \pi / 2$, the orientation of the platelets is perpendicular to the diffusion direction and $S' = 1$; for random orientation $S' = 0$.

![Figure 48 Values of the order parameter for three orientations of the platelets](image)

The Nielsen model for non-uniform orientation is then given by:

$$\frac{P}{P_u} = \frac{1 - \Phi}{\frac{1}{3} + \alpha(S' + \frac{1}{2})\Phi} \quad (20)$$

### 2.2.4 Other Permeation Models

The diffusion through a multiperforated single laminar was studied by Wakeham and Mason. They found that the resistance to diffusion through this system had a contribution from the need of the penetrant to enter the constriction into the pore/slit, and a contribution due to the length of the pore. This approach was
extended by Cussler et al.\textsuperscript{187} to multiple layers of parallel platelets of infinite third dimension, separated by slits. The result is simplified as:

\[
\frac{P}{P_u} = \left(1 + \frac{(\frac{\alpha}{2})^2 \Phi^2}{1 - \Phi}\right)^{-1}
\]

(21)

It is noted that Cussler et al. used particle aspect ratio $\beta = d/a = L/2W$. Here the aspect ratio is converted to the same as Nielsen model in case of any confusion.

Falla et al. developed the Wakeham and Mason model and found the following equations:

\[
\frac{P}{P_u} = \left(1 + \frac{(\frac{\alpha}{2})^2 \Phi^2}{1 - \Phi} + \frac{\alpha \Phi}{2\sigma} + 2(1 - \Phi)\ln\left(\frac{1 - \Phi}{2\sigma \Phi}\right)\right)^{-1}
\]

(22)

The second term of Equation (22), that involves $\alpha^2$, reflects the contribution of the tortuous path of the penetrant through the plates. The third term is due to the resistance to diffusion of the slits. The last part represents the constriction from the wide space between the plates into the narrow slits.

Moggridge et al.\textsuperscript{188} examined hexagonal flakes arranged in regular parallel arrays and found the change of permeability is shown as:

\[
\frac{P}{P_u} = \left(1 + \frac{2}{27} \left(\frac{\alpha}{2}\right)^2 \Phi^2\right)^{-1}
\]

(23)

The difference due to the specific platelet-shape is reflected by the coefficient (2/27), which reduces the effectiveness of the barrier.

### 2.2.5 Water Vapour Transmission Rate

#### 2.2.5.1 Introduction

The water vapour transmission rate (WVTR) is used to describe water barrier properties of a polymer. WVTR is actually the flux, which is the amount of water (Q) diffusing across unit area (A) in unit time (t), with units of g/(m\textsupersquare{2} day), as given by:
\[
WVTR = \frac{Q}{At} \quad (24)
\]

As shown in Figure 49, when the WVTR of a material is not too high, the water vapour permeation can reach a steady state and it is independent of sample thickness\(^{189}\).

Figure 49 Effect of film thickness and film area on normalised WVTR\(^{189}\)

Combining Equation (11) and (21), the water vapour permeability is given by:

\[
P = \frac{WVTR(I)}{\Delta p} \quad (25)
\]

Since thickness of films varies, the WVTR value is often normalised to a film of 25 \(\mu\)m or 1 mil(1/1000 inch) thickness, given by\(^{177,189,178}\):

\[
WVTR(\text{norm}) = WVTR(\text{raw}) \times \frac{l}{25} \quad (26)
\]

with the same unit as non-normalised WVTR. Normalised WVTR is sometimes
referred to as the water vapour permeation coefficient.

2.2.5.2 Measurements
The wet cup method described by ASTM E 96-95\textsuperscript{190} is often used to measure water vapour transmission rate. In this method, the test film covers a Petri dish filled with distilled water to maintain 100% relative humidity (RH). The mass of water lost from the dish is monitored as a function of time, and WVTR is calculated from the steady-state region. The dry cup test, a similar method described by ASTM E 96-95, has a desiccant, such as anhydrous calcium chloride, to maintain 0% RH inside the dish.

Several disadvantages of these cup testing methods have been recognised. Resistance to water vapour permeation from the air gap layer, and surface of the sample was reported\textsuperscript{191}. As reported by Hu et al.\textsuperscript{189} and Modern Controls, Inc.\textsuperscript{192}, the concentration of water is far less than 100% RH at the surface of the test films with high transmission rate because of the air gap. This causes inaccuracy in the test results.

The MOCON Permatran-W, developed by Modern Controls, Inc., is a new type of instrument designed for measuring WVTR of materials with different water barriers properties. As shown in Figure 50, the values obtained by MOCON were higher because of higher relative humidity concentration at the surface\textsuperscript{189}.
Figure 50 Comparison between WVTR obtained from wet cup test and MOCON 100K at 37°C

2.2.6 Water Vapour Transmission Rate of Biopolymers

Water permeability of a polymer is dependent on the polymer’s polarity, molecular weight, chain symmetry, crystallinity, orientation and temperature. Table 10 shows water vapour transmission rates of common biodegradable polymer films. There is more free volume in polymer at a higher temperature. The water molecules are more active as well. As a result, the WVTR is much higher.
<table>
<thead>
<tr>
<th>Film</th>
<th>WVTR (g/day/m(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T = 6°C</td>
</tr>
<tr>
<td>PHBV-6</td>
<td>1.8</td>
</tr>
<tr>
<td>PHBV-12</td>
<td>3.1</td>
</tr>
<tr>
<td>PHBV-18</td>
<td>3.5</td>
</tr>
<tr>
<td>PLA (annealed at 130°C)</td>
<td>27</td>
</tr>
<tr>
<td>PLA</td>
<td>54</td>
</tr>
<tr>
<td>PCL</td>
<td>41</td>
</tr>
<tr>
<td>Bionolle</td>
<td>59</td>
</tr>
<tr>
<td>BAK 1095</td>
<td>134</td>
</tr>
<tr>
<td>Cellulose acetate propionate</td>
<td>590</td>
</tr>
<tr>
<td>Cellulose acetate</td>
<td>1020</td>
</tr>
</tbody>
</table>

Table 10 Water vapour transmission rates of biodegradable polymer films\(^{13}\)

Biopolymers generally show poor water barrier properties compared to common commercial polymers. It is because biopolymers are polar polymers with hydrophilic groups. When the solubility parameter of a polymer is similar to water, the solubility is high, which in turn affects water vapour permeability according to Equation (11) in section 2.2.1.1. Degradation of many biopolymers includes a hydrolysis process, in which water is a reactant and exists within the polymer.

Crystallinity has been reported to have an obvious effect on WVTR of polymers. Tsuji et al.\(^{177}\) found the WVTR decreased rapidly from 230 to 130 g/day/m\(^2\) when crystallinity increased from 0 to 20%, as shown in Figure 51. A decrease in normalised WVTR in PLA films with an increase of crystallinity was also reported in studies by Shorgen\(^{13}\), Siparsky et al.\(^{21}\), Hu et al.\(^{189}\), and Tsuji et al.\(^{177}\).

Siparsky et al.\(^{21}\) cited the following equation to demonstrate the relationship between crystallinity and solubility as:

\[
S = S' (1 - \chi) \tag{27}
\]

where S and S’ are the solubility coefficient of semi-crystalline and total amorphous polymers respectively, and \(\chi\) is the crystallinity.
Siparsky et al\textsuperscript{21} discussed that cluster formation is an important factor that affects measured solubility. Clustering in a polymer/water binary system is the ordered structuring of a body of water within the polymer; it is stabilized by hydrogen bonding between the water molecules. Clustering leads to a low value of the diffusion coefficient.

Hydrolysis reactions should also be considered because this is essentially the mechanism by which degradation takes place. PLA is well established in biomedical applications by virtue of its biocompatibility and biodegradability. It is a polyester and undergoes hydrolysis reactions in which the ester bonds are cleaved and molecular weight is reduced. This process can take place in the presence of water alone but it is greatly accelerated by catalysts such as enzymes.
Siparsky et al\textsuperscript{21} investigated hydrolysis in PLA films at 90\% relative humidity and at temperatures between 20 and 50\ºC and found that the nonlinear behavior of the diffusion process is because of cluster formation instead of crystallinity, and hydrolysis in PLA films is a very slow process compared with water vapour diffusion.

Addition of fillers can also improve barrier properties of polymer. Thellen et al\textsuperscript{90} have reported a 50\% improvement in water vapour barrier compared with neat PLA when a loading of 5 weight \% nanoclay was used to make PLA nanocomposites that were prepared by twin-screw extrusion and converted to blown films. Zenkiewicz and Richert\textsuperscript{93} found the best result was a 60\% decrease water vapour permeability of a PLA nanocomposite containing 5 weight \% nanoclay to which 20 weight \% PMMA had been added. Rhim et al\textsuperscript{94} prepared PLA nanocomposites with increasing amounts of Cloisite 20A by solvent casting. It was found that with a high clay loading of 13 weight \%, the improvement in water vapour barrier was around 67\%. 
3 Experimental

3.1 Materials

Three grades of polylactide (PLA) polymer (Ingeo\textsuperscript{TM} 4060D, 4042D and 4032D) were supplied by NatureWorks\textregistered LLC (Minetonka, MN, USA). 4060D is an amorphous polymer with a glass transition temperature (Tg) of 55-60\textdegree C and a D content ratio of 1.4 wt.\%\textsuperscript{193}. 4032D is semi-crystalline with a melting point in the range 155-170\textdegree C, with a D content ratio of 12 wt.\%\textsuperscript{193}. The D content ratio of 4042D is 4.25 wt.\%\textsuperscript{193}. The specific gravity of PLA is 1.24 g/cm\textsuperscript{3}.

The molecular weights of PLA 4032D and 4060D are measured by using the Agilent 1260 Infinity GPC/SEC System. The system was calibrated by using polystyrene standards in molecular weight range of 3770-2950000 g/L. PLA samples were dissolved in THF for GPC at a concentration of 2 g/L and kept in an oven at 50 \textdegree C for 2 hours before the measurement. The flow rate was maintained at 1 ml/min at a column temperature of 30 \textdegree C. The Mark-Houwink constants used for PLA were \( K = 1.74 \times 10^{-5} \) and \( a = 0.74 \).

The molecular weight distribution of PLA 4032D is shown in Figure 52. Mark Houwink constants used in the experiment were taken as \( K = 1.74 \times 10^{-5} \) and \( a = 0.736 \) for THF. The peak reached a maximum at \( 8 \times 10^4 \) g/mol, with the detector response of 980 mV. The number average molecular weight of PLA 4032D is \( 36.7 \times 10^3 \) g/mol. The weight average molecular weight is \( 93.8 \times 10^3 \) g/mol. The viscosity average molecular weight is \( 155.1 \times 10^3 \) g/mol. The molecular weight distribution of PLA is narrow.
Figure 52 The molecular weight distribution of PLA 4032D

Figure 53 shows the narrow molecular weight distribution of PLA 4060D. The peak reached a maximum at $8 \times 10^4$ g/mol, with the detector response of 993 mV. In this case the number average molecular weight of PLA 4060D is $30.8 \times 10^3$ g/mol. The weight average molecular weight is $89.2 \times 10^3$ g/mol and the viscosity average molecular weight is $149.5 \times 10^3$ g/mol.
The Polybutylene succinate (PBS) used was supplied by IRe Chemical Ltd. It is a semi-crystalline polymer with a melting temperature of 115 °C. The density is 1.26 g/cm³.

The talc used in this study was JetFine® 3CC provided by Imerys Talc. It has a specific gravity of 2.78 g/cm³. The nanoclay used in this study was Cloisite® 30B obtained from Southern Clay Products (Gonzales, TX, USA). It is a montmorillonite layered silicate organically modified with a quaternary ammonium salt to improve compatibility with polymers. The organic modifier of Cloisite 30B is methyl tallow bis-2-hydroxyethyl ammonium cations, at a loading of 90 mEq/100g clay. It has a specific gravity of 1.98 g/cm³.

3.2 Sample Preparation

3.2.1 PLA of different crystallinity

Before processing, the PLA granules were dried at 60°C for 24 hours in a vacuum oven to remove excess moisture. Then melt blending was carried out.
in a counter-rotating mixer (Haake Rheomix OS, as shown in Figure 54) to eliminate boundaries between the granules. The total sample weight added to the mixer was 58g and mixing was carried out at 170°C for 10 minutes with a constant rotor speed of 60 rpm.

![Figure 54 Haake Polylab OS R600 torque rheometer](image)

Samples for water vapour permeability measurements were then prepared by compression moulding in a 20 ton hydraulic press. The materials were hot pressed at 180°C and the melt compressed for three minutes at 15 tons pressure, followed by cooling to room temperature over a period of three minutes at a pressure of 5 tons. The average thickness of the samples produced was 0.6 mm. The dimensions of the compression moulded sheet are shown in Figure 55. The centre part of the samples was used for WVTR measurement and the side edges were used for DSC.
Then PLA sheets were either quenched by water-cooled plates with 5 tons pressure for 3 min; or annealed at 100°C, 115°C, or 130°C for 5-40 minutes before being quenched to room temperature.

