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PET Nanocomposites Development with Nanoscale Materials

By
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I HEREBY RECOMMEND THAT THE DISSERTATION PREPARED UNDER MY SUPERVISION BY: Sung-gi Kim

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This research has concentrated on the development of methods for creating exfoliated clay nanocomposites with poly (ethylene terephthalate) (PET) for the purpose of improving barrier and other properties. For this purpose, extrusion blending and in situ polymerization were investigated. The melt extrusion was studied as a function of mobility of PET chain, affinity of clay modifier, and solid state polymerization (SSP). Three IVs of PET (0.48, 0.63, 0.74 dL/g) and three organic clays (Cloisite 10A, 15A, 30B) were melt blended with a twin screw extruder to evaluate variables on the properties. Addition of clay caused big molecular weight reduction after extrusion. Thermal stability experiments showed that the nanocomposites were sensitive to temperature. Fourier Transform Infrared (FTIR), however, indicated hydrolysis was the main reason for molecular weight reduction after extrusion. The SSP rate was decreased and crystallization rate became faster due to clay particles. There were basal spacing increases in PET/Cloisite 10A and
PET/Cloisite 30B, but PET/Cloisite 15A did not show any change. After SSP reactions, PET/Cloisite 10A and PET/Cloisite 30B nanocomposites had a new peak at low angle in X-ray diffracton (XRD), indicating more expansion of basal spacing.

In situ polymerization was investigated in detail as a function of time and temperature of polymerization, mode of addition of the clay in esterification and in polycondensation, ethylene glycol/terephthalic acid ratio (E/T), diethylene glycol (DEG) suppressor, reactor pressure, antioxidant, and metal stabilizer. There was a limitation to reach 0.60 dL/g IV when the clay was added into the reactor at PET melt polymerization conditions. Foam generation made the melt polymerization of nanocomposites difficult. The concentrations of carboxyl and hydroxyl end groups showed big differences from normal values of PET, due to severe thermal degradation during melt polymerization. This thermal degradation caused drastic decreases in melting points and made the SSP rates slower than the observed in the nanocomposites produced by the melt intercalation method. X-ray diffraction (XRD) results showed that Cloisite 30B had the best affinity with PET due to hydroxyl groups in PET and the modifier of clays, while strong hydrophobicity of Cloisite 15A caused the worst affinity with PET. Nanocomposites formed by the in situ polymerization method had more exfoliated nanostructures than those produced by the melt intercalation method, even though they had a small amount of clay agglomerations.

Aluminium dish and reactor experiments implied the reason of foam generation and how to reduce the foam amount. Several additives were evaluated to improve the nanocomposite properties. Among them, melt polymerization of E/T=1.2 bishydroxy ethylene terephthalate (BHET) with Cloisite 30B at 270 °C was the best conditions
for obtaining exfoliated nanostructures, considering all properties. The nanostructures analyzed by transmission electron microscopy (TEM) showed similar results with those of XRD, but TEM gave more detailed information compared with the results by XRD.

Tactoid and exfoliated nanocomposites were selected to evaluate the relationship between nanostructures and properties. Exfoliated nanocomposite had 11% improvement in tensile modulus and 29% improvement in oxygen permeability at 3 wt% of clay, while tactoid nanocomposite showed 2~7% improvement in tensile modulus and no improvement in oxygen permeability. According to the above results, it was found that the dispersion of clay platelets into single layers can have great impact on the properties even though the amount of clay was small. After stretching, improvements by the addition of clay particles were reduced, due to the structure change in the nanocomposites. Density, microscopy, and differential scanning calorimetry (DSC) results implied micro void generation during stretching.

The addition of 6 wt% clay in order to increase tortuous path length, was theoretically expected to produce 59% reduction in oxygen permeability, but only the permeability reduced by 37%, due to a small amount of intercalated nanostructure and more agglomeration of clay particles compared with that of 3 wt%. Low IV nanocomposite (0.39 dL/g), melt polymerized at 267 °C, improved the color of the nanocomposite. Cyclo hexane dimethanol (CHDM) was not a good monomer candidate for better nanocomposite, because color and oxygen permeability were worse than those of a control nanocomposite.
Dedication

This dissertation is dedicated to my parents, Jee-duck Kim and Hyun-bo Han, who have supported me spiritually and materially since I was born.
Words of Gratitude

I would like to express thanks to Dr. S.A. Jabarin, my adviser who gave me the direction of this research and chance to study in the Polymer Institute. Thanks are due to Mr. M. Mumford who prepared everything for the experimental facilities, to Ms. E.A. Lofgren for reviewing my dissertation and teaching me analysis techniques, to Dr. J. Brace, Dr. M. Cameron and Ms. J. Zydorczyk for their kind help. Especially, I give thanks to SK Chemicals for giving me a chance to study here. My thanks are due to Dr. A. Nadarajah, Dr. M. Coleman, Dr. D. Kim, and Dr. P. Burckel for serving on my dissertation committee.

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Chapter I

Introduction

Poly(ethylene terephthalate) (PET) is a semicrystalline polymer, which has wide application in beverage bottles, textiles, and electrical parts [1]. The incorporation of clay into PET can result in outstanding property improvement in terms of decreasing oxygen permeability in food packaging, increasing flame resistance in textiles, and increasing the modulus in injection molded parts. This can be done with less clay content than used in most conventional composites. Conventional fillers have been used to improve properties and reduce cost; however, there are limitations in their application due to phase separation, particle agglomeration, and heterogeneous distribution in the product [2]. Small size of clay minerals and clay surface treatments with chemicals in order to create an affinity between the clay surface and the polymer, can reduce those problems.

1.1 Nanocomposite

Polymer nanocomposites are mixtures of polymer and nanometer length scale particles, whereas, conventional polymer composites contain micrometer scale particles. The advantages of nanocomposites over macrocomposites include reduced filler amount and better properties than obtained for the conventional composites. Among the nanoscale materials used to form nanocomposite are clays, which can be swollen. Clay particles have high aspect ratios (ratio of length to width) and are composed of layered structures, so that the degrees of enhancement in properties
obtained can be varied according to the types of nanocomposite structures. There are three types [3,4,5,6] of polymer-clay nanocomposites. a) Tactoid structures are obtained when the interlayer space of the clay doesn’t expand, due to its poor affinity with the polymer. As a consequence, clay in this form plays little role in property enhancement and is used only for cost reduction. Property improvement in which tactoid structures are present, requires a loss of other properties as in the case of conventional fillers. b) Intercalated structures are obtained in the case of a little interlayer expansion of clay. In this case there is a well-ordered stacked multilayer structure as a result of some affinity between the polymer and the clay. The interlayer spaces of the clay are expanded as a few polymer chains penetrate the basal spacing of clay, but the shape of layered stack maintains. c) In the case of exfoliated structures, host clay layers have lost their registry and are well separated into single layers within a continuous polymer matrix. This is due to very good affinity between the polymer and clay (Figure 1.1). The three nanocomposite structures shown in Figure 1.1 could be observed separately or jointly in one sample.

Figure1.1 Three types of nanocomposite structures: a) tactoid (conventional composite), b) intercalation, and c) exfoliation structure
To make the nanocomposite most improved in properties, an exfoliated structure is required. The greatest dispersity of clay and interfacial interaction of clay platelets with polymer can be obtained in exfoliated structure. The proper hydrophobicity of clay and compatibility between organically modified clay and polymer are critical factors in nanocomposite formation [7]. Additionally, large interlayer spacing in clay and interaction ability between clay and polymer are the other factors which are considered to develop exfoliated nanostructures.

Properties that can be improved with the addition of clay include:

- Physical properties; modulus, dimensional stability, etc
- Barrier properties; reduced gas permeability to oxygen and carbon dioxide
- Chemical resistance
- Flame retardance and slow smoke emission
- Optical clarity increased over that of conventional filler
- Increased heat distortion temperature

1.2 Nanocomposite manufacturing methods

The preparation methods [7,8,9] of polymer clay-nanocomposites are divided into three categories according to starting materials and processing techniques. Their categories are solution intercalation, melt intercalation, and in situ polymerization methods.

Solution intercalation methods are used to develop a nanocomposite when the polymer is soluble to a solvent and clay layers are swellable in that solvent. Thermodynamically negative deviation in Gibbs free energy is needed when the solvent in the swollen interlayer of clay is exchanged with polymer. An entropy increase by desorption of solvent molecules occurs, while polymer chains move into
the layered clay from solution [10]. Sometimes only intercalation nanostructure is prepared for certain combinations of polymer-solvent. Disadvantages of this method are that most polymer-dissolving solvents are environmentally harmful and the amounts of solvent are very large. For this reason solution intercalation is hard to apply on a commercial scale.

Polymer and clay are mixed in the extruder under shear above the softening temperature of the polymer, in the case of melt intercalation. This method has several advantages over other methods: This method doesn’t use a solvent, so that makes it more environmentally acceptable and the residence time in high temperature is shorter than in the case of in situ polymerization. Commercial scale production can be applied with current industrial and processing techniques. This method can be applied if other methods are not suitable.

When clay is swelled with liquid monomer or polymerization occurs in the interlayer space of clay, in situ polymerization can be applied. Once the monomer is inserted into the interlayer space, the increase of chain length causes an expansion of the basal spacing of clay. This method creates an exfoliated nanocomposite structure more easily than other methods. As a result of good mobility of monomers, greater expansion of the basal spacing occurs to improve the nanocomposite properties.

1.3 Silicate

Silicate is a compound containing an anion in which electronegative ligands surround silicon atoms charging an electrical negative. Oxygen atoms are representative ligands in silicate. To become an electrically neutral compound, a silicate anion needs cations. Silica, SiO$_2$, is often confused with silicate, but this compound is considered as a mineral quartz with no negative charge [11,12]. Silicate
can be divided into several subclasses and one of them is bentonite. Bentonite is the rock or ore which contains the mineral montmorillonite/smectite group. The smectite group consists of several minerals including vermiculite, sauconite, talc, pyrophyllite, saponite, nontronite and montmorillonite [13].

Clay minerals for nanocomposites generally mean natural montmorillonite (MMT). Figure 1.2 shows examples of the structure of two materials which are swellable with the proper polar solvent. Polar solvents such as water can swell clay minerals, which contain alkali metal. Talc and kaolin can not swell since they do not contain an alkali metal. Solvation of polar solvent can expand the basal spacing of MMT and finally separate the stack of layers into individual layers (exfoliation).

Figure 1.2 Chemical structure of clays: a) montmorillonite, b) synthetic mica [6]
Clay minerals are made up of many crystalline sheets that can be categorized as tetrahedral and octahedral. Tetrahedral sheets are composed of silicon (Si$^{+4}$) and oxygen (O$^{2-}$) but octahedral sheets are made up of hydroxide (OH$^-$) and either aluminium (Al$^{3+}$) or magnesium (Mg$^{2+}$). If an octahedral sheet contains aluminium, it is called dioctahedral and if it contains magnesium trioctahedral [14]. The ratio of tetrahedral:octahedral is 1:2 in the case of MMT but that of kaolinite is 1:1.

The reason clay is negatively charged is that the oxygen atoms exposed to the surface of clay are not completely balanced by positive atoms, even though the positive (Si$^{+4}$, Al$^{3+}$, Mg$^{2+}$) and negative (O$^{2-}$, OH$^-$) charges are balanced, when one tetrahedral and octahedral join to form sheets. Another reason is isomorphic substitution of Al$^{3+}$ for some of the Si$^{+4}$ in the tetrahedral sheet. The negatively charged clay surface of clay can, therefore, hold cations and negative charges are counterbalanced with alkali or alkaline earth cations in the interlayer [15].

As the binding force [16] between stacking sheets of the clay is weaker, the clay mineral swells more easily with proper solvent. The strength of the binding force depends on cations in the interlayer. The sodium ion has a single positive charge so that its sheet binding ability is weak, whereas a calcium ion has a double positive charge and therefore its binding ability is strong. That binding ability of magnesium is intermediate. Another factor found to affect binding strength is the size of cations when the cations are hydrated. Sodium ion is strongly hydrated so that the distance between clay particles is increased due to the increase in hydration shell, but calcium ion is not strongly hydrated compared with sodium ion. Magnesium ion is highly hydrated ion but contains two positive charges, which makes magnesium keep the medium range of binding strength compared with sodium and calcium ions as shown in Figure 1.3. Therefore, it is easy for sodium ion to make exfoliated structure than
other cations with proper solvent.

Cation Exchange Capacity (CEC) is the ability of clay minerals to hold cations. Smectite has the bigger CEC values than kaolinite and illite. The CEC of smectite, kaolinite, and illite are 100, 9, 25 meq/100g respectively [16].

![Figure 1.3 Strength of attraction according to cations](image)

1.4 Organic clay

Natural montmorillonite is hydrophilic and a layered material. To render montmorillonite hydrophobicity to have compatibility with polymer, a cation exchange reaction is needed to replace sodium (or calcium or potassium) with cationic surfactants such as primary, secondary, tertiary and quaternary alkylammonium or alkylphosphonium cations (onium). When the clay surface is modified (organic clay is chemically modified natural clay), its surface energy is lowered and becomes more
organophilic than natural clay, which means organic clay can have more affinity with polymer than natural clay. After an ion exchange reaction, the basal spacing of organic clay is expanded due to the bulkiness of alkylammonium or alkylphosphonium cations. Additionally these cations can provide reacting functional groups with polymer or initiate polymerization of monomers depend on sorts of modifier of clay [17,18,19,20].

**Thermal stability of organic clay**

Natural and synthetic clay can be used as a catalyst [21] mainly at the platelet edge, normally 2~4% of total surface area of platelet. Hydroxyl groups at the edge of platelet and SiOH act as Bronsted acids, and partially coordinated Al$_{3+}$ acts as Lewis acid at the surface of a layer. Lewis acid sites can receive electrons from a molecule forming a new covalent bonding, coordinate a radical, and eliminate an electron from a vinyl group of a compound. In addition to temperature, this catalytic activity can be affected by the surface area of platelet edge, amount of agglomeration, and morphology of clay. High temperature is needed to prepare the nanocomposite for homogeneous mixing of clay and polymer and reaction of reactants regardless of preparation methods (melt intercalation or in situ polymerization). When the processing temperature or polymerization temperature is higher than the thermal decomposition temperature of organic clay modifier, thermal decomposition will occur and this causes interfacial force and affinity change between the clay surface and the polymer matrix. Sposito et al. [22] reported on the thermal degradation chemistry of organic clay, using a combination of high resolution TGA with Fourier transform infrared spectroscopy and mass spectroscopy (TG-FTIR-MS) and pyrolysis/GC-MS to evaluate non-oxidative thermal stability. They reported on the
degradation mechanism, major and minor factors to affect thermal stability, side products, and kinetics of decomposition of clay. They found thermal decomposition of the modifier in clay started from the parts having the smallest bond dissociation energy. Acidic parts of the clay has a catalytic effect on the initial decomposition of the modifier in clay, thus the thermal stability of clay is improved as the amount of ammonium salt is decreased. The overall stability of clay decreases, when the modifier intercalates into interlayers of montmorillonite. The onset point of decomposition is directly related to the thermal stability of the surfactant and catalytic sites of the clay. The dimensions of the interlayer strongly influence degradation kinetics, side product mass transfer, and the rate of volatilization, as shown by single and multi step decomposition of surfactant salts. One more important thing that was found is that organic clay can be used to form nanocomposites, even though thermal degradation of the modifier starts below the processing or reaction temperature. The onset point in TGA means the starting point of thermal degradation. Complex secondary reactions and retardation of degradation products due to modifier chain length and nanostructure, will occur at higher temperatures.

1.5 Nanostructure analysis

The most common techniques used to elucidate nanocomposite structures are wide angle X-ray diffraction (WAX or XRD) and transmission electron microscopy (TEM). Montmorillonite (MMT) is an aluminosilicate smectite clay, which has low concentrations of cations on the surface of clay, so that layers can be easily separated due to less interactions keeping the clay plates together. This can be compared with high surface concentrations of cations clay like vermiculite [23]. Three types of nanostructures can be analyzed with XRD. When basal spacing of the mixture is the
same to that of clay, this structure is tactoid (immiscible), which means no polymer chain is the inside of the gallery of clay. D-space is increased in intercalated nanostructure as interlayer space is expanded so that \( \Theta \) position in X-ray will be decreased (smaller value) according to Bragg equation [24]. \( \Theta \) is inversely proportional to basal spacing as shown in Bragg equation. Geometry of XRD in a periodical structure is illustrated in Figure 1.4. Exfoliated nanostructure shows no peak by XRD, indicating many polymer chains have penetrated and expanded the interlayer space far apart, disordering the regular stacks of clay layers so that X-ray cannot detect any regular structure.

\[
\begin{align*}
n \cdot \lambda &= 2d \cdot \sin \Theta \quad \text{(Bragg equation)} \\
\text{where,} & \quad n; \text{ integer}, \quad \lambda; \text{ wavelength}, \\
& \quad d; \text{ the separation of atomic plane (basal spacing or d-spacing in clay),} \\
& \quad \Theta; \text{ the angle between direction of travel of the wave and atomic plane}
\end{align*}
\]

Southern Clay Products Inc., one of the clay producers in the USA, reported the
characteristics of X-ray technique. No exhibition of an XRD by individual clay platelets indicates the exfoliated nanostructure. It is assumed that no peak detection in XRD spectra means the average distance from each platelet is at least 70Å apart. The aggregates of monomorillonite cause non-homogeneous dispersion which can reveal no peak in X-ray diffraction depending on the measurement location due to low concentration of clay. Therefore, the requirement of exfoliation is homogenous distribution of montmorillonite throughout a polymer matrix [13].

X-ray diffraction (XRD) is a useful technique for measuring basal spacing of clay, but sometimes XRD result can be misinterpreted due to sampling problems, orientation, and poor calibration of XRD instruments, especially at very low angles. Clay amount, clay order, and homogeneity can influence the XRD results. XRD doesn’t produce Bragg diffraction peaks when clay is not well ordered, therefore the disappearance of the XRD peak doesn’t confirm the presence of highly disordered and exfoliated structure of clay in the nanocomposite [25]. XRD results tell average basal spacing of the sample. Peak intensity depends on the amount of regular structure. When the amount of clay is smaller than 5 wt% or exfoliated structure is identified, XRD only data cannot be a criterion for clear nanostructure but TEM result should be used at the same time to overcome the limitation of XRD [26].

Diffraction and scattering

When the sample contains a regular structure (periodic structure, crystalline phase) the XRD is scattered consistently so that wavelength of X-ray and the phase relationship between the incident and scattered rays does not change. This process is called diffraction which is used in wide angle X-ray diffraction (WAXD). If a sample has an irregular structure (different electronic densities such as crystalline and
amorphous phase), X-ray diffraction gives inconsistent scattering (Compton scattering). Changes of the wavelength and phase relationship between incident and scattered rays are involved. This process is called simply scattering or diffuse X-ray diffraction effect, which is measured by small angle X-ray scattering [24]. The major application of WAXD is identification of polymer crystal size and perfection, the orientation of crystallite, and degree of crystallinity.

Inhomogeneities of atomic dimensions in a sample don’t affect Small angle (< 2°) X-ray diffraction (SAXS). The intensity of SAXS depends on electron densities of two or more phases. Therefore, the applications of SAXS include morphological domain measurements such as lamellae, spherulites, voids, particle size and shape measurements in solution, colloidal particle studies, and swollen polymer studies.
1.6 Polymerization of PET

PET can be prepared by transesterification of dimethyl terephthalate (DMT) with ethylene glycol (EG) or esterification of terephthalic acid (TPA) with ethylene glycol to produce transesterification of bishydroxyethyl terephthalate (BHET) produces PET and EG at higher temperature than the melting point of polymer and well above the boiling point of EG. Diethylene glycol (DEG) can be formed as a byproduct in the last stage of esterification or the early stage of transesterification of BHET. DEG contents can be varied according to temperature, residence time, sorts of catalyst, and TPA/EG ratio [1,27,28,29] The contents of copolymers change the thermal, physical and other properties of PET. All the conditions and steps for melt phase polymerization are shown in Figure 1.5.