3.2.2 PLA composites and nanocomposites

The PLA granules were heated at 60°C for 24 hours in a vacuum oven to remove moisture before processing. The PLA was then melt blended with 20 weight% of the JetFine® 3CC talc or Cloisite® 30B organoclay to make a masterbatch. Melt blending was carried out in a counter-rotating mixer (Haake Rheomix OS) to promote dispersive and distributive mixing. The total sample weight added to the mixer was 58g and mixing was carried out at 170°C for 10 minutes with a constant rotor speed of 60 rpm. The masterbatch was then diluted by adding dried PLA to form further compositions of 1%, 3%, 5% talc and 1% - 6% clay, based on the weight, and then mixed in the mixer at 170°C and 60 rpm for a further 10 minutes. The control PLA material was processed in the same way, so that it had the same thermal history as the PLA nanocomposites. Samples for water vapour permeability measurements were then prepared by compression moulding in a 20 ton hydraulic press. The materials were hot pressed at 180°C and the melt compressed for three minutes at 15 tons pressure, followed by
cooling to room temperature over a period of three minutes at a pressure of 5 tons.

3.2.3 PBS samples
First of all, the PBS granules were dried at 60°C for 24 hours in a vacuum oven. The PBS was then melt blended with 20 weight% of the Cloisite® 30B organoclay to make a masterbatch. Melt blending was carried out in Haake Rheomix OS, to promote dispersive and distributive mixing. A total sample weight of 58g was added to the mixer and mixing was carried out at 130°C for 10 minutes with a constant rotor speed of 60 rpm. The masterbatch was then diluted by adding dried PBS to form further compositions of 1%, 3%, and 5% clay, based on the weight, and then mixed in the mixer at 130°C and 60 rpm for a further 10 minutes. The control PBS material was processed in the same way, so that it had the same thermal history as the PLA nanocomposites. Samples for water vapour permeability measurements were then prepared by compression moulding in a 20 ton hydraulic press. The materials were hot pressed at 140°C and the melt compressed for three minutes at 15 tons pressure, followed by cooling to room temperature over a period of three minutes at a pressure of 5 tons.

3.3 Characterisation Techniques
3.3.1 X-Ray Diffraction
PLA and PBS nanocomposite samples were examined by wide-angle X-ray diffraction (WAXD) in order to investigate the extent of intercalation or exfoliation of the montmorillonite clay. X-Ray diffraction data were collected on a Brucker D8 Diffractometer using graphite-filtered Cu-Kα radiation (λ = 1.542nm) operated at 40 kV and 40 mA at a scanning rate of 2°/min from 0 to 40°(2θ). The diffractometer was controlled using Diffrac Plus XRD Commander and the raw data was manipulated using EVA software. The nanocomposite sheets were laid flat on an aluminium block, the height of which was adjusted so that the sample surface was the reference plane of the instrument.
3.3.2 Differential Scanning Calorimetry (DSC)
The melting and crystallisation behaviour of the composites was investigated using differential scanning calorimetry (DSC). Measurements were performed using a DSC Q200 (TA Instruments, USA) fitted with an auto-sampler and mechanical cooler. Samples of approximately 10~16 mg in mass were put into sealed aluminium pans and loaded into the auto-sampler. The PLA samples were heated from 20°C to 200°C at 10°C/min in a nitrogen atmosphere. Data was analysed using the TA universal analysis software package. All the values represent the average of 3 samples.

The amount of overall crystallinity was calculated using Equation 25.

\[ X_c = \frac{\Delta H_m - |\Delta H_c|}{\Delta H_{100}} \times 100\% \]  

(28)

where \( \Delta H_m \) (J/g) is the measured heat of fusion (melting enthalpy), \( \Delta H_c \) is the absolute value of enthalpy of cold crystallization, and \( \Delta H_{100} \) is the enthalpy of fusion for 100 % crystalline polymer. For PLA, \( \Delta H_{100} = 93 \) J/g. For composites of PLA, the weight fraction of the PLA (w) needs to be considered in calculating the percentage crystallinity.

The PBS samples were heated from 20°C to 150°C at 10°C/min, and cooled to room temperature at 10°C/min in a nitrogen atmosphere. The amount of overall crystallinity was calculated using Equation 25. For PBS, \( \Delta H_{100} = 200 \) J/g. For PBS composites, the weight fraction of the PBS needs to be considered in calculating the percentage crystallinity.

3.3.3 Cross Polarised Optical Microscopy
To study the crystalline morphology, the PLA films were observed under crossed polars in a Leica DM LM Binocular transmitted light microscope. Crystallinity behaviour of PLA was investigated by using polarised optical microscopy on a hot stage with a heating or cooling rate at 10 °C/ min between 30 and 200°C. Crystallinity behaviour of PBS with different thickness was also
investigated using polarised optical microscopy with a heating or cooling rate of 10 °C/ min between 30 and 150°C.

3.3.4 Transmission Electron Microscopy
Samples for transmission electron microscopy (TEM) were prepared by first cutting samples mixed by Haake Rheomix OS into a pencil-like point and then shaving off thin slices (approximately 100 nm thick) at room temperature using a Cambridge Instruments ultra-microtome fitted with a diamond edge blade. A reservoir of de-ionised water was used to contain the pieces of sample. The samples were then scooped onto a copper mesh and left to dry before being observed in a JEOL, JEM – 2000FX transmission electron microscope operated at an accelerating voltage of 100kV.

The aspect ratios of the talc and nanoclay filler particles within the PLA matrix were measured from the TEM micrographs using Image J® software.

3.3.5 Particle size measurement
Pure nanoclay, PLA with 20% nanoclay, and PLA with 2% nanoclay samples were dispersed in THF by stirring for 15min. Then particles in the solutions were measured in a Delsa™ Nano HC particle analyser by measuring the rate of fluctuations in laser light intensity scattered by particles. Three samples were measured for each formulation.

3.3.6 Water Vapour Permeability Measurements
Water vapour transmission rates (WVTR) through the various PLA and PBS sheets were measured using a MOCON (Modern Controls Inc., USA) Permatran-W@398 operated at 38°C and a relative humidity of 90%. Four samples were measured for each filler concentration.

The MOCON testing machine has two separate cells. Each cell is divided into two chambers. One chamber containing a source of water is separated from an
accumulation chamber by the sample under test as shown in Figure 56. The relative humidity (RH) within the accumulation chamber fluctuates between a low set-point and a high set-point in response to a periodic introduction of nitrogen.

![Diagram of an MOCOM Permatran-W 398 testing cell](https://example.com/diagram)

**Figure 56** An illustration of a MOCOM Permatran-W 398 testing cell

When a test begins, a set of valves open that allow a stream of dry nitrogen to flow through the upper chamber, taking water away until the low RH is reached. Then the valves close, and the humidity level within the chamber increases gradually as water permeates through the film. When the high RH set-point is reached, the valves open once again and the cycle repeats. The computer then records WVTR which is based on the number of seconds or minutes required for the RH within the chamber to reach the high set-point. When the WVTR is stable over repeated cycles, the testing system is at equilibrium and the measurement is taken.
4 Polylactide – Results and Discussion

4.1 Crystallinity and Morphology

4.1.1 Differential Scanning Calorimetry

Figure 57 shows a moulded sample of PLA 4060D. It is transparent and quite brittle because it is amorphous.

![Figure 57 A PLA 4060D sample](image)

Figure 58 shows the DSC first heating scan for PLA 4060D. The step change at 55°C corresponds to the glass transition temperature (T_g) of the polymer. The peak just after the step change is an enthalpic relaxation peak. There is no cold crystallisation temperature (T_c) or any melting point (T_m), thus confirming the amorphous nature of the samples.
NW 4042D has a very low crystallisation rate. Figure 59 shows the DSC trace (first heating scan) for a slowly cooled PLA 4042D sample. The glass transition temperature $T_g$ is 60°C and there is no obvious enthalpic relaxation peak. The exothermic peak at 120 °C corresponds to cold crystallisation on heating. The sample melted at 152 °C.
Figure 59 Differential scanning calorimetry curve of PLA 4042D

Figure 60 shows the DSC trace (first heating scan) for the crystallisable PLA 4032D that has been quenched. The glass transition temperature $T_g$ is 58°C and there is no enthalpic relaxation peak. The exothermic peak at 111 °C corresponds to cold crystallisation on heating above the $T_g$. There is a double melting peak at temperatures of 163 and 169 °C. The lower peak corresponds to melting of the $\beta$ phase, which is the disordered crystalline form, whereas the higher temperature peak corresponds to melting of the $\alpha$ phase, which is the ordered crystalline form.
Figure 60 Differential scanning calorimetry curve of quenched PLA 4032D

Figure 61 shows the DSC trace (first heating scan) for the crystallisable PLA 4032D annealed at 100 °C for 18 min. The step change at 56 °C corresponds to the glass transition temperature of the polymer. The cold crystallisation peak at 114 °C is flatter compared to the DSC curve of quenched PLA 4032D. The melting peak is at a temperature of 170 °C. There is a small peak at about 164 °C merging into the prime melting peak. It corresponds to melting of crystals in the α' phase.
Figure 61 DSC curve of PLA 4032D annealed at 100 °C for 18min

Figure 62 shows a moulded sample of annealed PLA 4032D. It is white and not transparent compared to the PLA 4060D samples. This is obviously because it is crystalline
Figure 63 shows the DSC trace (first heating scan) for the crystallisable PLA 4032D annealed at 115 °C for 25 min. The glass transition temperature $T_g$ is 55°C and there is no enthalpic relaxation peak either. The flat cold crystallisation peak is at 120 °C. The melting peak is at temperature of 167 °C. There is another smaller melting peak at about 169 °C that merges into the prime melting peak.
Figure 63 DSC curve of PLA 4032D annealed at 115 °C for 25 min

4.1.2 Crystallinity
Table 11 shows DSC data from an annealed PLA 4032D sample sheet in different positions. It can be seen that the glass transition temperatures and melting points are close between the centre part and the edge. Cold crystallisation temperature at the corner (position 5) is at 115 °C, which is slightly higher than the other parts. The degrees of crystallinity at the centre parts are 36.8±1.1%, but the degree of crystallinity at the position 4 is 19.1%, lower than the centre part. The degree of crystallinity at the corner is 31.2%, much closer to that at the centre part. Since the centre part is used for WVTR measurement, the degree of crystallinity of the corner part is considered as the degree of crystallinity of the whole sample sheet, i.e. Samples for DSC measurements were taken from position ‘5’.
Table 11 DSC data from an annealed PLA 4032D sample sheet in different positions

<table>
<thead>
<tr>
<th>position</th>
<th>Tg (ºC)</th>
<th>Tc (ºC)</th>
<th>Tm (ºC)</th>
<th>ΔHc (J/g)</th>
<th>ΔHm (J/g)</th>
<th>%crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>58</td>
<td>111</td>
<td>170</td>
<td>2.9</td>
<td>36.7</td>
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<tr>
<td>5</td>
<td>60</td>
<td>115</td>
<td>171</td>
<td>4.9</td>
<td>34.1</td>
<td>31.2</td>
</tr>
</tbody>
</table>

Table 12 shows degrees of crystallinity of PLA 4060D, PLA 4042D and PLA 4032D annealed in different conditions. It can be seen that PLA 4042D slow cooled samples have %crystallinity in the range of 1.7-4.4%. PLA 4032D quenched samples have %crystallinity between 5.4% and 12%. PLA 4032D samples annealed at 130 ºC for 5-20min have %crystallinity about 11-19%; samples annealed at 100 ºC for 18-25min cover the range of 30-44%; while samples annealed at 115 ºC reach a %crystallinity of 44%. PLA 4032D slow cooled samples achieved the highest %crystallinity from 43% to 51%.
<table>
<thead>
<tr>
<th>Polymer</th>
<th>Processing Procedure</th>
<th>% Crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA 4060D</td>
<td>Quenched or slow cooled</td>
<td>0</td>
</tr>
<tr>
<td>PLA 4042D</td>
<td>Quenched</td>
<td>0.8</td>
</tr>
<tr>
<td>PLA 4042D</td>
<td>Slow cooled</td>
<td>2.8±1.2</td>
</tr>
<tr>
<td>PLA 4032D</td>
<td>Quenched</td>
<td>8.2±3.4</td>
</tr>
<tr>
<td>PLA 4032D</td>
<td>Annealed at 130ºC for 5 minutes</td>
<td>14.2±3.1</td>
</tr>
<tr>
<td>PLA 4032D</td>
<td>Annealed at 100ºC for 18 minutes</td>
<td>32.5±3.5</td>
</tr>
<tr>
<td>PLA 4032D</td>
<td>Annealed at 115ºC for 25 minutes</td>
<td>41±4.1</td>
</tr>
<tr>
<td>PLA 4032D</td>
<td>Slow cooled</td>
<td>47.7±4.2</td>
</tr>
</tbody>
</table>

Table 12 Degrees of crystallinity of PLA annealed in different conditions

4.1.3 Crystalline Morphology

Figure 64 shows polarised optical micrograph of a slow cooled PLA 4032D sample. Since the slow-cooled sheet crystallised over a wide temperature range for long time (1 hour), some big spherulites appears. According to Yasuniwa et al.47, these big spherulites form at high temperature, with a slow nucleation rate. As the temperature decreased slowly, many small crystallites form and fill the gap between the big crystals. The double peak that appeared in the melting endotherm on the DSC curve also indicates that at least two different types of crystallites exist.
Figure 65 shows the spherulite morphology change of PLA 4032D annealed at 100 °C for 15min in polarised optical microscopy at a heating rate of 10 °C/min. It can be seen that at 40 °C there are at least 2 types of spherulites. When the sample is heated to 120 °C, the cold crystallisation peak has already appeared on the DSC curve (Figure 61). On the micrograph the number and size of large spherulites increase; meanwhile there is no obvious change in the area of tiny spherulites. At 158 °C there are even more large spherulites. The brightness of the image is increasing compared to the image at 120 °C. It indicates higher %crystallinity considering that the exposure settings of all images are the same. When the temperature increases to 167 °C, the area of tiny spherulites decreases and becomes blurred. However, the number of large spherulites does not change obviously; they are clearer as there are less tiny spherulites. In addition, bright rings appear around the large spherulites. At 169 °C, the whole image becomes dark, indicating melting of crystals. When the temperature reaches 172 °C, all crystals melt and the image is black.
Figure 65 PLA 4032D annealed at 100 °C for 15 min in hot staged polarised optical microscopy (a) at 40 °C, (b) at 120 °C, (c) at 158 °C, and (d) at 167 °C.