Although melt polymerization can increase molecular weight higher than molecular weight value (0.80dL/g) that process can cause resin quality problems due to the degradation coming from high temperatures and long residence times. Solid state polymerization (SSP) is done under relatively moderate thermal conditions. The important roles of solid state polymerization are to increase molecular weight with less thermal degradation than melt phase polymerization and to reduce the contents of byproducts such as acetaldehyde, oligomers, to acceptable levels. The normal SSP temperature is 200~230°C and this temperature can be changed according to melting point of PET [1]. Many variables can be involved in the SSP process. Precursor molecular weight, pellet size, and SSP temperature are the most important factors, because these factors influence SSP kinetics [30]. Low molecular weight, big pellet size, and low SSP temperature decrease SSP rate.

The basis for the concept that clay will be added in melt phase polymerization (in situ polymerization) is that the smaller monomer molecules can penetrate the
gallery of clay more easily than the bigger polymer molecules. Clay can be added
during the early stage of esterification or the early stage of transesterification of
BHET.

[1st step in melt polymerization]

\[
\text{DMT} + 2 \text{EG} \xrightarrow{\text{catalyst}} \text{BHET} + 2 \text{CH}_3\text{OH} \\
\text{TPA} + 2 \text{EG} \xrightarrow{\text{pressure}} \text{BHET} + 2 \text{H}_2\text{O}
\]

[2nd step in melt polymerization]

\[
\text{BHET} \xrightarrow{270 \sim 290 \degree \text{C}} \text{PET} + \text{EG}
\]

Where,
- DMT: \(\text{CH}_3\text{OOC} \overset{\text{O}}{\text{C}} \overset{\text{O}}{\text{C}} \overset{\text{O}}{\text{C}} \text{OCH}_3\)
- TPA: \(\text{HOOC} \overset{\text{O}}{\text{C}} \overset{\text{O}}{\text{C}} \overset{\text{O}}{\text{C}} \text{OOH}\)
- EG: \(\text{HOCH}_2\text{CH}_2\text{OH}\)
- BHET: \(\text{HOCH}_2\text{CH}_2\text{OOC} \overset{\text{C}}{\text{C}} \overset{\text{O}}{\text{C}} \overset{\text{O}}{\text{C}} \text{OCH}_2\text{CH}_2\text{OH}\)

Figure 1.5 Melt polymerization steps in PET and raw materials
1.7 Permeability

The improvement in barrier technology can be categorized into five areas [31]: 1. Vacuum deposited coatings (thin, transparent); 2. new barrier polymers; 3. blends of barrier polymers and existing polymers; 4. organic barrier coatings or adhesives; and 5. nanocomposite materials. One common target of these five technologies is to develop plastic bottles capable of protecting the contents from oxidation for at least six months. Some of these technologies have been commercially available, but others are still under development.

Barrier property improvements of PET with nanocomposites are still a developing area so that few articles have been reported. The addition of 3 wt% of organic clay reduced the permeability of PET nanocomposite film by half compared with that of a pure PET film [32]. Nanocomposites were polymerized through DMT and EG reaction and the film thickness was 25 micrometer. Natural clay was treated with an interlayer agent with carboxyl group in its structure. Oxygen permeability of PET nanocomposite film was considerably reduced by using clay-supported catalyst in the DMT and EG polymerization process [33]. The degree of improvement for the nanocomposite film, over that of the pure PET film, was factors of 11.3~15.6 depending on the clay amount (1~5 wt%). Thick films of 170 micrometers remained transparent up to a concentration of 5 wt% of clay, but their color was brown. Montmorillonite was reacted with chlorotitanium triisopropoxide to produce clay-supported catalyst.
1.7.1 Tortuous path model

Polymeric composites contain dispersed phase, which has a range of volume fractions, particle sizes, and particle shapes. This phase can be arranged randomly or regularly. Final properties can be affected by these factors so that a simplified mathematical expression is devised to predict the factor-property relationships under steady state, according to the type of fillers.

One of the most important factors, which have an effect on permeability, is the path length of permeant. The path length will be increased when impermeable fillers are added, whereas the surface area of matrix will be reduced proportional to the filler amounts. Tortuosity ($\tau$) is defined as: the ratio of the effective path length required for permeation, to actual composite film thickness. The reduction of area is proportional to the filler volume fraction.

Neilson [35,36] developed a tortuous path model (Figure 1.6), which can predict gas barrier properties when we use platelet particles to enhance barrier properties (reduce gas permeability). That model presents a general approximation for evaluating the effective tortuosity of systems containing asymmetric filler particles, especially platelet shapes, where the platelet length $L$ should be parallel to the composite surface.

$$\tau \approx 1 + \left(\frac{L}{2W}\right) \phi$$  \hspace{1cm} \text{(equation 2)}

where, $\tau$=tortuosity

$L$=length

$W$=width

$\phi$ =volume fraction of filler
According to equation (2), tortuosity will be affected by aspect ratio (L/W) and volume fraction of filler. To increase tortuosity to improve the barrier property of a nanocomposite, the filler has to have big aspect ratio and volume fraction in equation (2). The filler can have bigger volume fraction, when the density of filler has less density at a fixed weight % of filler. Clay has platelet shape so that this shape has bigger aspect ratio than spherical or rod type fillers.

Michaels, Bixler [37] and Barrer et al. [38] suggested an approximation relationship among the variables of tortuosity, volume fraction, and permeability in the conducting and continuous phase.

\[
\frac{P_c}{P_m} \approx \frac{\phi_m}{\tau} \quad \text{(equation 3)}
\]

where, 
\[P_c=\text{permeability of composite}\]
\[P_m=\text{permeability of matrix}\]
\[\phi_m=\text{volume fraction of matrix}\]
\[\tau=\text{tortuosity}\]

Combining equation (2) and (3) result in
Where, $P_{\text{nanocomposite}}$, the permeability of the resulting nanocomposite

$P_{\text{matrix}}$, the permeability of matrix

$\Phi$, the volume fraction of platelets

$\alpha$, the aspect ratio of the platelets

In this simple model, the reduction of permeability depends on the amount and the aspect ratio of the filler.

1.7.2. Modified models

R.K. Bharadwaj [39] suggested a barrier property model for polymer-layered silicate nanocomposite, considering the length and relative orientation of the silicate layers, and the state of the silicate aggregation. Clay platelets are assumed to be disks, with average diameters of 30–2000 nm and 1 nm widths. According to this model, longer sheets can reduce the dependency on the orientation, due to large length/width ratio so that when length is bigger than 500 nm, barrier property improvement in random orientation is almost similar to that of perpendicularly aligned sheets. Permeability in agglomerated platelets is strongly dependent on the degree of delamination for the shorter platelet clay. The best clay for reduced gas permeability, is longer sheets (length should be longer than 500 nm). With the viewpoint of tortuosity, there is less orientation dependence, and less effect by delamination of clay
platelets if they don’t consider affinity of clay with polymer.

Xu at el. [40] proposed a relative permeability model, considering an increased path length due to platelets and chain segment immobility using semicrystalline polymer permeability. They found that intercalated and/or incompletely exfoliated nanostructure and dispersed tactoids (consisting of several layers) can improve gas barrier property. Gas permeability on exfoliated nanostructure is more sensitive to agglomeration, than is an intercalated one. In the case of a confined matrix, however, relative permeability decreases more drastically for intercalated structures than for an exfoliated one. This result could be caused by a very few exact results for chain segment mobility data, which came from the effects of crystallization on the diffusion constant. This model takes into account the platelet ordering, dispersion, layer thickness, gallery height, layer length, layer volume fraction, and chain segment immobility factor. Their model accords with the experimental result, when the volume fraction of clay is bigger than 1%. It becomes similar to Nielsen’s formula, when the clay length is much bigger than the lateral distance between platelets, and the chain segment mobility factor is not considered.
1.8 Literature review of PET nanocomposites

1.8.1 In situ polymerization

1.8.1.1 Surface treatment of Montmorillonite clay with chemicals

Ke et al. [34] prepared organic clay with intercalated reagent through refinement and powdering of natural clay, then reacted it with PET monomers in the reactor to form PET nanocomposite. The nanocomposite pellets were compressed into 1-2 mm film at 270 °C. The PET nanocomposite showed 3 times faster crystallization rate, 20-50 °C higher heat distortion temperature, 3 times bigger modulus than those of pure PET, when 5 wt% clay was added. The clays were distributed in the PET matrix uniformly and only 4 wt% agglomerated clay particles were detected. The strip belt morphology was observed, where PET chains are intercalated into the expanded interlamellar space. The interaction between clay and PET molecular chains improved several properties of nano-PET, compared with PET properties, but not to the greatest degree. Less improvement than expectation may be caused by the low content of clay (maximum 5 wt% in this paper), the agglomeration of clay, and weak interfacial force between clay and PET due to agglomerated clay particles.

Barbee et al. [41] performed numerous experiments changing many variables. Oxygen permeability has been improved by 22% with 2 wt% of clay addition, after cation exchange reaction of natural montmorillonite with octadecyl bis (polyoxyethylene) amine. Organic clay was added to the early stage of the polycondensation reaction of BHET, then melt polymerized at 280 °C up to higher than IV 0.60 dL/g. XRD did not showed any peak. At the second experiment, octadecyl methyl (ethoxylated) ammonium chloride was used to prepare organic clay and then the clay was crushed into 10 μm particle size. An 87% reduction in oxygen
permeability was obtained at 8.9 wt% clay, but diethylene glycol (DEG) content was 12 mole% and IV was 0.26 dL/g after melt polymerization. Oxygen permeability was reduced by 32% when the same organic clay was 2.2 wt%. Longer residence time in the reactor and clay amount increase caused the DEG content to increase in melt polymerization. A 20 minute increase in residence time at 280°C caused a 4.3 mole% increase in DEG. They revealed that clay particle caused a reduction of the rate of transesterification, shown by methanol accumulation amount. Addition of cyclohexan dimethanol (CHDM) as a third monomer increased oxygen permeability slightly, but dimethyl naphthalate usage as a monomer instead of DMT reduced oxygen permeability by 50%. Comparative examples pointed that no improvement in permeability of nanocomposite film up to 6 wt% clay addition was achieved when PET is melt blended with clay in an extruder. Clay particles are agglomerated, basal distance is less than 20 nm, and few individual platelets are observed in TEM indicating poor dispersion and/or delamination in melt blended nanocomposite.

1,2,4-Benzenetricarboxylic anhydride (TMA) was used by Kim et al. [42] to enhance the reaction of clay with PET. Esterification of TMA and the mixture of ethylene glycol and montmorillonite produce a trimellitate ester oligomers (TEO). When the equivalent ratio of montmorillonite and clay was changed from 1:3 to 1:1.5, WAXS results showed that the peak location moved to a smaller angle indicating the expansion of interlayer spacing of clay in TEO. The dispersibility of the clay in the TEO was investigated by Transmission Electron Microscopy (TEM). The clay particles were well dispersed and layers of clay were delaminated. After melt polymerization, the dispersion of clay particles was kept in a submicron level.
1.8.1.2 Clay surface treatment with catalyst

Tsai et al. [43] developed a polymerization catalyst intercalation method in order to pull the monomers or oligomers inside of clay gallery during melt polymerization. The probability of polymerization happening inside of the gallery of the layered clay will be increased, when the surface of the clay is treated with polymerization catalyst, because the ends of functional group react with each other on the spot where the catalyst is located. The interlayer space will expand more as the molecular weight of PET increases. This invention makes the clay layers readily exfoliated and uniformly dispersed in the PET matrix. Antimony catalyst solution was added into the mixture of montmorillonite and EG kept at 80 °C. It was then, stirred for 4 hrs, centrifuged, washed with water, dried, and ground. After melt polymerization using antimony reacted montmorillonite mentioned above, the basal spacing of the resultant nanocomposite was measured as 103 Å with TEM where X-ray could not detect any peak indicating delamination of clay layer.

Choi et al. [44] reported oxygen permeability was decreased by factor of 11.3 at 1 wt% of clay and by 15.6 factors at 5 wt% of clay. They reacted with natural montmorillonite in a suspension of chlorotitanium triisopropoxide and anhydrous tetrahydrofuran to prepare clay-supported catalyst. Melt polymerization then proceeded through the ester interchange reaction of DMT and polycondensation of BHET. Thermal Gravimetric Analysis (TGA) result showed clay-supported catalysts do not degrade up to 600 °C while the mixture of catalyst and montmorillonite begins to degrade after temperature of 120 °C have been reached. X-ray diffraction, however, showed that the PET nanocomposite has a peak at 5.80°, which means that the intercalation of PET chain into the clay interlayer space occurred, but exfoliation
Ke et al. [45] prepared organic clay by processing the natural montmorillonite with quaternary ammonium salt containing Cl- and –COOH in its structure. They expected that the carboxyl groups in the interlayer spaces of the organic clay layer would react with the hydroxyl groups in the PET chains and that polymerization would accelerate the exfoliation of the clay layers. They also expected that stretching the product into a film would orient clay particles in the stretching direction, and thus improve its gas barrier properties. X-ray did not detect any peak due to the limitation of wide angle, while TEM measured interlayer distances of about 25 nm. Oxygen permeability of 25 μm nanocomposite film was reduced to 50% of that of pure PET film with the addition of 3 wt% organic clay.

1.8.1.3 Nanocomposite fiber

Property and draw ratio relationships were examined by Chang et al. [8, 46] to prepare nanocomposite fibers. They used an in situ polymerization method with organoclay. Normally the sodium cations of clay are substituted for alkyl ammonium cations to give organophilicity with polymer, but thermal stability of that cations are not good enough to resist PET processing temperature (280 °C). Thermally stable organoclay was prepared by these researchers through an ion exchange reaction of natural montmorillonite with dodecyl triphenyl phosphonium chloride. Dimethyl terephthalate (DMT) was used as a monomer, instead of terephthalic acid (TPA) to melt polymerize nanocomposites with varying clay contents from 0 to 3 wt%. All the samples were extruded through a capillary rheometer, to stretch the nanocomposite fibers. X-ray results showed basal spacing of organic clay was increased to 36.08 and
18.20 Å from 11.99 Å, the basal spacing of natural clay. Before stretching 3 wt% organic clay, a peak was observed at d=17.25 Å. The intensity of this peak become stronger as clay was added from 1 wt% to 3 wt%. When the draw ratio was increased from 3 to 16, however, no clear peaks appeared. The appearance of a peak would have implied homogeneous dispersion and exfoliation of the clay. According to SEM pictures of nanocomposite fibers, higher draw ratio (DR=16) fibers contained smaller domain sizes clay (80-100 nm in size) than found in samples with a lower draw ratio (DR=3, 30-50 nm in size). A clear clay phase was observed as draw ratio was increased up to 16, implying excess stretching of the fiber. Clays were well dispersed in the PET matrix, although agglomerated clays were detected in TEM photographs. Higher contents of clay nanocomposites contained more agglomeration of clay. Tensile strength was linearly increased from 46 to 71 MPa at DR=1, when clay amount increased from 0 to 3 wt%, and tensile modulus become 1.8 time higher than that of pure PET. This improvement, however, disappeared when the fibers were stretched up to 16 times. The authors suggested the decrease in tensile strength and modulus, at high stretch ratios, is related to debonding and void generation in the nanocomposites. Imperfect matrix and filler interfaces, cannot resist the large interfacial stress such as tensile stress so that yielding or/and debonding can occur when the specimen is stretched. They reported that the residual weight at 600 °C was 21 % in the case of 3 wt% clay addition when thermal stability is evaluated in TGA under N₂. In the case of pure PET residual weight was 1 wt%. They noted that the 20% increase in residual amount in the case of nanocomposite results from the improved thermal stability due to clay particles. These particles provided a heat insulation effect, thus the reduced mass transportation rate of volatile product was caused by clay particles [47].
1.8.1.4 Surface treatment of mica clay

Saujanya et al. [48,49,50] developed a PET nanocomposite with expandable fluorine mica and compatibilizer, instead of montmorillonite by in situ polymerization. The size of mica (6 μm) is bigger than that of montmorillonite (~200nm) and mica has 2.5 times higher negative charge. The higher negative charge can cause greater expansion of the mica gallery, due to more adsorption of bulky and long compatibilizer. This can then help polymer chain penetrate the gallery space more easily. One more thing they considered was the compatibilizer which can connect the PET chain to the surface of the clay. PET is not polar enough to interact with clay surface in the manner of a nylon-clay nanocomposite, where strong interaction exists through ionic and hydrogen bonding. In addition to good thermal stability of phosphonium cation at 275 °C, the reactive compatibilizer, 10-[3.5-bis(methoxycarbonyl)phenoxy]decyltriphenylphosphonium bromide, holds functional groups, which can react with the monomer of PET by transesterification of dimethyl isophthalate group. They can also react with the negatively charged mica surface by the triphenylphosphonium group to achieve both exfoliation of the mica in the PET matrix and strong adhesion of PET chain to mica surface. The cation exchange reaction was done with compatibilizer and mica through several steps in order to intercalate the basal spacing of mica with compatibilizer so that the 0.96 nm basal spacing of mica becomes 3.20, 1.65, and 1.11 nm. This intercalated mica was melt polymerized with BHET, oligomer of PET, to form PET nanocomposite. X-ray result showed that exfoliation in the PET nanocomposite was not achieved satisfactorily, even in the case of the nanocomposite containing the compatibilizer. Flexural modulus, however, was improved up to 1.7 times of pure PET at 8 wt % mica/BHET and 1.2 times for compatibilizer/BHET(mmol/g). In the case of the nanocomposite
without compatibilizer, flexural modulus was increased only by 10% at the same formulation. $^{13}$C-NMR confirmed the reaction of BHET and compatibilizer. No reaction between those parts in the case without compatibilizer was presumed by existence of particles in polarization microscope. Compatibilizer was found to accelerate the crystallization rate and make the Avrami exponent (n) smaller.

1.8.2 Melt intercalation

Barber at el. [51] investigated the effect of ionomers on nanostructure and properties as exfoliation agents of organic montmorillonite. The goal of this research was to increase the number of ionic interactions between the negatively charged sodium sulfonate group of the exfoliation agent and the positively charged clay edge. SAX result showed that the increase of sulfonate groups in PET caused the decrease of scattering peak intensity. The greatest improvement in tensile modulus resulted from the nanocomposite including organic clay and ionomer. They produced intercalated nanocomposite with this technique, and tensile modulus was improved more as the ionomer contents and clay contents were increased. 50% improvement in tensile modulus was achieved when 5 wt% organic clay and 5.8mole% sodium solfonate group were added to the PET.

Davis at el. [52] reported the effects of melt compounding condition and organic modifier of clay on nanostructure. N,N-dimethyl-N,N-dioctadecylammonium treated clay nanocomposite showed brittle behavior and black color, due to the low decomposition temperature (250 °C) of clay. The 1,2-dimethyl-3-N-hexadecyl imidazolium treated clay nanocomposite revealed good dispersion and delamination as a result of the high degradation temperature (350 °C) of this clay. The synthesis of
modifier on the surface of montmorillonite was confirmed by the basal spacing change of the organic clay itself. X-ray result of the nanocomposites showed weaker, broader and lower peak locations, when compared with the peak locations of organically treated clay. The authors mentioned the inconsistency of the result of X-ray and TEM. This result came from restrictions of X-ray in that X-ray could not detect the level of dispersion and delamination, but only indicate a intercalated structure. The tactoid structures can be detected by XRD, even though the concentration is very low, because that structure is well defined in XRD. This tactoid structure can be the cause of peak broadness in XRD, due to wide distributions of tactoid sizes in the nanocomposite. Sometimes this broadness makes analyzer hard to distinguish the baseline.

Sanchez-Slois et al. [53] used pentaerythritol and maleic anhydride to achieve compatibility between montmorillonite and PET. Natural montmorillonite modified with a quaternary ammonium salt was melt mixed in a co-rotating twin screw extruder under nitrogen, to prevent hydrolysis and oxidation with air. Organic clay has 31.5 Å as its basal spacing and all nanocomposites showed similar non-exfoliated basal spacing. The specimen was cut from bottles. A 30 % improvement in tension strength and a 31% increase in Young’s modulus were attributed to the compatibility of clay and the PET matrix, especially when pentarythritol was used as compatibilizer. The viscoelastic behavior was affected by interaction between clay and PET, due to polarity change.