When the melted sample was cooled in the hot stage microscope at a cooling rate of 10 °C/min, nothing can be seen until the temperature dropped to 80 °C, then few tiny spherulites appeared. However, when the sample was held at 100 °C, the crystallisation speed was much faster. As shown in Figure 66, spherulites were seen after 1 min. After 9 min the tiny spherulites had grown to fill the whole area, but there are no large spherulites found in the image.
Figure 66 PLA 4032D at 100 °C after melting in the hot stage polarised optical microscopy (left) in 1min, and (right) in 9min

4.2 Effect of crystallinity on water vapour transmission rate

4.2.1 Relationship between WVTR and crystallinity

Figure 67 shows water transmission rate of a PLA 4032D quenched sample as a function of time. At the beginning the water transmission rate jumped to a high point, as residual water was driven out of the sample by pressure. Then water transmission rate dropped significantly as most residual water had been moved. After that the water transmission rate increased slowly. At around 400 minutes it reached a steady state. The water vapour transmission rate (WVR) is the water transmission rate multiplied by thickness of the sample per unit of mil (i.e. per 25µm):

\[ \text{WVTR} = \text{WTR} \times \frac{l}{25} \]  

(29)

In this case, the WVTR of this sample is:

\[ \text{WVTR} = 7.09 \times 0.72 / 25 \]
\[ = 201 \text{ g/(m}^2 \text{ day)} \]
Table 13 shows degree of crystallinity and WVTR of different PLA samples. NW 4060D and NW 4042D do not have much crystallinity and the water vapour transmission rate is relatively high. The average WVTR of NW 4060D is $206 \pm 13$ g.mil/m$^2$.day. NW 4032D samples have high degrees of crystallinity, and the WVTR values are lower. The NW 4032D sample slowly cooled from the melt has the highest degree of crystallinity of 51.5%; and the lowest WVTR of 70 g.mil/m$^2$.day.
<table>
<thead>
<tr>
<th>Samples</th>
<th>Crystallinity%</th>
<th>WVTR (g. mil/m². day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NW 4060D</td>
<td>0</td>
<td>206 ± 13</td>
</tr>
<tr>
<td>NW 4042D quenched</td>
<td>0.8</td>
<td>205</td>
</tr>
<tr>
<td>Slow cooled</td>
<td>2.8 ± 1.2</td>
<td>204 ± 10</td>
</tr>
<tr>
<td>NW 4032D quenched</td>
<td>8.1 ± 3.3</td>
<td>186 ± 13</td>
</tr>
<tr>
<td>Slow cooled</td>
<td>47.9 ± 4.3</td>
<td>82 ± 18</td>
</tr>
<tr>
<td>Annealed at 130°C</td>
<td>14.2 ± 3.2</td>
<td>162 ± 12</td>
</tr>
<tr>
<td>5min</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Annealed at 100°C</td>
<td>32.3 ± 3.9</td>
<td>141 ± 8</td>
</tr>
<tr>
<td>18min</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Annealed at 115°C</td>
<td>41.0 ± 4.2</td>
<td>91 ± 4</td>
</tr>
<tr>
<td>25min</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 13 Crystallinity and WVTR of PLA samples

Figure 68 Shows the WVTR of PLA samples with different crystallinity. It is found that WVTR continuously decreases with increasing crystallinity. When %crystallinity of the sample reached 51%, WTVC is only 1/3 of that of the amorphous polymer. There is possible linear relationship between WVTR and crystallinity.
4.2.2 Linear Model

According to the two-phase model developed by Micheals et al., water molecules cannot be absorbed by the PLA crystalline regions. The solubility of crystalline PLA (S) equals to solubility of its amorphous volume fraction, as described in Equation (27).

\[ S = S_0 (1 - \chi) \]

Where \( S_0 \) is solubility of amorphous PLA, and \( \chi \) is degree of crystallinity.

Assuming the spherulites do not affect diffusivity, so \( D = D_0 \). By combining Equation (11) and (27), the permeability coefficient of crystalline polymer \( P \) is:

\[ P = S D = P_0 (1 - \chi) \]  

(30)

where \( P_0 \) is the permeability coefficient of amorphous PLA. Hence this explains the linear relationship between permeability and crystallinity.

Figure 69 shows the relationship between WVTR and %crystallinity for the linear explanation. The equation of the trend line is:
WVTR = -266 x + 207
= 207(1-1.29x)
= 207(1 - x0.29)

The linear approach has a good fit to the experimental data, with the coefficient of determination $R^2$ equal to 0.96.

It is notable that the WVTR drops faster as %crystallinity increases. According to Equation (31), WVTR reaches zero when PLA has a degree of crystallinity of 77.5%. One explanation is given by Micheals et al.\textsuperscript{174,175,176}. They suggested that the crystalline phase both increases the effective path length of diffusion and reduces the polymer chain mobility in the amorphous phase. This lead to a higher activation energy of diffusion. In addition, Tsuji et al.\textsuperscript{177,178} suggested that there are "restricted" amorphous regions between the normal amorphous phase
and crystals. These restricted amorphous regions have higher resistance to water vapour permeation, since crystals reduce the polymer chain mobility in the amorphous phase and water molecules cannot pass through these areas. According to Equation (31), the restricted amorphous region should equal to 29% of the crystalline phase volume fraction. However, there is no other solid evidence of the existence of or the effect of the restricted amorphous region. Therefore, another approach is needed for the experimental data.

4.2.3 Nielsen Tortuosity Model
Since crystals are spherulites, the aspect ratio is 1. The crystals can be considered that they are uniformly and completely dispersed in the polymer. Thus the Nielsen model can be applied in this case.

According to the Nielsen tortuosity model, the diffusivity \( D \) of crystalline PLA is:

\[
D = \frac{D_0}{\tau} = \frac{D_0}{1 + \frac{1}{2} \chi} \quad (32)
\]

From Equation (27), the solubility of crystalline PLA \( S \) is:

\[
S = S_0 (1 - \chi)
\]

Combining Equation (27) and (32), the permeability coefficient of crystalline polymer \( P \) is:

\[
P = S D = \frac{1 - \chi}{1 + \frac{1}{2} \chi} P_0 \quad (33)
\]

Where \( P_0 \) is the permeability coefficient of amorphous PLA.

As shown in Figure 47, when the aspect ratio of filler equals to 1, the line appears to be quite straight. Figure 70 shows the relationship between WVTR and crystallinity using the Nielsen Model. The approach also has a good fit to the experimental data, with the coefficient of determination \( R^2 \) equal to 0.95.
Figure 70 Relationship between WVTR and crystallinity in an approach of Nielsen model

Although the coefficient of determination $R^2$ for the Nielsen tortuosity model is 0.95, and is slightly lower than that for the linear approach, WVTR does not drop to zero until the degree of crystallinity reaches 100%.
4.3 Conclusion

NW 4060D PLA is an amorphous polymer. It is hard to crystallise even being annealed or cooled slowly.

NW 4042D PLA forms a few tiny crystallites when it is annealed or slow cooled. The melting temperature of these tiny crystallites is 152°C, lower than the other two PLA grades.

NW 4032D PLA has high crystallisation ability. The %crystallinity of this PLA can be more than 50% with low cooling rate over a wide temperature range, and at least two different types of crystallites may form in this condition. There is a double melting peak at temperatures of 163 and 169 °C in the DSC curve of quenched PLA. The lower peak corresponds to melting of the β phase, which is the disordered crystalline form, whereas the higher temperature peak corresponds to melting of the α phase, which is the ordered crystalline form. In annealed PLA the melting peak of disordered crystalline form disappears.

It is found that WVTR continuously decreases with increasing crystallinity. When %crystallinity of the sample reached 51%, WVTR is only 1/3 of that of the amorphous polymer.

The linear approach has a good fit to the experimental data, with the coefficient of determination $R^2$ equal to 0.96.

However, the data also gave a statistically significant fit ($R^2$ of 0.95) to the ‘tortuous path’ model, assuming that the crystals are impermeable filler particles with an aspect ratio of 1. This model predicts that the water vapour permeability reaches zero at 100% crystallinity, which is a more reasonable outcome.

It was found that the tortuous path model could also be used to explain published data (from Lasoski and Cobbs) on the water permeability of
polyethylene terephthalate. First it was necessary to convert density crystallinity to DSC crystallinity and then the PET data fitted the tortuous path model, with a regression coefficient, $R^2$, of 97.
5  PLA Composites – Results and Discussion

5.1  Talc

PLA NW 4032D composites with 1%, 3%, 5% talc were mixed using the Haake followed by compression moulding. The morphology of the nanocomposites was investigated using transmission electron microscopy (TEM). The melting and crystallisation behaviour of the composites was investigated using differential scanning calorimetry (DSC). Water vapour transmission rates (WVTR) through the PLA sheets were measured using a MOCON.

5.1.1  Filler Morphology

Figure 71 shows transmission electron micrographs of PLA composites with 1%, 3% and 5% talc mixed by Haake Rheomix OS at the magnifications of 30K and 200K. It is found that the talc was well dispersed in the PLA matrix. With a higher concentration of talc, more talc with multi-layers can be found on the image of PLA with 5% talc at the magnification of 200K.

There is evidence of filler alignment in PLA with 1 wt.% talc. When the concentration of talc goes higher, the talc particles are aligned in the flow direction of the polymer melt. For example, most talc particles oriented in the direction from top left to bottom right on the image of PLA with 3% talc at the magnification of 30K. Also many talc particles oriented in the direction from bottom left to top right in the image of PLA with 5% talc at the magnification of 30K.
Figure 71 Transmission electron micrographs of PLA composites with 1%, 3%, and 5% talc at magnifications of 30K(left) and 200K(right)
By using ImageJ® software, the average particle length and thickness of the talc in PLA with 3% talc were measured on Figure 72. 20 different talc particles were chosen randomly on the whole picture. The average particle length is 161±17nm and the average particle thickness is 19±3nm. Therefore, the average aspect ratio of this talc is 8.

![Image of PLA composite with 3% talc at 30K magnification]

Figure 72 Transmission electron micrographs of PLA composites with 3% talc at magnifications of 30K

The average particle length and thickness of the talc in PLA with 1% and 5% talc were measured using the same method. The results are shown in Table 14. The aspect ratios of talc are only slightly different, the variations of WVTR they cause can be ignored in the Nielsen model when the content of talc is no more than 5%. Therefore the aspect ratio of talc is considered as 7 in the following discussion.
<table>
<thead>
<tr>
<th>samples</th>
<th>average particle length(nm)</th>
<th>average particle thickness(nm)</th>
<th>aspect ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1% talc</td>
<td>93±25</td>
<td>15±3</td>
<td>6</td>
</tr>
<tr>
<td>3% talc</td>
<td>161±17</td>
<td>19±3</td>
<td>8</td>
</tr>
<tr>
<td>5% talc</td>
<td>148±30</td>
<td>20±5</td>
<td>7</td>
</tr>
</tbody>
</table>

Table 14 Aspect ratios of talc in PLA composites

5.1.2 Differential Scanning Calorimetry

Figure 73 shows the DSC trace (first heating scan) for the PLA NW4032D composite with 1% talc. The glass transition temperature \( T_g \) is at 60ºC and there is a small enthalpic relaxation peak. The exothermic peak at 99 ºC corresponds to cold crystallisation on heating above the \( T_g \). This peak is 12 ºC lower than that of pure PLA NW4032D samples (as shown in Figure 60). There is a small exothermic peak at 155 ºC. It corresponds to phase transformation from the disordered \( \beta \) phase to the ordered \( \alpha \) phase. Then the crystals in \( \alpha \) phase melt at 170 ºC, as for pure PLA.
Figure 73 Differential scanning calorimetry curve of PLA NW4032D composite with 1% talc

Figure 74 shows the DSC trace (first heating scan) for the PLA NW4032D composite with 3% talc. The glass transition temperature $T_g$ is at 56$^\circ$C and there is no enthalpic relaxation peak. The exothermic peak at 96 $^\circ$C corresponds to cold crystallisation on heating above the $T_g$. This peak is slightly lower than that for PLA with 1% talc. The small exothermic peak corresponding to phase transformation from the $\beta$ phase to the $\alpha$ phase can also be found at 155 $^\circ$C. The polymer composite also melts at 170 $^\circ$C.
The DSC trace (first heating scan) for the PLA NW4032D composite with 5% talc is shown in Figure 75. The glass transition temperature $T_g$ is at 59 °C. The exothermic peak at 93 °C corresponds to cold crystallisation on heating above the $T_g$ and again it is slightly lower than PLA with 3% talc. The small exothermic peak corresponding to phase transformation from the $\beta$ phase to the $\alpha$ phase and the melting temperature are the same as that of PLA with 1% and 3% talc.
Table 15 shows general thermal properties of PLA composites with talc. The amount of overall crystallinity was calculated using Equation 34.

\[ X_c = \frac{\Delta H_m - \Delta H_c}{\Delta H_{100} \times w} \times 100\% \quad (34) \]

Where \( w \) is the weight fraction of the PLA.

It is found that the proportion of talc does not change the glass transition temperature. However, it obviously decreases the cold crystallisation temperature, as talc is a nucleating agent for PLA. The largest reduction was in going from pure PLA to 1% talc. When there was a 12 °C drop in the cold crystallisation temperature. When more talc was added, the cold crystallisation peak occurred at a lower temperature. In addition, talc shows an effect on the melting of crystals in the disordered \( \beta \) phase, as crystals in \( \beta \) form transfer to \( \alpha \) form in PLA/talc.
### Table 15 Thermal properties of PLA composites with talc

<table>
<thead>
<tr>
<th>Samples</th>
<th>Tg (°C)</th>
<th>Tc (°C)</th>
<th>Tm (°C)</th>
<th>%crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PLA</td>
<td>58±2</td>
<td>111±2</td>
<td>163±1</td>
<td>1.2±0.8</td>
</tr>
<tr>
<td>PLA +1% talc</td>
<td>60±1</td>
<td>99±1</td>
<td>170</td>
<td>2.1±1.0</td>
</tr>
<tr>
<td>PLA +3% talc</td>
<td>56±2</td>
<td>96±1</td>
<td>170</td>
<td>4.4±1.3</td>
</tr>
<tr>
<td>PLA +5% talc</td>
<td>59±1</td>
<td>93±1</td>
<td>170</td>
<td>5.7±1.2</td>
</tr>
</tbody>
</table>

#### 5.1.3 Relationship between WVTR and content of talc

Water vapour transmission rates (WVTR) of quenched PLA NW 4032D and PLA composites samples were measured by using the MOCON at 38 °C and 90% RH. At least 5 specimens were measured for each formulation. It should be noticed that the MOCON was recalibrated before the PLA control and composites were tested to improve its accuracy. As a result, the WVTR of pure PLA NW 4032D appears to be lower than the previous results.

Table 16 shows the degree of crystallinity and WVTR of PLA composites with various levels of talc. NW 4032D is a crystallisable grade of PLA, and talc increases the degree of crystallisation. With more talc added, the degree of crystallinity of PLA becomes higher. For a 5 weight% addition of talc, the degree of crystallinity of the composites increases to 5.7±1.2%.

### Table 16 WVTR of PLA composites with talc

<table>
<thead>
<tr>
<th>Samples</th>
<th>Crystallinity%</th>
<th>WVTR(g.mil/m2.day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PLA</td>
<td>1.2±0.8</td>
<td>181±3</td>
</tr>
<tr>
<td>PLA +1% talc</td>
<td>2.1±1.0</td>
<td>170±6</td>
</tr>
<tr>
<td>PLA +3% talc</td>
<td>4.4±1.3</td>
<td>161±4</td>
</tr>
<tr>
<td>PLA +5% talc</td>
<td>5.7±1.2</td>
<td>143±5</td>
</tr>
</tbody>
</table>
WVTR of PLA composites are plotted in Figure 76. It is found there is a significant reduction in WVTR with increasing clay content. For a 5 weight% addition of talc, there was found to be a reduction in WVTR of 21%.

![Figure 76 WVTR of PLA composites with talc](image)

5.1.4 Nielsen Model fit

Talc is a platy filler. The transmission electron micrographs of PLA/talc composites show that the talc particles are aligned in the direction of melt flow. Therefore the Nielsen tortuosity model can apply.

According to the Nielsen model, the diffusivity \( D \) of PLA/talc composite is:

\[
D = \frac{D_0}{\tau} = \frac{D_0}{1 + \frac{\alpha}{2} V_f} \quad (35)
\]

Where \( V_f \) is the volume fraction of talc, \( \alpha \) is the aspect ratio of talc and this
equals to 7 according to the measurement from the transmission electron micrograph in Figure 72.

Since water has much lower solubility in talc compared with the PLA matrix, the solubility of PLA/talc composite (S) is given by:

\[ S = S_0 \left(1 - V_f\right) \quad (36) \]

Combining Equations (35) and (36), the permeability coefficient of PLA/talc composite \( P \) is:

\[ P = S D = \left(\frac{1-V_f}{1+3.5V_f}\right)P_0 \quad (37) \]

Where \( P_0 \) is the permeability coefficient of pure PLA.

As the volume fraction of talc is required for the Nielsen tortuosity model, it is converted from weight fraction by using following equation:

\[ V_f = \frac{W_f/\rho_f}{W_f/\rho_f+W_p/\rho_p} \quad (38) \]

Where \( W_f \) and \( W_p \) are the weight fraction of talc and PLA. \( \rho_f \) and \( \rho_p \) are the densities of talc and PLA.

The density of talc is 2.78 g/cm\(^3\), and the density of PLA is 1.24 g/cm\(^3\). With 1% talc, the volume fraction of talc \( V_f \) is:

\[ V_f = \frac{0.01/2.78}{0.01/2.78 + 0.99/1.24} = 0.5\% \]

With 3% talc, the volume fraction of talc \( V_f \) is:

\[ V_f = \frac{0.03/2.78}{0.03/2.78 + 0.97/1.24} = 1.4\% \]

With 5% talc, the volume fraction of talc \( V_f \) is:
\[ V_f = \frac{0.05/2.78}{0.05/2.78 + 0.95/1.24} = 2.3\% \]

By using Equation (37), the theoretical WVTR is calculated from the Nielsen tortuosity model. For example, for PLA composite with 1% talc, the theoretical permeability coefficient of PLA/talc composite \( P \) is:

\[ P = \frac{1 - 0.005}{1 + 3.5 \times 0.005} \times 181 = 177 \text{ (g.mil/m2.day)} \]

All the calculated results are shown in Table 17. It is found that the theoretical values are not in agreement with the experimental values.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Vf (%)</th>
<th>Theoretical value (g.mil/m2.day)</th>
<th>Experimental value (g.mil/m2.day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PLA</td>
<td>0</td>
<td>181</td>
<td>181±3</td>
</tr>
<tr>
<td>PLA +1% talc</td>
<td>0.5</td>
<td>177</td>
<td>170±6</td>
</tr>
<tr>
<td>PLA +3% talc</td>
<td>1.4</td>
<td>170</td>
<td>161±4</td>
</tr>
<tr>
<td>PLA +5% talc</td>
<td>2.3</td>
<td>164</td>
<td>143±5</td>
</tr>
</tbody>
</table>

Table 17 WVTR of PLA/talc composites calculated by the Nielsen tortuosity model

The data is plotted in Figure 77. The experimental values are all lower than the values predicted by the Nielsen tortuosity model. With more talc added, the difference between the experimental values and the theoretical values is larger. This is probably because talc acts as a nucleating agent in the PLA composites. It increases the crystallinity of PLA, as shown in Table 16. The crystals will also cause a reduction in the water vapour transmission rate, as already discussed in section 4.3. This effect should be included to get a better theoretical prediction of the water vapour permeability results.
5.1.5 Combined Effect of crystallinity and filler on WVTR

5.1.5.1 Mathematical Approach

According to Equation (33), the predicted WVTR reduction due to crystallinity is given:

\[ \Delta P_1 = P_0 - \frac{1 - \chi}{1 + 2\chi} P_0 \quad (39) \]

And according to Equation (37), the predicted WVTR reduction due to talc filler is given:

\[ \Delta P_2 = P_0 - \frac{1 - V_f}{1 + 3.5V_f} P_0 \quad (40) \]

Assume crystallinity and filler have individual effects on WVTR. Then the predicted WVTR of crystallinity and filler is:

\[ P = P_0 - \Delta P_1 - \Delta P_2 \quad (41) \]
WVTR of pure amorphous PLA is calculated based on WVTR of pure PLA with 1.2% crystallinity as:

\[ P_0 = \frac{181}{\left(1 - 0.012\right) \frac{1}{1 + 0.012/2}} = 184 \text{ (g.mil/m2.day)} \]

The results of calculations are shown in Table 18:

<table>
<thead>
<tr>
<th>crystallinity%</th>
<th>talc%</th>
<th>(\Delta P_1)</th>
<th>(\Delta P_2)</th>
<th>Predicted value (g.mil/m2.day)</th>
<th>Experimental value (g.mil/m2.day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2</td>
<td>0</td>
<td>3</td>
<td>0</td>
<td>181</td>
<td>181±3</td>
</tr>
<tr>
<td>2.1</td>
<td>0.5</td>
<td>6</td>
<td>1</td>
<td>177</td>
<td>170±6</td>
</tr>
<tr>
<td>4.4</td>
<td>1.4</td>
<td>12</td>
<td>4</td>
<td>168</td>
<td>161±4</td>
</tr>
<tr>
<td>5.7</td>
<td>2.3</td>
<td>15</td>
<td>6</td>
<td>162</td>
<td>143±5</td>
</tr>
</tbody>
</table>

Table 18 Predicted WVTR of PLA/talc composites calculated using the mathematical approach

Figure 78 Comparison of experimental values with those calculated by mathematic approach
The data is plotted in Figure 78. The experimental values are all lower than predicted values as well, confirming that crystallinity and filler have a combined effect on the barrier property of PLA.

5.1.5.2 Nielsen model combining crystallinity and content of talc
Since water has much lower solubility in both crystals and talc compared with the PLA matrix, the solubility of PLA/talc composite \( S \) is given by

\[
S = S_0 \left(1 - \chi - V_f \right) \tag{42}
\]

Assume the diffusivity (D) of PLA/talc composite equals:

\[
D = \frac{D_0}{\tau} = \frac{D_0}{1 + \frac{\chi}{2} + \frac{\chi^2}{2} V_f} \tag{43}
\]

Therefore the permeability coefficient of PLA/talc composite \( P \) is:

\[
P = S D = \left(\frac{1 - \chi - V_f}{1 + \frac{\chi}{2} + \frac{\chi^2}{2} V_f}\right) P_0 \tag{44}
\]

By using Equation (44), the theoretical WVTR is calculated. For example, for PLA composite with 1% talc, the theoretical permeability coefficient of PLA/talc composite \( P \) is:

\[
P = \left(\frac{1 - 0.021 - 0.005}{1 + 0.5 \times 0.021 + 3.5 \times 0.005}\right) \times 184
\]

\[= 174 \text{ (g.mil/m2.day)}\]

All the calculated results are shown in Table 17.

<table>
<thead>
<tr>
<th>crystallinity%</th>
<th>talc%</th>
<th>Predicted value (g.mil/m2.day)</th>
<th>Experimental value (g.mil/m2.day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2</td>
<td>0</td>
<td>181</td>
<td>181±3</td>
</tr>
<tr>
<td>2.1</td>
<td>0.5</td>
<td>174</td>
<td>170±6</td>
</tr>
<tr>
<td>4.4</td>
<td>1.4</td>
<td>162</td>
<td>161±4</td>
</tr>
<tr>
<td>5.7</td>
<td>2.3</td>
<td>153</td>
<td>143±5</td>
</tr>
</tbody>
</table>

Table 19 Predicted WVTR of PLA/talc composites calculated using the Nielsen model combining crystallinity and content of talc
The data is plotted in Figure 79. The predicted values are closer to experimental values, giving a better approach to the measured results. In PLA with 5% talc, there is a high chance that talc and crystals fold in layers which significantly increase the length of tortuous path. Thus it leads a strong combining effect of talc and crystallinity on WVTR.

![Graph showing predicted WVTR of PLA/talc composites](image)

**Figure 79** Predicted WVTR of PLA/talc composites calculated using the Nielsen model combining crystallinity and content of talc

### 5.1.5.3 Calculation of Tortuosity Factor

The solubility of PLA/talc composite (S) is given in Equation (42),

$$ S = S_0 \ (1 - \chi - V_t) $$

According to the Nielsen tortuosity model, the diffusivity (D) of PLA/talc composite is:

$$ D = \frac{D_0}{\tau} $$
The permeability coefficient of PLA/talc composite P is:

\[ P = S D = \left( \frac{1 - \chi - V_f}{\tau} \right) P_0 \]  
(43)

Thus the tortuosity factor \( \tau \) can be calculated using the following equation:

\[ \tau = \left( 1 - \chi - V_f \right) \cdot \frac{P_0}{P} \]  
(44)

The results of calculations are shown in Table 20. The tortuosity factor continually increases with increasing content of talc, as both crystallinity and talc increase the length of tortuous path. The relationship between tortuosity factor and content of crystallinity/talc requires more work to be done.