1.8.3 Mechanism of clay intercalation into PET

Matayabas Jr. and Turner [9] reported the mechanism of exfoliation of
montmorillonite in a PET matrix, the degree of improvement in permeability, comparison of nanocomposite preparation method, and applications of nanocomposite. First, the way of inserting clay into PET was to use swelled clay. Ethylene glycol can swell sodium montmorillonite, because ethylene glycol and clay are both hydrophilic, so that this mixture became a gel [40]. Exfoliation of clay, which was prepared by mixing of montmorillonite and ethylene glycol, can be maintained if proper polymerization conditions are selected. Oxygen permeability of 10 mil thick film obtained by compression molding, was reduced from 11.6 to 7.2 (cm³ mil/100 in² day atm) when clay amount was increased from 0 to 2 wt%. Polar polymers such as polyvinylpyrrolidone or polyvinyl alcohol can be used to prepare the gels. A second way of exfoliating clay in PET is to use organoclay in melt polymerization. Proper selection of organoclay can give affinity of the montmorillonite to the PET oligomer, so that some parts of the oligomer of PET are inserted into the gallery and then basal spacing of the clay expands as melt and solid state polymerization proceeds. They suggested a critical molecular weight of PET oligomer in melt polymerization, to form exfoliated structures after polymerization.

They mentioned a melt compounding method that can improve gas permeability, but the degree of improvement is less than that achieved by in situ polymerization. One more disadvantage of melt compounding is the severe thermal degradation that occurs during compounding so that the final molecular weight of the product is not enough to make bottles, especially if the amount of clay bigger than 2 wt %. This degradation cannot be overcome by using high molecular weight PET (IV 1.0 dL/g).
1.9 Other polymer nanocomposites

1.9.1 Polypropylene nanocomposite

Polypropylene (PP) is one of the most widely used polyolefin polymers in food packaging, textile, plastic parts, and containers. To develop PP-montmorillonite nanocomposite, two hurdles should be overcome. The first is that PP doesn’t have any polar group in its backbone and PP is one of the most hydrophobic polymers so that its affinity with montmorillonite is poor. Second is the insertion of a suitable monomer into the interlayer space of organically modified clay and then expansion of that space during polymerization or insertion of polymer chain during melt mixing of organophilic clay and PP in the extruder.

One approach to develop PP nanocomposite is to use the compatibilizer in the melt mixing method, where the compatibilizer includes some amount of polar groups to form hydrogen bonds with the oxygen of the silicate surface and contains the ability to be miscible with PP. The miscibility and expansion of the clay gallery depend on the composition of PP, chemical groups of the compatibilizer, and sorts of clay modifier. The Toyota CRD group [54] improved the dynamic storage moduli of PP by ~50% at the composition of 70% PP, 22% maleic anhydride-PP compatibilizer, and 8wt% octadecylammonium treated montmorillonite.

Another approach includes (i) inserting polar monomer into the gallery of clay using solvent followed by polymerization of the monomer, (ii) intercalating polar maleic acid-modified PP into the interlayer space in solvent to prepare a master batch, and (iii) blending the master batch and PP in the extruder. The reason to do these three steps is that the separation of stacked clay layers into single layers is so difficult. Hydrophobic hectorite, hydrophobic montmorillonite, and hydrophobic mica were used with maleic anhydride, according to the above procedure. Hectorite/maleic
anhydride-PP compatibilizer/PP nanocomposite showed the best nanostructure in WAXS (faint peak at 4° and gradual increase of intensity at low angle) and 35 % increase in modulus at 3 wt% clay. Mica/maleic anhydride-PP compatibilizer/PP nanocomposite showed a peak at 3°, gradual increase of intensity at low angle in WAXS, and 67% increase in bending modulus at 3 wt% clay. TEM results are consistent with WAXS results. Stronger physical properties were obtained, even though nanostructure is not better in the case of mica/maleic anhydride-PP compatibilizer /PP nanocomposite, because mica seems to be more rigid than montmorillonite [55].

1.9.2 Nylon nanocomposite

In 1976 for the first time, Nylon nanocomposite, applicable for a conventional molding method, was obtained with two step reaction by Fujiwara and Sakamoto [56]. An ion exchange reaction of the sodium ion in montmorillonite with a protonated aminocarboxylic acid and aminocarboxylic acid-montmorillonite complex made the basal spacing of the intermediate 15.2 Å at first step. Basal spacing was then increased up to 69.8 Å with ε-caprolactam intercalation into the clay gallery and in situ polymerization at second step. This method, however, was not applicable to industrial production due to its high cost.

Practical development of nylon nanocomposites with in situ polymerization was prepared from a swellable synthetic mica containing an optimized ion exchange capacity and ε-caprolactam. Nanocomposite formation consisted of four steps. Basal spacing of synthetic mica was 9.6 Å. During the first step, ε-caprolactam, water and synthetic mica were mixed at 80 °C, and basal spacing became 15.3 Å, because ε-caprolactam penetrated into the gallery of mica. ε-caprolactam was hydrolyzed into
aminocaproic acid and some proportions of that were protonated during the second stage. This protonated aminocaproic acid caused an ion exchange reaction with sodium ion between the clay layers that means protonated amonocaproic acid was introduced into the gallery of the clay. The basal spacing was increased to 20.6 Å. At third stage, the ε-caprolactam addition reaction was continued and basal spacing increaseed up to no detection of a peak in WAXS. The ion exchange reaction reached 95 % (equilibrium state) and the sodium ion was extracted from the gallery to form salts with the carboxyl end group. At the final stage, polymerization was continued to produce a nylon nanocomposite. The reaction temperatures of the third and fourth stages were 260 ℃. The total reaction time was similar to that of conventional hydrolytic polymerization of nylon 6. The nanocomposite was purified with water and dried as nylon 6 [11]. A 50 % increase of flexural modulus and strength, 65 % reductiont in film oxygen permeability, but a 25 times decrease in elongation were obtained at 4 wt% silicate addition.

1.10 Rationale and objectives

Nanostructure dependency on molecular weight of PET is one of area of study in this research. To evaluate the dependency of nanostructure on molecular weight, different molecular weight PET will be used in melt intercalation method, and polycondensation time and solid state polymerization time will be varied in in situ polymerization method.

The most important factor required to increase the basal spacing of the clay is how to expand the interlayer spaces of the clay. More expansion of the clay gallery can result in more interaction between the clay surfaces and polymer chains, and more chains can penetrate into interlayer space of the clay. Montmorillonite has a
large concentration of oxygen on its surface. Oxygen in clay can interact through hydrogen bonding with hydroxyl groups or carboxyl groups of PET. Hydroxyl groups in the edge of clay platelets also can interact with those groups of the PET through hydrogen bonding.

Another important thing is the selection of clay. Modifier of the clay will play an important role in nanostructure formation, because the sorts of clay modifier will decide the thermal stability, the affinity with PET, and the improvement of properties.

Monomer will be the candidate to increase the basal spacing of the clay in the case of in situ polymerization methods. Ethylene glycol has hydroxyl group and the size is less than 10 Å, whereas the length of interlayer space of an organic montmorillonite is 20-30 Å. A better nanostructure would be expected with in situ polymerization than that obtained with melt intercalation method due to the smaller size of the monomer unit in comparison to that of the polymer.

The size of cyclohexane dimethanol (CHDM) is bigger than that of ethylene glycol and the material has a three dimensional structure, that is a mixture of chair and boat structures. CHDM is also hydrophilic like ethylene glycol. If CHDM can penetrate the gallery of the clay, the distance between clay platelets would become bigger than the distance of platelets when ethylene glycol used. CHDM is another monomer that can expand the basal spacing of the montmorillonite more than that obtained by ethylene glycol.

The overall objective of this project is to develop exfoliated PET nanocomposites. When exfoliated structures are obtained, significant barrier and physical property improvement are expected. Homogeneous dispersion of clay into single platelets in PET matrix is not frequently met in the literature. In this research,
an in situ polymerization method is selected to develop exfoliated PET nanocomposites and several organic clays have been used. The current research investigates in detail how to set up the polymerization process and the resultant effect on nanocomposite properties, in terms of nanostructures, physical properties, thermal properties, and barrier properties. According to these considerations, the detailed objectives are categorized into three parts.

First, a melt intercalation method will be evaluated for the comparison with in situ polymerization results. The main concerns are the effect of molecular weight and the effect of modifier of the clay on nanostructure. This experiment will also includes the degree of molecular weight reduction after extrusion, end group concentration change after extrusion, solid state polymerization effect on nanostructure, and thermal characteristics of nanocomposites.

The second step of this study will be to focus on in situ polymerization. Several studies [2,8,34,41,43,48-50] were reported about PET nanocomposite by in situ polymerization method but few studies mentioned detailed results such as difficulties in melt polymerization, the effect of polymerization variables on properties, the reason of degradation during polymerization, and the relationship between additives and properties. End group and composition analysis will be performed to evaluate the degradation during melt polymerization. Melting point can be used as an indicator for the degree of side reaction, and the best conditions for melt polymerization will be set up with the melting point of nanocomposites. An additional purpose is to find out optimum melt polymerization process, which can form better nanostructure according to chemical structure of the modifier of 3 clays in melt polymerization.
The third objective is the comparison of two cases, tactoid and exfoliated nanostructure. The dependency of properties on sorts of nanostructure is not well known. Nanostructure, physical properties, gas permeability and characteristics of each case will be examined to relate nanostructures to properties.

Another main objective in this part is to investigate the effect of stretching on properties of two nanocomposites using sheet and stretched film samples. The stretching process is performed between the glass transition temperature and crystallization temperature and causes several property changes in the case of pure PET. Stretching nanocomposites will give more understandings about the processing-properties relationships in the nanocomposites. Additionally, further improvements of melt polymerization process to get better nanostructure in final products and investigations of factors that affect properties will be followed.

1.11 Clay selection for this research

The organo-montmorillonites which have been used in this research are Cloisite 10A, 15A, and 30B from Southern Clay Products Inc.. Advantages of each of these clays are described below: Cloisite 10A has a benzene ring structure, which indicates the possibility of its compatibility with the PET benzene ring structure. Cloisite 15A has the biggest basal spacing therefore the PET chains can more easily penetrate the interlayer spacing. Cloisite 30B has two hydroxyl groups in the modifier, which gives the possibility of compatibility with hydroxyl group of PET and interaction with carboxyl group of PET. In addition to the existence of hydroxyl group, Cloisite 30B contains the smallest cation exchange capacity (CEC) among 3 clays so that separation of platelet is easier than other 2 clays (Table 1.1). Figure 1.7 shows the
difference in hydrophobicity of clays. Modifier structures of three clays are given in Figure 1.8 [13]. (Tallow is a compound consisting of C, H, and O so that tallow is organophilic like fat.)

Table 1.1 Factor comparisons of three clays for basal spacing expansion

<table>
<thead>
<tr>
<th>Factors</th>
<th>Cloisite 10A</th>
<th>Cloisite 15A</th>
<th>Cloisite 30B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basal spacing</td>
<td>19.2 Å</td>
<td>31.5 Å</td>
<td>18.5 Å</td>
</tr>
<tr>
<td>Compatibility*</td>
<td>+</td>
<td>0</td>
<td>++</td>
</tr>
<tr>
<td>Modifier conc.</td>
<td>125 meq/100g</td>
<td>125 meq/100g</td>
<td>90 meq/100g</td>
</tr>
<tr>
<td>Interaction force*</td>
<td>0</td>
<td>0</td>
<td>+</td>
</tr>
<tr>
<td>hydrophobicity</td>
<td>low</td>
<td>high</td>
<td>very low</td>
</tr>
</tbody>
</table>

*; +(positive effect), -(negative effect)

Figure 1.7 Hydrophobicity comparisons of clays
Figure 1.8 Modifier structures of three clays.

HT is Hydrogenated Tallow (~65% C18; ~30% C16; ~5% C14). T is Tallow (~65% C18; ~30% C16; ~5% C14) [13]
Chapter II
Experimental

2.1 Materials

Commercially available poly (ethylene terephthalate) (PET), Voridian Aqua WA314, was used for melt intercalation of the clay with a twin screw extruder. The intrinsic viscosity of WA314 was 0.74 dL/g. Two low IV PETs with similar compositions were produced and provided by SK Chemicals. These resins were used to evaluate the initial PET molecular weight effect on melt intercalation with clay. The IV values of the two resins were 0.48 dL/g and 0.63 dL/g. Cloisite 10A, 15A, and 30B clays were purchased from Southern Clay Products, Inc., and used as received without further chemical treatment. Table 2.1 contains element of analysis results obtained for three clays. Cyclohexane dimethanol, antimony trioxide, cobalt acetate, phosphoric acid, triphenyl phosphate, and tetramethylammonium hydroxide were purchased from Fischer Scientific. Ethylene glycol was purchased from May’s chemical company and Wellman Inc. Terephthalic acid was kindly donated from Amoco chemical company. Free samples of Irganox 1010 and Irganox HP2225 were supplied by Ciba Specialty Chemicals, Antifoam H-10 from Dow Corning. Table 2.2 shows all the chemical names and their usages in this research.

2.2 Twin screw extrusion

PET and clays (weight fractions of clays were 2, 3, 4, 5%) were compounded
with a Werner & Pfleiderer ZSF-30 co-rotating twin screw extruder (equipped with a vacuum pump) at 275 °C and 200 rpm for melt intercalation in order to obtain a more homogeneous dispersion of clay particles in a PET matrix. Before extrusion, PET samples were dried in a Conair CD60 desiccant dryer at 140°C overnight and the clays were vacuum dried at 120°C overnight. Dry blending, mixing the PET and clays in the metal bucket for 3 min, was performed just before loading the mixtures of PET and clay into the hopper of the extruder. Nanocomposite strand coming out from the die was quenched through a water bath, and then cut into pellets with a pelletizer at 50 rpm. The residence time in the extruder was measured by the time interval between the time when the mixture enters the entrance of extruder barrel and the time extrudate comes out of the die. The residence time was 3~5 minute.

<table>
<thead>
<tr>
<th>Element</th>
<th>Cloisite 10A</th>
<th>Cloisite 15A</th>
<th>Cloisite 30B</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>41.27</td>
<td>38.38</td>
<td>46.22</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>14.36</td>
<td>12.82</td>
<td>16.03</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.21</td>
<td>2.83</td>
<td>3.51</td>
</tr>
<tr>
<td>MgO</td>
<td>1.58</td>
<td>1.47</td>
<td>1.82</td>
</tr>
<tr>
<td>CaO</td>
<td>0.06</td>
<td>0.03</td>
<td>0.08</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.43</td>
<td>0.12</td>
<td>0.46</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.03</td>
<td>0.04</td>
<td>0.05</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.08</td>
<td>0.07</td>
<td>0.09</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>&lt;0.01</td>
<td>0.02</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>MnO</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Ba,ppm</td>
<td>20</td>
<td>14</td>
<td>42</td>
</tr>
<tr>
<td>Ni,ppm</td>
<td>&lt;20</td>
<td>30</td>
<td>&lt;20</td>
</tr>
<tr>
<td>Zr,ppm</td>
<td>86</td>
<td>85</td>
<td>109</td>
</tr>
</tbody>
</table>

Table 2.1 Elements in clay supplied by Southern Clay Products, Inc.
Table 2.2 Chemical names and usages in this research

<table>
<thead>
<tr>
<th>Name</th>
<th>Usage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Terephthalic acid (TPA)</td>
<td>Monomer</td>
</tr>
<tr>
<td>Ethylene glycol (EG)</td>
<td>Monomer</td>
</tr>
<tr>
<td>Cyclohexan dimethanol (CHDM)</td>
<td>Monomer for copolymer</td>
</tr>
<tr>
<td>Antimony trioxide</td>
<td>Catalyst</td>
</tr>
<tr>
<td>Cobalt acetate</td>
<td>Colorant</td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td>Metal stabilizer</td>
</tr>
<tr>
<td>Triphenyl phosphate (TPP)</td>
<td>Metal stabilizer</td>
</tr>
<tr>
<td>Tetramethylammonium hydroxide (TMAH)</td>
<td>DEG suppressor</td>
</tr>
<tr>
<td>Irganox 1010</td>
<td>Antioxidant</td>
</tr>
<tr>
<td>Irganox HP2225</td>
<td>Antioxidant</td>
</tr>
<tr>
<td>Antifoam H-10</td>
<td>Foam reducer</td>
</tr>
</tbody>
</table>
2.3 Intrinsic viscosity

Intrinsic viscosities (IV) of the samples were measured by the conversion of melt viscosity into intrinsic viscosity. Melt viscosities were measured at a temperature of 280 °C and shear rate of 10 rad/sec, using a Rheometrics viscoelastic tester with parallel-parallel plate geometry. A calibration curve was obtained from the correlation equation between intrinsic viscosity, for which 60/40 phenol/tetrachloroethane solvents system was used, and melt viscosity as shown in Figure 2.1. Three PETs and four nanocomposite samples (3 wt% clay addition) were used to get a correlation equation. Linear correlation equation was IV = 0.126*ln(melt viscosity[Pa*s] at 10 rad/sec) -0.040

Figure 2.1 Correlation between ln(melt viscosity[Pa*s] at 10 rad/sec) and intrinsic viscosity. Circles are the data of PETs and diamonds are those of nanocomposites
2.4 Solid state polymerization

The precursor samples were crystallized at 150°C for 2hrs before solid state polymerization to prevent the pellets from sticking during solid state polymerization. A reactor from Buhler, with a 1000g sample capacity, was used to perform solid state polymerization. The cylindrical, stainless steel reactor was equipped with N₂ gas inlet below the sample chamber to pass preheated N₂ gas through the pellet bed during solid state polymerization. The N₂ gas was used to distribute heat evenly throughout the sample chamber and to remove volatile products from the pellet. Reaction time was counted after the resin temperature reached 210°C and it took 1.5 hrs to preheat the sample up to this temperature from room temperature at the conditions of 2000 liter/hr flow rate and 0.3 bar N₂ pressure.

2.5 Thermal stability

A Rheometrics viscoelastic tester with parallel plate geometry was used to measure the melt viscosity as a function of time. The measurements were done under nitrogen or air at 280 °C and 10 rad/sec for 20 min. Prior to the melt viscosity measurements, all samples were vacuum dried at 140 °C overnight. Normalized melt viscosity, melt viscosities were divided by the maximum melt viscosity value, was used to compare the degree of degradation in melt state.