<table>
<thead>
<tr>
<th>Crystallinity%</th>
<th>Talc%</th>
<th>Experimental value (g.mil/m2.day)</th>
<th>( \tau )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2</td>
<td>0</td>
<td>181±3</td>
<td>0.006</td>
</tr>
<tr>
<td>2.1</td>
<td>0.5</td>
<td>170±6</td>
<td>1.056</td>
</tr>
<tr>
<td>4.4</td>
<td>1.4</td>
<td>161±4</td>
<td>1.078</td>
</tr>
<tr>
<td>5.7</td>
<td>2.3</td>
<td>143±5</td>
<td>1.186</td>
</tr>
</tbody>
</table>

Table 20 Tortuosity factors calculated according to experimental values

### 5.2 Nanoclay

#### 5.2.1 Nanocomposite Morphology

##### 5.2.1.1 X-ray Diffraction

The wide-angle X-ray diffraction (WAXD) traces from Cloisite® 30B nanoclay, PLA and PLA nanocomposite containing 3 weight% of nanoclay are shown in Figure 80. The signal due to nanoclay has a 2θ value of 4.8°, which corresponds to an interlayer spacing of 18.4 Å. In the trace from the PLA nanocomposite, it is seen that the peak has shifted to give a 2θ value of 2.6°. This corresponds to an interlayer spacing of 34 Å and thus demonstrates a widening of the clay interplanar spacing, showing that intercalation has occurred.

This result is in agreement with other published WAXD data for PLA.
nanocomposites. For example, Thellen et al.\textsuperscript{90} have reported that the interplanar spacing in montmorillonite layered silicates was 18.7 Å and this increased to 32 Å in PLA nanocomposites produced by blown film extrusion. McLauchlin and Thomas\textsuperscript{196} have reported that Cloisite® 30B nanoclay has an interplanar spacing of 18.1 Å and this increased to 34.8 Å in intercalated PLA nanocomposites produced by solvent casting.

![Figure 80 Wide-angle X-ray diffraction traces from nanoclay, PLA and PLA + 3 weight% nanoclay](image)

Figure 80 Wide-angle X-ray diffraction traces from nanoclay, PLA and PLA + 3 weight% nanoclay
5.2.1.2 Transmission Electron Microscopy

Transmission electron micrographs of PLA nanocomposites containing 1, 3 and 5 weight % clay at low and high magnifications are shown in Figure 81. These micrographs indicate that the clay particles are well dispersed and aligned in the flow direction of the polymer melt. The lines in the micrograph are the edges of the clay platelets. In PLA containing 1% nanoclay, clays have good exfoliation within the polymer matrix. With a higher concentration of clay, the spacing between nanoclay platelets is lower.

The average length of the nanoclay platelets within the PLA matrix was measured from the TEM micrographs using Image J® software. The average thickness of a single clay platelet is 1.6 nm. The average value of the length for nanoclay is 80 nm. Hence the average aspect ratio (length/thickness) is taken as 50 and this was the value used in the tortuosity calculations in section 5.2.4.

The average particle length and thickness of the nanoclay in PLA with 1% and 5% nanoclay were measured using the same method. The results are shown in Table 21. It can be found that the average particle length and thickness of nanoclay in PLA with 5% nanoclay is higher than the other samples. However, the aspect ratios of nanoclay are only slightly different, so that the variations of WVTR they cause can be ignored in the Nielsen model when the content of nanoclay is no more than 5%. Therefore the aspect ratio of nanoclay is considered as 50 in the following discussion.

<table>
<thead>
<tr>
<th>samples</th>
<th>average particle length(nm)</th>
<th>average particle thickness(nm)</th>
<th>aspect ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1% nanoclay</td>
<td>80±23</td>
<td>1.7±0.8</td>
<td>47</td>
</tr>
<tr>
<td>3% nanoclay</td>
<td>80±19</td>
<td>1.6±0.2</td>
<td>50</td>
</tr>
<tr>
<td>5% nanoclay</td>
<td>92±30</td>
<td>1.8±0.7</td>
<td>51</td>
</tr>
</tbody>
</table>

Table 21 Aspect ratios of nanoclay in PLA composites
Figure 81 Transmission electron micrographs of PLA nanocomposites containing 1, 3 and 5 weight % clay at low and high magnifications
5.2.1.3 Nanoclay Particle Size Measurement

Pure nanoclay, PLA with 20% nanoclay, and PLA with 2% nanoclay samples were dispersed in THF by stirring for 15min. Then particles in the solutions were measured in a Delsa™ Nano HC particle analyser. PLA dissolved in THF, so the particle measured is just the nanoclay. The results are shown in Table 22, where $Z_{\text{intensity}}$, $Z_{\text{volume}}$, and $Z_{\text{number}}$ are the peaks of particle size in intensity, volume and number distributions. It is found that nanoclay dispersed in the 20% sample is smaller than pure nanoclay; the particle size is about 1/5 of the size measured for pure nanoclay. The particle size of PLA + 2% nanoclay is even smaller, only about half of the particle size measured in the 20% sample. The results indicate that the nanoclay is well dispersed after the 2$^{nd}$ mixing in the Haake. The particle size measured for PLA + 2% nanoclay is about 36±3nm. This is an average particle size and does not take account of the fact that the particles are plate-like with a high aspect ratio.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Particle size, $Z_{\text{intensity}}$ (nm)</th>
<th>Particle size, $Z_{\text{volume}}$ (nm)</th>
<th>Particle size, $Z_{\text{number}}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>nanoclay [0.25g/L]</td>
<td>426±21</td>
<td>350±59</td>
<td>310±74</td>
</tr>
<tr>
<td>PLA+20%nanoclay [1g/L]</td>
<td>78±8</td>
<td>74±8</td>
<td>71±7</td>
</tr>
<tr>
<td>PLA+2% nanoclay [1g/L]</td>
<td>41±6</td>
<td>38±4</td>
<td>36±3</td>
</tr>
</tbody>
</table>

Table 22 Particle size of PLA/nanoclay solutions

5.2.2 Differential Scanning Calorimetry

Figure 82 shows the DSC trace (first heating scan) for the PLA NW4032D composite with 1% nanoclay. The glass transition temperature $T_g$ is at 56°C. The exothermic peak at 100 ºC corresponds to cold crystallisation on heating above
the $T_g$, which is similar to PLA with 1% talc. It occurs 14 °C lower than for pure PLA NW4032D samples. There is a small exothermic peak at 156 °C. It corresponds to phase transformation from the disordered $\beta$ phase to the ordered $\alpha$ phase. Then the crystals in the $\alpha$ phase melt at 170 °C, the same as pure PLA.

Figure 82 Differential scanning calorimetry curve of PLA NW4032D composite with 1% nanoclay

Figure 83 shows the DSC trace (first heating scan) for the PLA NW4032D composite with 3% nanoclay. The glass transition temperature $T_g$ is at 56°C. The exothermic peak at 100 °C corresponds to cold crystallisation on heating above the $T_g$. The small exothermic peak corresponding to phase transformation from the $\beta$ phase to the $\alpha$ phase can be found at 155 °C. The polymer composite also melts at 170 °C.
The DSC trace (first heating scan) for the PLA NW4032D composite with 5% nanoclay is shown in Figure 84. The glass transition temperature $T_g$ is at 55 °C. The exothermic peak at 99 °C corresponds to cold crystallisation on heating above the $T_g$. The small exothermic peak corresponding to phase transformation and the melting temperature are the same as that of PLA with 1% and 3% nanoclay. Then the polymer composite melts at 169 °C.
Table 23 summarizes the DSC data from the PLA 4032D nanocomposites. It can be seen that there is no significant change in glass transition temperature ($T_g$) with addition of nanoclay. There is, however, a significant reduction in the cold crystallisation temperature ($T_c$). This indicates that the nanoclay platelets can facilitate nucleation of PLA crystallites. Furthermore, the disappearance of the lower temperature melting point ($T_m$) with addition of nanoclay indicates that the nanoclay particles promote formation of the ordered crystalline phase.

Compared with PLA composites with talc, PLA/nanoclay samples also show a significant reduction in the cold crystallisation temperature. However, the $T_c$ does not further decrease as the content of nanoclay increases. They all have the small exothermic peak corresponding to phase transformation from the $\beta$ phase to the $\alpha$ phase, and the melting temperatures are all about 170 °C. With more talc added, the degree of crystallinity of PLA becomes higher. Nanoclay also
increases crystallinity of PLA. But unlike talc, the content of nanoclay does not have a strong effect on crystallinity. For example, the samples of PLA with 6% nanoclay have crystallinity of 2.1±1.7%, only slightly higher than the samples of PLA with 1% nanoclay, which have crystallinity of 1.8±0.8%.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Tg(°C)</th>
<th>Tc(°C)</th>
<th>Tm(°C)</th>
<th>%crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PLA 4032D</td>
<td>58±1</td>
<td>111±2</td>
<td>164±1, 170±1</td>
<td>1.2±0.8</td>
</tr>
<tr>
<td>PLA+1%nanoclay</td>
<td>56±1</td>
<td>100±1</td>
<td>170±1</td>
<td>1.8±0.8</td>
</tr>
<tr>
<td>PLA+2%nanoclay</td>
<td>58±1</td>
<td>100±1</td>
<td>170±1</td>
<td>2.4±1.8</td>
</tr>
<tr>
<td>PLA+3%nanoclay</td>
<td>56±1</td>
<td>100±1</td>
<td>170±1</td>
<td>1.7±1.0</td>
</tr>
<tr>
<td>PLA+4%nanoclay</td>
<td>58±2</td>
<td>100±2</td>
<td>169±1</td>
<td>2.1±2.1</td>
</tr>
<tr>
<td>PLA+5%nanoclay</td>
<td>57±2</td>
<td>98±1</td>
<td>169±1</td>
<td>2.2±2.1</td>
</tr>
<tr>
<td>PLA+6%nanoclay</td>
<td>56±1</td>
<td>98±2</td>
<td>168±1</td>
<td>2.1±1.7</td>
</tr>
</tbody>
</table>

Table 23 DSC data from the PLA 4032D nanocomposites

5.2.3 Relationship between WVTR and content of nanoclay

Water vapour transmission rates (WVTR) as measured through the PLA sheets processed from the crystallisable PLA 4032D, are shown in Table 24. Four samples were measured for each data point. It is found that there is a significant reduction in WVTR with increasing clay content, which starts to level off at clay additions above 5 weight %. It should be noticed again that the MOCON was recalibrated before the PLA control and composites were tested to improve its accuracy. As a result, the WVTR of pure PLA NW 4032D appears to be slightly different from section 4.3.1.
<table>
<thead>
<tr>
<th>Samples</th>
<th>WVTR (g-mil/m²-day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PLA 4032D</td>
<td>181 ± 4</td>
</tr>
<tr>
<td>PLA+1% nanoclay</td>
<td>153 ± 8</td>
</tr>
<tr>
<td>PLA+2% nanoclay</td>
<td>144 ± 5</td>
</tr>
<tr>
<td>PLA+3% nanoclay</td>
<td>130 ± 4</td>
</tr>
<tr>
<td>PLA+4% nanoclay</td>
<td>115 ± 4</td>
</tr>
<tr>
<td>PLA+5% nanoclay</td>
<td>108 ± 5</td>
</tr>
<tr>
<td>PLA+6% nanoclay</td>
<td>98 ± 2</td>
</tr>
</tbody>
</table>

Table 24 Water Vapour Transmission Rates of PLA Nanocomposites

The data is plotted in Figure 85. Although 4032D is a crystallisable grade of PLA, samples were cooled quickly in the compression moulding machine and so significant crystallisation did not take place. Hence the reduction in permeability is due to the effect of the nanoclay. For a 5 wt% addition of nanoclay, there was found to be a reduction in WVTR of 40%. This result compares with data reported by Thellen et al.\textsuperscript{90}, who incorporated 5 wt% of organically modified montmorillonite into plasticised PLA blown films and reported a 50% improvement in water vapour barrier.
5.2.4 Nielsen Model fit

Nanoclay is platy filler. The transmission electron micrographs of PLA/nanoclay composites show that the nanoclay aligns in the direction of melt flow. Therefore the Nielsen tortuosity model can apply.

According to the Nielsen tortuosity model, the diffusivity (D) of PLA/nanoclay composite is as:

$$D = \frac{D_0}{\tau} = \frac{D_0}{1 + \frac{\alpha}{2}V_f}$$  \hspace{1cm} (45)$$

Where $V_f$ is the volume fraction of nanoclay. $\alpha$ is the aspect ratio of nanoclay, which equals to 50 according to the measurement on the transmission electron micrograph in section 5.2.1.2.
Since water has much lower solubility in nanoclay compared to PLA matrix, the solubility of PLA/ nanoclay composite (S) is as:

\[ S = S_0 (1 - V_f) \] (46)

Combine Equation (45) and (46), permeability coefficient of PLA/ nanoclay composite \( P \) is:

\[ P = S D = \left( \frac{1-V_f}{1+25V_f} \right) P_0 \] (47)

Where \( P_0 \) is the permeability coefficient of pure PLA.

As the volume fraction of nanoclay is required for the Nielsen tortuosity model, it is converted from weight fraction by using following equation:

\[ V_f = \frac{W_f/\rho_f}{W_f/\rho_f + W_p/\rho_p} \] (48)

Where \( W_f \) and \( W_p \) are the weight fraction of nanoclay and PLA. \( \rho_f \) and \( \rho_p \) are the densities of nanoclay and PLA.