2.6 Carboxyl and hydroxyl end group concentration using FTIR

Carboxyl end group concentration of PET nanocomposite can be determined by a Fourier Transform Infrared (FTIR) technique [57,58]. This technique is based on that the areas of IR peaks that are proportional to the concentration of carboxyl end group. Kim et al. [30] used the intensity of IR peak with several modifications of
FTIR technique using peak area. The principle is to use calibration line between normalized intensity difference from FTIR ($\Delta N_{\text{COOH}}$) and carboxyl end group content from titration. The IR peak intensity was used to calculate the end group concentration in this research. Compression molding machine with a set of polished flat metal was used to make cylindrical pellet into squeezed thin film. To prepare FTIR measurement, all the samples were vacuum dried at 140 °C for solid stated pellet and at 80 °C for amorphous pellet. Normalization of intensity ($N_{\text{COOH}}$) was done after the intensity at 3714 cm$^{-1}$ was set zero to eliminate thickness effect; Normalization of the intensity at 3268 cm$^{-1}$ with the intensity at 3995 cm$^{-1}$ for the carboxyl end group concentration. Thinner than 0.3 mm thickness gave the better reproducibility and 4~5 samples were measured to get an average. Equation (5) was used to calculate $\Delta N_{\text{COOH}}$.

$$
\Delta N_{\text{COOH}} = N_{\text{COOH}} - N_{\text{COOH}}^d
$$

$$
= \left[ I_{3268\text{cm}^{-1}} - I_{3714\text{cm}^{-1}} \right]_{\text{sample}} - \left[ I_{3268\text{cm}^{-1}} - I_{3714\text{cm}^{-1}} \right]_{\text{deuterated-sample}}
$$

(equation 5)

Deuterated sample (Figure 2.2) was prepared with the reaction of deuterium oxide and sample at 50 °C for more than 48 hrs for the zero level of end group. All the samples were dried before deuteration. Similar calibration curve [30] between normalized intensity difference from FTIR and carboxyl end group content from titration was used shown as in Figure 2.3; COOH (titration)=20.659*\( \Delta N_{\text{COOH}} \). Hydroxyl end group was measured with the same way of carboxyl end group using FTIR except that the intensity at 3268 cm$^{-1}$ was replaced by 3545 cm$^{-1}$.

$$
\text{OH}=26.0*\Delta N_{\text{OH}}
$$
Figure 2.2 FTIR spectra for deuterated PET and PET. –OH is located at 3545 cm\(^{-1}\) and –COOH is located at 3268 cm\(^{-1}\)

Figure 2.3 Calibration line between Carboxyl end group content from titration and normalized intensity difference from FTIR, \(\Delta\text{Ncooh}\) (Diamond points are data of PET nanocomposites and circle points are those of PETs)
Figure 2.4 shows FTIR spectra of three clays, three nanocomposites and pure PET. All nanocomposites, prepared by in situ polymerization, have the peak at 3630 cm\(^{-1}\) and three clays also contain the same peak. All nanocomposites and clays were dried at 140°C overnight. The clay was mixed with KBR before FTIR measurement (95% KBR and 5% clay) using porcelain bowl, and then the mixture was compression molded into thin film. From these results, it is known that the peak at 3630 cm\(^{-1}\) was from the clay. Hongping et al. [87] reported the peak near this location is related to OH stretching vibrations of the structural OH groups in the clay.

Figure 2.4 FTIR spectra of three clays, three nanocomposite and pure PET. 1) 30B nanocomposite, 2) 15A nanocomposite, 3) 10A nanocomposite, 4) pure PET, 5) the mixture of 95% KBR and 5% Cloisite 30B, 6) the mixture of 95% KBR and 5% Cloisite 10A, , 7) the mixture of 95% KBR and 5% Cloisite 15A
Titration of carboxyl end group

a) Weigh 4.0 g NaOH and make the solution using 3~5 ml pure water with 1000ml flask. Fill up the 1000 ml level with benzyl alcohol and stir till the mixture becomes transparent.

b) Weigh 0.1000 g of phenol red indicator and add into 100 ml flask. Add 20 ml ethanol to make a solution, and then fill up the level with pure water.

c) Weigh 0.0500 g of amidosulfamic acid using 50 ml flask and add 30~50 ml pure water to make a solution. Put two drops of phenol red and titrate with 0.1N NaOH.

\[
\text{Factor (F)} = \frac{A \times \text{purity of sulfamic acid}}{(N \times V \times 97.09)} \quad \text{(equation 6)}
\]

Where, \( A \)= weight of amidosulfamic acid (sulfamic acid) (g)

\( N \)=concentration of NaOH (0.1N)

\( V \)= volume of NaOH for titration

d) Weigh 0.1000 g of powder sample (less than 40 mesh) and put the powder sample into a solution tube. Add 10 ml benzyl alcohol with pipet. Make that mixture a solution at 200°C with stirring, under nitrogen purge for 10 minutes. Cool down the solution with air blow. Move the solution to a 50 ml beaker and add 5 ml chloroform, and wash the solution tube with 5 ml chloroform. This 5 ml chloroform should be added into 50 ml beaker. Add two drops of indicator and titrate the solution with NaOH prepared at a); yellow → red.

The same procedure will be performed without sample to determine a blank.

\[
\text{COOH} = \frac{[(B-C) \times 1/1000 \times N \times F]}{D} \quad \text{(equation 7)}
\]

where, \( B \) and \( C \)= the amount of NaOH (ml) and that for blank

\( N \)= the concentration of NaOH (N)

\( F \)=factor, \( D \)= the weight of sample (g)
2.7 Melt polymerization

Nanocomposite was melt polymerized in bench scale polymerization system (RTI Engineering Co., Ltd., South Korea) equipped with 2 reactors (Esterification reactor and Polycondensation reactor). Each reactor has 3 liter capacity so that 1~2 kg PET resin per batch can be produced. An anchor type stirrer was installed in the esterification reactor, whereas the polycondensation reactor was equipped with a helical type stirrer to increase stirring efficiency (Figure 2.5). The PET melt polymerization process consists of 2 steps (esterification and polycondensation). TPA and EG are reacted at 220~245 °C under 1 kgf/cm² of N₂, to produce water and BHET as products in the esterification reaction step. The polycondensation reaction was performed at 270~280 °C under high vacuum (1~2 torr). The amounts of additives for the polycondensation reaction were 250 ppm Sb, 30 ppm Co, and 20 ppm P. These were added in the last stage of esterification or in the early stage of the polycondensation reaction. These three additives were put into the reactor at the same time with stirring and nitrogen flowing. Before adding additives, antimony trioxide was mixed with ethylene glycol and heated up to 150 °C for 2 hrs to form antimony glycolate. Cobalt acetate was mixed with hot ethylene glycol to prepare a solution.

In this research, two processes were used to evaluate the affinity of the three clays with monomers or oligomers of PET, and the effect of the residence time of the clay in the reactor on nanostructure (Figure 2.6). The first process has been designated as the ES clay addition process. This process contains esterification and polycondensation steps with clay addition at the early stage of the esterification reaction. The second process has been designated as PC clay addition process and includes only the polycondensation step. In this process the clay was added at the early stage of polycondensation reaction as illustrated in Figure 2.6. 1 Kg of
terephthalic acid and 35 g clay were mixed in powder form to obtain good dispersion and then mixed with 560 g of ethylene glycol in the esterification reactor for the ES clay addition process, then heated to esterification temperature (Figure 2.7). Theoretically 1197 g of PET nanocomposite can be produced at these conditions. The mole ratio of ethylene glycol/terephthalic acid was 1.5, which was the standard ratio for PET melt polymerization in this reactor. Crushed BHET of 1250 g was dried at 130°C overnight, then melted at 250°C for 2 hrs under nitrogen (0.2 kgf/cm² pressure). After BHET melting, catalyst, colorant, stabilizer, and 35 g dried clay were put into the PC reactor with nitrogen flow to prevent thermo-oxidation during the PC clay addition. The polycondensation reaction was done at 280 °C under a vacuum of 1~2 torr.

![Figure 2.5 Schematic diagram of melt polymerization reactor](image)
Figure 2.6 Detailed processes of ES clay addition and PC clay addition

Figure 2.7 Heating profile of esterification reaction. Standard PET esterification reaction takes 5~6 hrs
Many clay agglomerations were observed on the surface of nanocomposite strands, when clay was added in the same way as the catalyst addition (ordinary) as shown in Figure 2.8. The source of these agglomerations can be explained in terms of mixing conditions. A helical stirrer occupies more space than the anchor type stirrer so that some amounts of clay were left on the surface of helical stirrer flights without mixing with BHET after powdered clay was added through the additive addition cap. This unmixed clay was heated on the surface of stirrer and then thermally degraded in the form of dark brown agglomeration. The thermally degraded clay started to be mixed with melted resin when the IV of the resin reached about 0.3 dL/g. This is because the melt resin goes up the helical stirrer flights from that IV until the polycondensation reaction is finished. The actual clay amounts in PET nanocomposite could be affected by the agglomeration of clay and XRD measurements can detect the agglomeration, which will be considered as the part of no affinity with PET. Theses agglomerations due to the degraded clay on the surface of stirrer were found during the melt polymerization of nanocomposites at PET conditions. To reduce the agglomeration of the clay in nanocomposites, a funnel was used to reduce the amount of clay on the surface of stirrer flight. Figure 2.8 showed the concept and the result of the funnel method. The clay addition with funnel was applied from Chapter 3.3. The reason, the clay addition with funnel was developed, was to reduce the amount of clay agglomerations and to disperse clay particles in PET matrix more uniformly. Otherwise, nanocomposite properties can be affected by the clay addition method, instead of the affinity of the organic clay.
Figure 2.8 Concept of ordinary clay addition method and funnel method;

(a) ordinary method, (b) funnel method, (c) strand surface with ordinary method, (d) strand surface with funnel method
2.8 NMR spectrometer

Composition of nanocomposite and PET were determined by Varian VXRS-400 MHz H MNR. A mixture of 70/30 (wt%/wt%) deuterated chloroform/trifluoroacetic acid were used to make solutions with samples.

- Spectrometer receiver frequency or field strength = 400 MHz
- Spectra width or spectral frequency window = 6000 Hz
- Nucleus = 1H
- Original points count = 16384
- Points count = 16384
- Acquisition time = 2.7 (sec)
- Relaxation delay = 2 (sec)
- Pulse = 29.5°
- Numbers of transients = 64
- Line broadening = 0.5 Hz
- FT size = 65536
- Temperature = 29 °C

2-9. DSC measurement

A Perkin Elmer DSC-7 (Shelton, CT), differential scanning calorimeter, was used to monitor glass transition (Tg), crystallization (Tc1, Tc2) and melting temperatures (Tm) of samples at a scanning rate of 10 °C/min(heating rate) and 5 °C/mn (cooling rate) under a nitrogen atmosphere. Tc1 is crystallization temperature of glass phase heated from 40 °C to 300 °C and Tc2 is crystallization temperature of melt phase cooled from 300 °C to 100 °C.
2.10 Single screw extrusion

A laboratory scale Brabender single screw extrusion was performed to obtain the ribbon sheets with the following parameters: screw diameter D=19 mm, L/D=22/1, and compression ratio=3/1. Before extrusion, pellets were dried in a vacuum oven overnight at 140 °C. Extrusion temperature was 280 °C and screw speed was 80 rpm. An extruded sheet was quenched with winder cooling rolls to get uniform thickness of amorphous sheet. All the sheet samples were kept in constant temperature and constant relative humidity (25 °C and 50 % R.H.)