As density of nanoclay is 1.98 g/cm\(^3\), and density of PLA is 1.24 g/cm\(^3\), with 1% nanoclay, the volume fraction of nanoclay \( V_f \) is:

\[ V_f = \frac{0.01/1.98}{0.01/1.98 + 0.99/1.24} = 0.6\% \]

With 3% nanoclay, the volume fraction of nanoclay \( V_f \) is:

\[ V_f = \frac{0.03/1.98}{0.03/1.98 + 0.97/1.24} = 1.9\% \]

With 5% nanoclay, the volume fraction of nanoclay \( V_f \) is:

\[ V_f = \frac{0.05/1.98}{0.05/1.98 + 0.95/1.24} = 3.2\% \]
By using Equation (47), the theoretical WVTR is calculated from the Nielsen tortuosity model. For example, for PLA composite with 1% nanoclay, the theoretical permeability coefficient of PLA/nanoclay composite \( P \) is:

\[
P = \left( \frac{1 - 0.006}{1 + 25 \times 0.006} \right) \times 181
\]

\[
= 156 \text{(g.mil/m2.day)}
\]

All the calculated results are shown in Table 25. It is found that the theoretical values are not quite the same as the experimental values, and lie just below the experimental values.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Vf (%)</th>
<th>Theoretical value (g.mil/m2.day)</th>
<th>Experimental value (g.mil/m2.day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PLA</td>
<td>0</td>
<td>181</td>
<td>181 ± 4</td>
</tr>
<tr>
<td>PLA +1% nanoclay</td>
<td>0.6</td>
<td>156</td>
<td>153 ± 8</td>
</tr>
<tr>
<td>PLA +2% nanoclay</td>
<td>1.3</td>
<td>134</td>
<td>144 ± 5</td>
</tr>
<tr>
<td>PLA +3% nanoclay</td>
<td>1.9</td>
<td>120</td>
<td>130 ± 4</td>
</tr>
<tr>
<td>PLA +4% nanoclay</td>
<td>2.5</td>
<td>109</td>
<td>115 ± 4</td>
</tr>
<tr>
<td>PLA +5% nanoclay</td>
<td>3.2</td>
<td>97</td>
<td>108 ± 5</td>
</tr>
<tr>
<td>PLA +6% nanoclay</td>
<td>3.8</td>
<td>89</td>
<td>98 ± 2</td>
</tr>
</tbody>
</table>

Table 25 WVTR of PLA/nanoclay composites calculated by the Nielsen tortuosity model
The values predicted from the Nielsen model are compared with the measured values in the plot of permeability versus clay volume fraction in Figure 86. The trend line predicted by the Nielsen model lies just below that of the experimental data. Hence the experimental data give a reasonably good fit to the Nielsen model, which predicts the maximum improvement in barrier properties, assuming that the clay platelets are 100% intercalated or exfoliated and perfectly aligned.

Experimental WVTR values of PLA/talc composites are lower than the theoretical values predicted from Nielsen model. However, experimental WVTR values of PLA/nanoclay composites are higher. This is because talc acted as nucleating agent in processing and sufficiently improved crystallinity of PLA, and crystallinity further reduced permeation of water. Nanoclay did not increase crystallinity as much as talc, therefore crystallinities did not have a strong effect on WVTR in PLA/nanoclay samples and the reduction of water permeation is due to the nanoclay itself.

![Figure 86 Comparison of Measured Values with those predicted from the Nielsen model.](image)
5.2.5 Calculation of Tortuosity Factor

The solubility of PLA/nanoclay composite (S) is given in Equation (42),

\[ S = S_0 (1 - \chi - V_f) \]

According to the Nielsen tortuosity model, the diffusivity (D) of PLA/nanoclay composite is:

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

The permeability coefficient of PLA/nanoclay composite \( P \) is:

\[ P = S D = \left( \frac{1 - \chi - V_f}{\tau} \right) P_0 \]

Thus the tortuosity factor \( \tau \) can be calculated using Equation (44):

\[ \tau = (1 - \chi - V_f) \cdot \frac{P_0}{P} \]

The results of calculations are shown in

<table>
<thead>
<tr>
<th>Crystallinity%</th>
<th>Vf (%)</th>
<th>Experimental value (g.mil/m2.day)</th>
<th>( \tau )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2</td>
<td>0</td>
<td>181 ± 4</td>
<td>1.006</td>
</tr>
<tr>
<td>1.8</td>
<td>0.6</td>
<td>153 ± 8</td>
<td>1.176</td>
</tr>
<tr>
<td>2.4</td>
<td>1.3</td>
<td>144 ± 5</td>
<td>1.233</td>
</tr>
<tr>
<td>1.7</td>
<td>1.9</td>
<td>130 ± 4</td>
<td>1.367</td>
</tr>
<tr>
<td>2.1</td>
<td>2.5</td>
<td>115 ± 4</td>
<td>1.529</td>
</tr>
<tr>
<td>2.2</td>
<td>3.2</td>
<td>108 ± 5</td>
<td>1.614</td>
</tr>
<tr>
<td>2.1</td>
<td>3.8</td>
<td>98 ± 2</td>
<td>1.77</td>
</tr>
</tbody>
</table>

Table 26. The tortuosity factor continuous increases with increasing content of nanoclay.
<table>
<thead>
<tr>
<th>τ</th>
<th>Vf</th>
<th>∆τ</th>
<th>∆Vf</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.4</td>
<td>1.3</td>
<td>144 ± 5</td>
<td>1.233</td>
</tr>
<tr>
<td>1.7</td>
<td>1.9</td>
<td>130 ± 4</td>
<td>1.367</td>
</tr>
<tr>
<td>2.1</td>
<td>2.5</td>
<td>115 ± 4</td>
<td>1.529</td>
</tr>
<tr>
<td>2.2</td>
<td>3.2</td>
<td>108 ± 5</td>
<td>1.614</td>
</tr>
<tr>
<td>2.1</td>
<td>3.8</td>
<td>98 ± 2</td>
<td>1.77</td>
</tr>
</tbody>
</table>

Table 26 Tortuosity factors of PLA nanocomposites calculated according to experimental values

Tortuosity factor $\tau$ of PLA nanocomposites as a function of volume % nanoclay is plotted in Figure 87. It appears to be a linear relationship between permeability and content of nanoclay, as:

$$\frac{\Delta \tau}{\Delta Vf} = 19.4$$

And the equation of the trend line is:

$$\tau = 1.02 + \frac{38.8}{2} Vf$$
Figure 87 Tortuosity Factor $\tau$ of PLA Nanocomposites as a Function of volume % Nanoclay
5.3 Conclusion

**Talc**

It is confirmed that the talc was well dispersed in the PLA matrix using transmission electron microscopy (TEM). The talc particles are aligned in the flow direction of the polymer melt.

The DSC data showed that the proportion of talc does not change the glass transition temperature. However, it obviously decreases the cold crystallisation temperature. As more talc was added, the cold crystallisation occurred at a lower temperature. Talc acts as a nucleating agent. In addition, talc shows an effect on the melting of crystals in the disordered β phase. Crystals in the β phase transfer to the ordered α phase in PLA/talc composites before melting.

The experimental values of water vapour permeation rate are all lower than the values predicted by the Nielsen tortuosity model. With more talc added, the difference between the experimental values and the theoretical values becomes larger. This is because talc acts as a nucleating agent in the PLA composites and it increases crystallinity of PLA. The crystalline regions also cause a reduction in the water vapour transmission rate. This needs to be taken into account.

**Nanoclay**

It was confirmed that the nanocomposite structures were intercalated wide-angle X-ray diffraction (WAXD). Results from WAXD analysis showed that the clay interlayer spacing increased from 1.84 to 3.4 nm. TEM micrographs indicated that the clay particles were well dispersed and aligned in the flow direction of the polymer melt. Using image processing software it was found that the thickness of a single clay platelet was 1.6 nm. The average length of the nanoclay platelets within the PLA matrix was measured from the TEM micrographs and found to be 80 nm, thus giving an average aspect ratio (length/thickness) of 50.
The DSC data showed that addition of nanoclay had no effect on the glass transition temperature ($T_g$). However, there was a significant reduction in the cold crystallisation temperature ($T_c$), indicating that the nanoclay platelets facilitated nucleation of PLA crystallites. The disappearance of the lower temperature melting point ($T_m$) with addition of nanoclay also showed that the nanoclay particles promoted formation of the ordered crystalline phase.

Measured values of water vapour permeability of the PLA nanocomposites were compared with values from the Nielsen tortuosity model. The trend line predicted by the Nielsen model lay just below that of the experimental data, showing a reasonably good fit given that the model assumes that the clay platelets are 100% intercalated or exfoliated and perfectly aligned. Nanoclay did not increase crystallinity as much as talc, therefore crystals did not have a strong effect on WVTR in PLA/nanoclay samples and the reduction of water permeation is due to the nanoclay.
6 Polybutylene Succinate – Results and Discussion

The PBS granules supplied by IRe Chemical Ltd. were pre-dried and then melt blended. Then the product was compressed using the same mould as used for the PLA samples. PBS nanocomposites with 1%, 3% and 5% nanoclay were also mixed using the Haake followed by compression moulding. The melting and crystallisation behaviours of the pure samples and composites were investigated using differential scanning calorimetry (DSC) and cross polarised optical microscopy. The morphology of the nanocomposites was investigated using transmission electron microscopy (TEM). Wide-angle X-ray diffraction (WAXD) was also used to investigate the extent of intercalation or exfoliation of the nanoclay. Water vapour transmission rates (WVTR) through the PBS sheets were measured using a MOCON.

6.1 Crystallinity and Morphology

6.1.1 Pure PBS

6.1.1.1 Differential Scanning Calorimetry

Figure 88 shows a moulded sample of pure PBS. It is white and not transparent. The sample is much softer compared with PLA samples, since the glass transition temperature of PBS is much lower than room temperature.
Figure 89 shows the differential scanning calorimetry curve of pure PBS granules during the 1st and 2nd heating runs. The glass transition temperature $T_g$ is below zero, which was not in the range of measurement. PBS melts at 126 °C. During cooling from 160 °C to 20 °C at a cooling rate of 10 °C/min, PBS crystallises at 87°C, with a strong exothermic peak. This indicates that PBS crystallises much easier and faster than PLA. During the 2nd heating, PBS melts at 118°C. However, the melting peak is different from the one in the 1st heating run as there seems to be a small peak merged into the main peak at about 110°C.
Figure 89 Differential scanning calorimetry curve of pure PBS granules during the 1st heating (upper) and 2nd heating (lower) scan.

Figure 90 shows the differential scanning calorimetry curve of quenched PBS. During the 1st heating run, there is a small exothermic peak at 100±1°C. It may correspond to phase transformation of PBS crystals, as was the case for PLA. PBS melts at 115±1 °C. During the cooling PBS crystalises at 88 °C, the same as
PBS granules. During the 2nd heating run, there are two melting peaks at 108 °C and 116 °C. The lower peak may correspond to melting of the less ordered crystalline form, whereas the higher temperature peak may correspond to melting of ordered crystalline form. These two forms of PBS crystals have been discovered by Ichikawa et al. According to their work, the β form appears with application of stress.

Figure 90 Differential scanning calorimetry curve of quenched PBS during the 1st heating (upper) and 2nd heating (lower) scans
Figure 91 shows the differential scanning calorimetry curve of PBS annealed at 100 °C for 10 min. During the 1st heating scan, PBS melts at 118 °C, with a broad melting peak instead of the small exothermic peak before melting shown in the DSC of quenched PBS. This indicates that the less ordered crystal form mainly melts in annealed PBS. During the cooling PBS crystalises at 87 °C. During the 2nd heating scan, there are two melting peaks at 106 °C and 115 °C, similar to quenched PBS.

Figure 91 Differential scanning calorimetry curve of annealed PBS during the 1st heating (upper) and 2nd heating (lower)
Table 27 shows degrees of crystallinity of pure PBS samples. Quenched PBS already has degree of crystallinity of 29.7±2.3%, which is much higher than quenched PLA. By annealing the degree of crystallinity can be further increased to about 42%.

<table>
<thead>
<tr>
<th>Samples</th>
<th>1st heating</th>
<th>2nd heating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Granules</td>
<td>35.8±2.7%</td>
<td>34.9±0.8%</td>
</tr>
<tr>
<td>Quenched</td>
<td>29.7±2.3%</td>
<td>36.6±1.4%</td>
</tr>
<tr>
<td>Annealed</td>
<td>41.9±2.5%</td>
<td>35.6±1.5%</td>
</tr>
</tbody>
</table>

Table 27 Degrees of crystallinity of pure PBS samples

6.1.1.2 Crystalline Morphology

Figure 92 shows the crystalline morphology change of pure PBS film in polarised optical microscopy at a heating rate of 10 °C/min. It can be found that PBS spherulites are tiny. When the sample is heated to 105 °C, spherulites seem to have changed, as many impurity particles disappear and the colour of the image becomes blue. This change lasts until 110 °C, then PBS spherulites starts to melt at 113 °C, as the whole image suddenly becomes black.
When the melted sample was cooled on the hot stage at a cooling rate of 10 °C/min, nothing changed until the temperature dropped to 93°C, then a lot of tiny spherulites suddenly appeared. Spherulites formed very fast and at 90°C they had already filled the whole area. The amount of birefringence continued increasing until about 57 °C as the image goes brighter. PBS spherulites are all very tiny. There is no large spherulite observed in the photos.
Figure 93 Cooling of pure PBS film in hot staged polarised optical microscopy at 100 °C, 93 °C, 90 °C, and 57 °C

6.1.2 PBS Nanocomposites
6.1.2.1 Differential Scanning Calorimetry

Figure 94 shows the DSC trace (first heating scan) for the PBS composite with 1% nanoclay. The glass transition temperature $T_g$ is out of the temperature range of the test. There is a small exothermic peak at 100 °C. It corresponds to phase transformation from a disordered phase to an ordered phase, which is similar to the quenched PBS. Then the crystals of α phase melt at 115 °C.
Figure 94 Differential scanning calorimetry curve of PBS composite with 1% nanoclay

Figure 95 shows the DSC trace (first heating scan) for the PBS composite with 3% nanoclay. The small exothermic peak corresponding to phase transformation from a disordered phase to an ordered phase can be found at 98°C. The polymer composite melts at 116 °C.
The DSC trace of first heating scan for the PBS composite with 5% nanoclay is shown in Figure 96. Phase transformation of crystals occurs at 99°C. The polymer composite melts at 115 °C.
Figure 96 Differential scanning calorimetry curve of PBS composite with 5% nanoclay

Table 28 summarizes the DSC data from the PBS nanocomposites. It can be seen that there is no significant change in phase transformation temperature ($T_1$) and melting temperature with addition of nanoclay. The degree of crystallinity does not change much. For PBS with 5% nanoclay, the degree of crystallinity is lower than pure PBS. This is because pure PBS already has a high degree of crystallinity. It is difficult for the polymer chains between nanoclay particles to form crystals. As a result, the degree of crystallinity decreases slightly.

Compared to PLA composites with nanoclay, the nanoclay platelets have negligible effect on nucleation of PBS crystallites. This is because PBS forms crystals easier and faster than PLA. Quenched PLA has $1.2\pm0.8\%$ crystallinity, but quenched PBS has $29.7\pm2.3\%$ crystallinity. As a result, nanoclay cannot accelerate nucleation of PBS crystals. Furthermore, the content of nanoclay does not have a strong effect on crystallinity in both PLA and PBS. Samples of PLA with more nanoclay have slightly higher degrees of crystallinity, while the degree of crystallinity in PBS samples with 5% nanoclay is lower.
<table>
<thead>
<tr>
<th>Samples</th>
<th>T_i(°C)</th>
<th>T_m(°C)</th>
<th>%crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PBS</td>
<td>100±1</td>
<td>116±1</td>
<td>29.7±2.3</td>
</tr>
<tr>
<td>PBS+1%nanoclay</td>
<td>100±1</td>
<td>115±1</td>
<td>30.1±1.2</td>
</tr>
<tr>
<td>PBS+3%nanoclay</td>
<td>98±1</td>
<td>116±1</td>
<td>29.6±1.2</td>
</tr>
<tr>
<td>PBS+5%nanoclay</td>
<td>99±1</td>
<td>115±1</td>
<td>27.3±1.5</td>
</tr>
</tbody>
</table>

Table 28 DSC data from the PBS nanocomposites

6.1.2.2 Crystalline Morphology
Figure 97 shows the crystalline morphology change of PBS composite with 3% nanoclay in polarised optical microscope at a heating rate of 10 °C/min. When the sample is heated to 108 °C, crystals seem to have changed, as the colour of the image becomes slightly darker. Then PBS crystals start to melt at 113 °C, as the whole image suddenly becomes dark. At 116 °C tiny crystal totally disappeared, with some white particles left, which may be nanoclay aggregations.
Figure 97 PBS composite with 3% nanoclay in hot staged polarised optical microscopy at, 105 °C, 108 °C, 113 °C, and 116 °C

Figure 98 shows the crystallisation of PBS composite with 3% nanoclay in hot stage polarised optical microscope at a cooling rate of 10 °C/min. The sample did not change until the temperature dropped to 95°C, then a lot of tiny crystals suddenly appeared. At 90°C they have already filled the whole area. The degree of crystallinity continued increasing until about 80 °C as the image goes yellow. There is no big spherulite observed on the photos, as was the case for pure PBS. Compared to PLA, PBS has a high nucleation rate but relatively low crystal growth rate. So the effect of nanoclay on crystallinity is not strong in PBS, as speed of crystallisation depends more on growth rate of crystals in PBS.
6.2 Filler Morphology

6.2.1.1 X-ray Diffraction
The wide-angle X-ray diffraction (WAXD) traces from Cloisite® 30B nanoclay, PBS and PBS nanocomposite containing 3 weight% of nanoclay are shown in Figure 99. The signal due to nanoclay has a 2θ value of 4.8°, which corresponds to an interlayer spacing of 18.4 Å. In the trace from the PBS nanocomposite, it is seen that the peak has shifted to give a 2θ value of 3.0°. This corresponds to an interlayer spacing of 29 Å and thus demonstrates a widening of the clay interplanar spacing, showing that intercalation has occurred.

Figure 98 Cooling of PBS composite with 3% nanoclay in hot staged polarised optical microscopy at 95 °C, 90 °C, 88 °C, and 80 °C
Figure 99 Wide-angle X-ray diffraction traces from nanoclay, PBS and PBS + 3 weight% nanoclay

6.2.1.2 Transmission Electron Microscopy
Transmission electron micrographs of PBS nanocomposites containing 3 and 5 weight % clay at magnifications of 50k and 200k are shown in Figure 100. It was found that PBS kept shrinking in the TEM because it is very soft with a low melting point. As a result, it was difficult to capture a clear image and nanoclay particles came closer to each other in the shrunken PBS samples. These micrographs show that the clay particles are not as well dispersed as in the PLA nanocomposites. The lines in the micrograph are the edges of the clay platelets. In PBS containing 3% nanoclay, some clay is exfoliated within the polymer matrix. With a higher concentration of clay, the spacing between nanoclay platelets is lower.
Figure 100 Transmission electron micrographs of PBS nanocomposites containing 3 and 5 weight % clay at magnifications of 50k (left) and 200k (right)

A more detailed view of the clay platelet structure can be seen in Figure 101. This shows a 5 weight % nanoclay sample at 200k magnification. By using Image J® software, the average thickness of a single clay platelet is measured to be 1.6±0.2 nm, and the length for nanoclay is measured to be 80±19 nm. Hence the average aspect ratio (length/thickness) of nanoclay is taken as 50.
6.3 Water Vapour Permeability

6.3.1 Relationship between WVTR and content of nanoclay
Water vapour transmission rates (WVTR) of quenched pure PBS and PBS composite samples were measured by using the MOCON. At least 3 specimens were measured for each formulation. Measured WVTR of PBS composites with nanoclay are shown in Table 29. It is found that there is a significant reduction in WVTR with increasing clay content.
<table>
<thead>
<tr>
<th>Samples</th>
<th>Crystallinity%</th>
<th>WVTR (g.mil/m2.day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PBS</td>
<td>29.7±2.3</td>
<td>192±4</td>
</tr>
<tr>
<td>PBS+1% nanoclay</td>
<td>30.1±1.2</td>
<td>175±6</td>
</tr>
<tr>
<td>PBS +3% nanoclay</td>
<td>29.6±1.2</td>
<td>159±5</td>
</tr>
<tr>
<td>PBS +5% nanoclay</td>
<td>27.3±1.5</td>
<td>150±9</td>
</tr>
</tbody>
</table>

Table 29 WVTR of PBS composites with nanoclay

WVTR of PBS composites are plotted on Figure 102. It is found there is a significant reduction in WVTR with increasing clay content. For a 5 weight% addition of talc, there was found to be a reduction in WVTR of 22%.

Figure 102 Water vapour transmission rates (WVTR) of PBS nanocomposites as a function of weight % nanoclay
6.3.2 Nielsen Model fit

The aspect ratio of nanoclay equals to 50 according to the measurement on the transmission electron micrograph. Therefore Equation (47) can be also used to calculate permeability coefficient of PBS/ nanoclay composite $P$, as:

$$P = S \cdot D = \frac{1-V_f}{1+25V_f} P_0$$

Where $P_0$ is the permeability coefficient of pure PBS.

As the volume fraction of nanoclay is required for the Nielsen tortuosity model, it is converted from weight fraction by using following equation:

$$V_f = \frac{W_f/\rho_f}{W_f/\rho_f + W_p/\rho_p} \quad (49)$$

Where $W_f$ and $W_p$ are the weight fraction of nanoclay and PBS. $\rho_f$ and $\rho_p$ are the densities of nanoclay and PBS.

As density of nanoclay is 1.98 g/cm$^3$, and density of PBS is 1.26 g/cm$^3$. With 1% nanoclay, the volume fraction of nanoclay $V_f$ is:

$$V_f = \frac{0.01/1.98}{0.01/1.98 + 0.99/1.26} = 0.6\%$$

With 3% nanoclay, the volume fraction of nanoclay $V_f$ is:

$$V_f = \frac{0.03/1.98}{0.03/1.98 + 0.97/1.26} = 1.9\%$$

With 5% nanoclay, the volume fraction of nanoclay $V_f$ is:

$$V_f = \frac{0.05/1.98}{0.05/1.98 + 0.95/1.26} = 3.2\%$$

By using Equation (47), the theoretical WVTR is calculated by the Nielsen tortuosity model. For example, for PBS composite with 1% nanoclay, the
theoretical permeability coefficient of PBS/nanoclay composite P is:

\[
P = \left( \frac{1 - 0.006}{1 + 25 \times 0.006} \right) \times 192
\]

\[= 165 \text{(g.mil/m}^2\text{.day)}
\]

All the calculated results are shown in Table 30. It is found that the theoretical values are lower than the experimental values.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Vf (%)</th>
<th>Theoretical value (g.mil/m2.day)</th>
<th>Experimental value (g.mil/m2.day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure BBS</td>
<td>0</td>
<td>192</td>
<td>192±4</td>
</tr>
<tr>
<td>PBS +1% clay</td>
<td>0.6</td>
<td>164</td>
<td>175±6</td>
</tr>
<tr>
<td>PBS +3% clay</td>
<td>1.9</td>
<td>127</td>
<td>159±5</td>
</tr>
<tr>
<td>PBS +5% clay</td>
<td>3.2</td>
<td>103</td>
<td>150±9</td>
</tr>
</tbody>
</table>

Table 30 WVTR of PBS/nanoclay composites calculated by the Nielsen tortuosity model

The data is plotted in Figure 103. The experimental values are all higher than the values predicted by the Nielsen tortuosity model. With more nanoclay added, the difference between the experimental values and the theoretical values becomes larger. This is because all PBS samples have very high degrees of crystallinity. And so the nanoclay is not as well dispersed as it was in the PLA nanocomposites. Hence there is not as great a reduction in the water vapour permeability.
Figure 103 Comparison of measured values with those predicted from the Nielsen model.

6.3.3 Calculation of Tortuosity Factor

WVTR of pure amorphous PBS is calculated based on WVTR of pure PBS with 29.7% crystallinity as:

$$P_0 = \frac{192}{(1-0.297) + 0.297 / 2} = 313.67 \text{ (g.mil/m2.day)}$$

By using Equation (44) The tortuosity factor $\tau$ can be calculated as:

$$\tau = (1 - \chi - Vf) \cdot \frac{P_0}{P}$$

The results are shown in Table 31. Then tortuosity Factor $\tau$ of PBS nanocomposites as a function of volume % nanoclay is plotted in Figure 87. It appears to be a linear relationship between permeability and nanoclay in PBS nanocomposites, as:

$$\frac{\Delta \tau}{\Delta V_f} = 7.69$$
And the equation of the trend line is:

$$\tau = 1.19 + \frac{15.4}{2} V_f$$

<table>
<thead>
<tr>
<th>Crystallinity</th>
<th>Talc Vf(%)</th>
<th>Experimental value (g.mil/m2.day)</th>
<th>$\tau$</th>
</tr>
</thead>
<tbody>
<tr>
<td>29.7</td>
<td>0</td>
<td>192±4</td>
<td>1.15</td>
</tr>
<tr>
<td>30.1</td>
<td>0.6</td>
<td>175±6</td>
<td>1.24</td>
</tr>
<tr>
<td>29.6</td>
<td>1.9</td>
<td>159±5</td>
<td>1.35</td>
</tr>
<tr>
<td>27.3</td>
<td>3.2</td>
<td>150±9</td>
<td>1.45</td>
</tr>
</tbody>
</table>

Table 31 Tortuosity factors of PBS nanocomposites calculated according to experimental values

Figure 104 Tortuosity Factor $\tau$ of PBS Nanocomposites as a Function of volume % Nanoclay
6.3.4 In comparison with PLA composites

Figure 105 shows comparison of WVTR reduction rates $P/P_0$ of PBS and PLA nanocomposites. It is found that although same type and amount of nanoclay was added in PBS and PLA, the effect on WVTR is totally different. For a 3.2 volume % addition of nanoclay (5 weight %), there was found to be a reduction in WVTR of 40% in PLA; but there was only a reduction of 22% in PBS. This is because PLA and PBS have different crystallisabilities. Nanoclay in amorphous polymers such as PLA creates a long tortuosity path which results a high reduction of water vapour permeability. However, there is a combining effect of crystals and nanoclay in highly crystalline polymers such as PBS, and the tortuosity path does not increase as much as in amorphous polymers, which gives a low reduction of water vapour permeability. More experiments are needed to investigate how water vapour permeability changes when both crystallinity and contents of filler are changed.

![Figure 105 Comparison of WVTR of PBS and PLA nanocomposites](image-url)
Figure 106 shows comparison of tortuosity factors of PBS and PLA nanocomposites. Although crystallinity of PLA and PBS nanocomposites does not change obviously, $\Delta \frac{\tau}{\Delta V_f}$ of PBS nanocomposites is lower than that of PLA nanocomposites. This difference is related to crystallinity. PLA nanocomposites has much lower crystallinity% than PBS, and this leads to a higher slope of the line.

Figure 106 Comparison of tortuosity factors of PBS and PLA nanocomposites
6.4 Conclusion

DSC data shows that PBS crystalises much easier and faster than PLA. During the 1st heating of quenched PBS, there is a small exothermic peak at 100±1°C corresponding to phase transformation of PBS crystals. PBS melts at 115±1 °C. During cooling PBS crystallises at 88 °C. During the 2nd heating run, there are two melting peaks at 108 °C and 116 °C. The lower peak corresponds to melting of the less ordered crystalline form, whereas the higher temperature peak corresponds to melting of the ordered crystalline form. Polarised optical microscopy shows PBS crystals are all very tiny. PBS melt starts to crystalise between 93°C and 90°C, and the nucleation process is very fast.

The DSC data from the PBS nanocomposites shows that there is no significant change in phase transformation temperature (T₁) and melting temperature with addition of nanoclay. The degree of crystallinity slightly decreases with addition of 5% nanoclay. This is because it is difficult for the polymer chains between nanoclay particles to form crystals. As a result, the degree of crystallinity only decreases slightly. Polarised optical microscopy confirmed that PBS has a high nucleation rate but relatively low crystal growth rate compared to PLA.

According to TEM and wide-angle X-ray diffraction (WAXD) results, the PBS nanocomposite structures were intercalated. Results from WAXD analysis showed that the clay interlayer spacing increased from 1.84 to 2.9 nm. TEM micrographs indicated that the clay particles were aligned in the flow direction of the polymer melt. The average thickness of a single clay platelet is 1.6±0.2 nm. The average value of the length for nanoclay is 80±19 nm. Hence the average aspect ratio (length/thickness) is taken as 50.

There is a significant reduction in WVTR with increasing clay content. The experimental values are all higher than the values predicted by the Nielsen tortuosity model. With more nanoclay added, the difference between the experimental values and the theoretical values is larger. This is because all PBS
samples have very high degrees of crystallinity. And so the nanoclay is not as well dispersed as it was in the PLA nanocomposites. So it is not effective in reducing water vapour permeability.

By comparing WVTR reduction rates $P/P_0$ of PBS and PLA composites, it is found that although the same type and amount of nanoclay was added in PBS and PLA, the effects on WVTR are totally different. This is because PLA and PBS have different crystallisabilities. Nanoclay in amorphous polymers such as PLA creates a long tortuosity path which results a high reduction of water vapour permeability. However, all PBS samples have very high degrees of crystallinity, there is a combined effect of crystals and nanoclay and the tortuosity path does not increase as much as in amorphous polymers. The nanoclay in PBS is not as well dispersed as it was in the PLA nanocomposites. Hence there is not as great a reduction in the water vapour permeability.
7 Conclusions and further work

7.1 Conclusions

7.1.1 Crystallinity and water vapour permeability in Pure PLA

PLA films were prepared from three different grades of commercial PLA with different ratios of L-lactide and D-lactide to give a range of crystallinities from 0 to 50%. Samples were produced by melt compounding followed by compression moulding and annealing at different temperatures and for different times to give the range of crystallinities required. Crystallinity was measured by differential scanning calorimetry (DSC).

Water vapour transmission rates through the films were measured at 38°C and at a relative humidity of 90%. It was found that the measured values of WVTR decreased linearly with increasing crystallinity of the PLA from 0 to 50%. The data showed a good fit to a linear trend line with a regression coefficient, $R^2$, of 0.96. This result was readily explained in terms of the effect of crystallinity on the solubility of water vapour in polymers: water is insoluble in the crystalline regions and so the solubility coefficient (S) of a semi-crystalline polymer is equal to the solubility coefficient of the amorphous fraction. The linear relationship predicts zero permeability when the crystallinity reaches about 78%.

However, the data also gave a statistically significant fit ($R^2$ of 0.95) to the ‘tortuous path’ model, assuming that the crystals are impermeable filler particles with an aspect ratio of 1. This model predicts that the water vapour permeability reaches zero at 100% crystallinity, which is a more reasonable outcome.

It was found that the tortuous path model could also be used to explain published data (from Lasoski and Cobbs) on the water permeability of polyethylene terephthalate. First it was necessary to convert density crystallinity to DSC crystallinity and then the PET data fitted the tortuous path model, with a regression coefficient, $R^2$, of 0.97.
7.1.2 PLA composites with talc
The talc was confirmed to be well dispersed in the PLA matrix using transmission electron microscopy (TEM). The talc particles are aligned in the flow direction of the polymer melt.

The proportion of talc does not change the glass transition temperature according to the DSC results. However, talc decreases the cold crystallisation temperature of PLA. As more talc was added, the cold crystallisation occurred at a lower temperature. Talc also acts as a nucleating agent. In addition, it shows an effect on the melting of crystals in the disordered β phase. Crystals in the β phase transfer to the ordered α phase in PLA/talc composites before melting.

The experimental values of water vapour permeation rate are all lower compared with the values predicted by the Nielsen tortuosity model. The difference between the experimental values and the theoretical values becomes larger with higher content of talc. This is because talc acts as a nucleating agent in the PLA composites and it increases crystallinity of PLA. The crystalline regions also cause a reduction in the water vapour transmission rate. This needs to be taken into account.

7.1.3 PLA composites with nanoclays
The nanocomposite structures were found to be intercalated using wide-angle X-ray diffraction (WAXD). Results from WAXD analysis showed that the clay interlayer spacing increased from 1.84 to 3.4 nm. The clay particles were well dispersed and aligned in the flow direction of the polymer melt as shown in TEM micrographs. Using image processing software the average thickness and length of a single clay platelet was measured from the TEM micrographs and found to be 1.6 nm and 80 nm, hence giving an average aspect ratio (length/thickness) of 50.

The DSC data showed that addition of nanoclay had no effect on the glass
transition temperature \((T_g)\). However, there was a significant reduction in the cold crystallisation temperature \((T_c)\). This indicates that the nanoclay platelets facilitated nucleation of PLA crystallites. The disappearance of the lower temperature melting point \((T_m)\) with addition of nanoclay also showed that the nanoclay particles promoted formation of the ordered crystalline phase.

Measured values of water vapour permeability of the PLA nanocomposites were compared with values from the Nielsen tortuosity model. The experimental results are all slightly higher than the theoretical values predicted by the Nielsen model showing a reasonably good fit given that the model assumes that the clay platelets are 100% intercalated or exfoliated and perfectly aligned. Nanoclay does not have a strong effect on crystallinity of PLA compared with talc, therefore crystallinity does not obviously change WVTR in PLA/nanoclay samples and the reduction of water permeation is due to the nanoclay.

### 7.1.4 Polybutylene Succinate

PBS crystallises much easier and faster than PLA. During the 1st heating of quenched PBS in DSC result, a small exothermic peak appears at 100±1ºC corresponding to phase transformation of PBS crystals. PBS melts at 115±1 ºC. During cooling crystals form at 88 ºC. During the 2nd heating run, there are two melting peaks at 108 ºC and 116 ºC. The lower peak corresponds to melting of the less ordered crystalline form, whereas the higher temperature peak corresponds to melting of the ordered crystalline form. PBS spherulites are all very tiny in the images of polarised optical microscopy. PBS melt starts to crystallise between 93ºC and 90ºC, and the nucleation progress is very fast.

According to the DSC data from the PBS nanocomposites, there is no significant change in phase transformation temperature \((T_1)\) and melting temperature with addition of nanoclay, as found for the pure quenched PBS. The degree of crystallinity slightly decreases with addition of 5% nanoclay. This is because the polymer chains between nanoclay are difficult to form crystals. Polarised optical
microscopy confirmed that PBS has a high nucleation rate but relatively low crystal growth rate compared to PLA.

Wide-angle X-ray diffraction (WAXD) results show that the PBS nanocomposite structures were intercalated. It is found that the clay interlayer spacing increased from 1.84 to 2.9 nm in WAXD analysis. TEM micrographs indicated that the clay particles were aligned in the flow direction of the polymer melt. The average thickness of a single clay platelet is 1.6±0.2 nm. The average value of the length for nanoclay is 80±19 nm. Hence the average aspect ratio (length/thickness) is taken as 50.

There is a significant reduction in WVTR with increasing clay content. However, the experimental values are all higher than the values predicted by the Nielsen tortuosity model. With more nanoclay added, the difference between the experimental values and the theoretical values is larger. This is because all PBS samples have very high degrees of crystallinity. And so the nanoclay is not as well dispersed as it was in the PLA nanocomposites. So it is not effective in reducing water vapour permeability.

7.1.5 Comparison of PLA and PBS

DSC data shows that PBS crystalize much easier and faster than PLA.

The glass transition temperature of PBS is much lower than PLA. There is more free volume in PBS and water molecules can easily pass through. However, PBS is much more crystalline. As a result, pure PLA and PBS films have not much difference in water vapour transmission rate.

By comparing WVTR reduction rates $P/P_0$ of PBS and PLA composites, it is found that although the same type and amount of nanoclay was added in PBS and PLA, the effects on WVTR are totally different. This is because PLA and PBS have different crystallisabilities. Nanoclay in amorphous polymers such as
PLA creates a long tortuosity path which results in a high reduction of water vapour permeability. However, there is a combining effect of crystallinity and nanoclay in highly crystalline polymers such as PBS, and the tortuosity path does not increase as much as in amorphous polymers. The nanoclay was not well dispersed in PBS. As a result, nanoclay in PBS gives a low reduction of water vapour permeability.
7.2 Further Work

The following work is suggested in future:

1. Study the effect of orientation of PLA and PBS on water vapour permeation rate. Orientation improves the barrier properties of polymer, as drawing can condense the amorphous phase and reduce the free volume. For crystalline polymers, orientation may modify the distribution and direction of crystals. This can lead to a change of the path length for diffusion of gases and affect gas permeation. However, the effect of orientation of PLA and PBS on water vapour permeation rate is still not clear at the moment.

2. Study how water vapour permeability changes when both crystallinity and content of filler are changing. This can be achieved by using different fillers and annealing at different temperature for various times. Addition of both talc and nanoclay to PLA or PBS is also recommended as they have different aspect ratios. An improved model of permeation may be discovered by investigating the relationship between polymer/talc/nanoclay content ratio and WVTR.

3. Study the crystallisation behaviours and barrier properties of PBS/PLA blends, and their composites. PBS/PLA blends can improve processing properties and mechanical properties of the material. These two polymers have different crystallisabilities and barrier properties, so the crystallisation behaviour and barrier properties of the blends are very interesting to be investigated.

4. Investigate properties of PBS and its composites. PBS is a new biopolymer which draws a lot of attention recently. Further investigation is still required for a better understanding of this polymer, as there are very few publications on properties of PBS until now.
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Appendix

Interpretation of Data on Poly(ethylene terephthalate)

The following discussion comes from a paper submitted for publication with co-author N. L. Thomas (section 1.3).

Poly(ethylene terephthalate) (PET) is another polymer that can be thermally treated to produce a range of crystallinities from zero up to 40% or 50%. One of the earliest studies on the effect of crystallinity on the moisture permeability of PET was carried out by Lasoski and Cobbs. They prepared amorphous PET film by extrusion and quenching. Polymer of increased crystallinity was then prepared by annealing samples of the amorphous film (restrained in frames) at temperatures from 100 to 200°C for various times. The crystallinity of the films was determined by density measurements. Water vapour permeability was measured by the ‘cup method’ at 39.5 °C.

Data showing the relationship between water permeability and crystallinity from the paper by Lasoski and Cobbs are plotted in Figure. Here it can be seen that the data give a good fit to a linear model with a regression coefficient, $R^2$, of 0.97. However, the data do not fit the tortuous path model. In their paper, Lasoski and Cobbs concluded that the best fit of their data was to the square of the amorphous volume fraction, but there appears to be no theoretical justification for this.
The key to interpreting the data of Lasoski and Cobbs comes in a publication by Polyakova et al\cite{Polyakova}, who investigated the effect of crystallisation from the glassy state (cold crystallisation) on the oxygen barrier properties of copolyesters based on ethylene terephthalate. These authors have reported that, for PET and copolymers of ethylene terephthalate, the crystallinity obtained from density measurements was not equal to the crystallinity obtained from DSC measurements when the samples were prepared by cold crystallisation. In fact their data show a very significant difference between the two measurements: the ratio of density crystallinity to DSC crystallinity was found to be around 0.75. The discrepancy between density crystallinity and DSC crystallinity was explained in terms of de-densification of the amorphous phase. This was reported to be a characteristic of cold crystallisation but not of melt crystallisation.

Figure A Water Vapour Permeability of PET versus Density Crystallinity – Data from Lasoski and Cobbs \cite{Lasoski}
Returning to the data of Lasoski and Cobbs, it is apparent that their PET films for permeability measurement were prepared by cold crystallisation and crystallinity was determined by density measurements. In Figure , the density crystallinity data of Lasoski and Cobbs has been converted to DSC crystallinity data by dividing by 0.75. It is now evident that the data fit the tortuous path model, with a regression coefficient, $R^2$, of 97.

![Figure B Water Vapour Permeability of PET versus DSC Crystallinity – Data from Lasoski and Cobbs](Image)

Finally, in Figure C, the normalised water vapour permeability data for both PLA and PET are plotted as a function of DSC crystallinity. They overlay each other and both fit the tortuous path model with an aspect ratio of 1.
Figure C Comparison of the Relative Water Vapour Permeability Data of PLA and PET and the Fit to the Tortuous Path Model