2.11 Biaxial stretching

A T.M. Long Co. Inc. Film Stretcher was used to prepare the films of 2x2, 3x3, 3.5x3.5 stretch ratios. Three film stretching temperatures (90, 100, 110 °C) and 2 stretching rates of 100 and 50%/sec were evaluated to establish the best conditions for preparing the PET nanocomposite films. It was found that 100 °C and 100 %/s were the best stretching conditions for obtaining the most transparent nanocomposite films.

2.12 Oxygen permeability

The oxygen transmission rate, the rate of oxygen gas passing through a unit of a film or sheet per unit of time at specified conditions of the sample, under steady-state conditions, at specific temperature and pressure, was measured using a MoCon OxTran 1050 oxygen permeation analyzer. The value of Hewlett Packard multimeter was transmitted to a computer through the data acquisition unit. This method is a coulometric method, which follows ASTM D 3985.

Aluminium film for sample supporting was used in the cases where the sheet and 2x2 stretched film size of samples were too small for the sample holder. Epoxy
adherent prevented leaks between the sample sheet/film and the aluminium film. 3×3 and 3.5×3.5 stretched films were used without support of aluminium film. The oxygen permeable areas of stretched films were 50 cm². The areas of samples, which needed aluminium film support, were 5 cm².

2.13 Clay content

An electric multiple unit furnace of Hevi Duty Electric Co. was used to measure the ash content of nanocomposite materials. Nanocomposites and pure PET were burned at the conditions of 900 °C and for 1 hr to burn out the matrix polymer completely, which is similar to ASTM 5630-94, but longer time was needed. Clays were also burned to measure the residual amount of the clay without polymer. Moisture absorption started when porcelain was taken out from the furnace. Four minutes of storage in desiccator was required to cool the temperature of porcelain without moisture absorption then weighed to measure the weight of burned material and porcelain itself. The weight of dried porcelain was measured before ash content was measured. The balance can weigh the sample to the 0.0001 g. Equation (8) was used to calculate clay contents.

\[
\text{ash, mass \%} = \frac{(W_3-W_1) \times 100}{(W_2-W_1)} \quad \text{(equation 8)}
\]

where, \(W_1\) = mass of sample crucible (g)

\[
W_2 = \text{mass of sample crucible (g) + mass of sample (g)}
\]

\[
W_3 = \text{mass of sample crucible (g) + ashed mass of sample (g)}
\]
Three clays were burned to calculate the residual amount of the clay. The results were similar to the results from the clay company.

<table>
<thead>
<tr>
<th></th>
<th>Cloisite 10A</th>
<th>Cloisite 15A</th>
<th>Cloisite 30B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment</td>
<td>60.5</td>
<td>56.0</td>
<td>68.3</td>
</tr>
<tr>
<td>Clay company data</td>
<td>61</td>
<td>57</td>
<td>70</td>
</tr>
</tbody>
</table>

Table 2.3 Clay ash contents from this experiment and clay company (unit; weight %)

Ash content at different clay amount

Cloisite 15A was extruded with PET (WA 314) in twin screw extruder changing clay amounts (2, 3, 4, 5 wt%). Figure 2.9 showed the linearity between the clay addition amount and the ash residual. The increase of clay amounts didn’t affect the analysis result of the ash residual up to 5 wt%.

![Figure 2.9 Relationship between the clay addition amount and the clay residual in nanocomposites](image)

$$y = 1.009x - 0.102$$

$$R^2 = 0.997$$
2.14 Density and crystallinity

Densities of the films and sheets were measured at 25°C with a density gradient column filled with aqueous calcium nitrate solutions. Two columns, one for amorphous and the other is for crystalline PET, were used to measure the densities of the nanocomposite films and sheets. This method follows ASTM D792-91. Volume fraction crystallinity (f) was calculated from the density values using the following relationship.

\[
\text{Crystallinity (f)} = \frac{(d-d_a)\times 100}{(d_c-d_a)}
\]  
(equation 9)

where, 
\(d\) = sample density
\(d_a\) = the density of amorphous PET (1.333 g/cc)
\(d_c\) = the density of completely crystalline PET (1.455 g/cc) [30]

2.15 Optical microscopy

To investigate the presence of impurities and residual stress in the sheets and films at 50 × 1.25 magnification ratio, a Carl Zeiss Inc microscope equipped with Sony CCD-IRIS/RGB color video camera was used. Polarizer and analyzer were used to detect the refraction of two orthogonal vibrational components in a beam.

2.16 Instron tester

Tensile modulus, strength and maximum strain were measured with an Instron 4400R tester according to ASTM D 638 type IV. The specimen for this study was prepared with dog bone die and press. Test conditions are 2 in/min crosshead speed, 50% humidity, and 23°C temperature. Specimen dimensions of sheets were 6.5 inch length, 2 inch gage length, and 0.5 inch width. Thickness of every specimen was measured with micrometer. 5~10 specimens were measured per one sample and
averaged. All the samples were conditioned under 25 °C and 50 % RH before measuring tensile properties.

2.17 Basal space measurement by Wide Angle X-ray Diffraction

The basal spacing of nanocomposites and clays were determined by a wide angle x-ray diffraction technique using Xpert PRO (PAN analytical) facility; Nickel filter, K-alpha (1.541 Å), scan speed (0.2 °/min), in the range of 2θ=1.6°~7°. All samples were ground into fine powder. The optimum particle size for measurement using XRD is 1~10 μm. Large particles can result in unpredictable spikes but too small particles lead to line broadening of the result. The particle size of the ground samples was bigger than the optimum size so compression molding with cylinder type flat metal at room temperature was done to make 0.3 mm thin sheet which can increase the XRD intensity and get better resolution as shown in Figure 2.10.

![Figure 2.10 The effect of powder and thin sheet on XRD peak intensity and resolution](image)
Before using the PANanalytical Xpert PRO X-ray (“Xpert PRO”) to measure the basal spacing of nanocomposite samples (Chapter 3.2 -3.5), a Scintag Inc XDS 2000 (“XDS 2000”) powder diffractometer was used to measure the interlayer space of melt intercalation samples (Chapter 3.1). The radiation source of XDS 2000 is copper of 0.154 nanometers. A liquid nitrogen cooled germanium solid state detector is used to capture the scattered X-ray beam. Xpert PRO gives stronger intensity than XDS 2000. Stronger intensity in XRD results will reduce misunderstanding about nanocompostructures, especially clay contents is small.

2.18 Transmission Electron Microscopy (TEM)
Cross-sectional TEM specimens of PET nanocomposite were prepared as described below. The pellet samples were embeded in epoxy resin (eponfix purchased from Electron Microscopy Sciences) in a capsule. After curing the epoxy resin, the embedded samples were ultramicrotomed using a diamond knife to produce thin specimens for high-resolution transmission electron microscopy (HR TEM) study. The slicing speed and thickness were set at 1 mm/s and 70 Å, respectively. The thin sections were then located onto a carbon coated microgrid. The HR TEM study was carried out with a JEOL JEM 3010 TEM (Cooperative Center for Research Facilities in Sungkyunkwan University, South Korea) was used to investigate nanostructure. Accelerating voltage was 300 kV, vacuum was 1.0 x 10^-7 torr, and the resolution of TEM was 0.2 nm point-to-point.

2.19 Color measurement

Hunterlab Color/Difference Meter D25-2 was employed for color measurement. The color measured was expressed by the CIE Lab color space values which follow
CIE Illuminant D65. Color L is the degree of lightness and the range is from 100 (white) to 0 (black), a is the degree of redness (+) and greenness (-), and b is that of yellowness (+) and blueness (-).
Chapter III

Results and Discussion

3.1 Melt intercalation

3.1.1 Nanocomposite IV after melt intercalation

3.1.1.1 Clay amounts and sorts effect on IV drop with IV 0.74 dL/g PET

Three different sorts of clays were used to evaluate the modifier effect of the clay on nanostructure in PET. The modifier of Cloisite 10A clay has a benzene ring structure and medium range of hydrophobicity, that of Cloisite 15A clay has the largest basal spacing and high hydrophobicity, and the modifier of Cloisite 30B clay contains hydroxyl groups and low hydrophobicity. The purpose of using three clays for evaluation is to know which chemical structure of modifiers has the best affinity with PET and which factor has the largest effect on resultant nanostructure.

The melt viscosity differences between strands of pure PET and nanocomposites coming from the extruder were observed during extrusion so that IV of the strand was measured to examine IV differences between before and after extrusion. All the drying and extrusion conditions for samples were the same.

PET/clay nanocomposites were melt-blended with IV 0.74 dL/g PET at various clay contents using the three clays. Addition of clay caused a bigger IV drop than that observed for pure PET, even though a small amount clay was added. Figure 3.1 shows changes in IV as a results of extruding PET containing various concentration of Cloisite 15A clay; 0.13 dL/g IV drop is observed at 2 wt% Cloisite 15A , whereas
only a 0.06 dL/g IV drop is recorded in the case of pure PET. This trend was consistent for the three clays shown as in Figure 3.2. PET/15A nanocomposites showed the least IV drop, while PET/30B nanocomposites showed the greatest IV drop. An increase of clay amounts results in a slight increase of IV (Figure 3.1 and 3.2). Matayabas Jr and Turner [9] reported that the addition of clay caused a big IV drop and the IV drop was increased with the increase of clay amounts. My results showed that the melt viscosity increased with the increase of clay amounts, but their result was the opposite of mine. These differences seem to be caused by the use of different organic clay, Clayton APA versus Cloisite 15A. Pristine montmorillonite is treated with various chemicals through an ion exchange reaction, which assigns different thermal resistance. Xie et al. [59] researched thermal degradation of organically treated montmorillonite, and suggested four decomposition regions with respect to the temperature using a thermal gravimetric analyzer (TGA): the free water was released in the region below 200 °C; organic substances evolved in the region between 200-500 °C; structural water was released in the region between 500-800 °C; organic carbon reacted in the region between 800-1000 °C. They reported that the onset temperature of thermal degradation did not mean that the clay could not be used to form the nanocomposite at that temperature. Davis et al. [52] mentioned that the sorts of organic modifiers in montmorillonite can affect its thermal stability, dispersion, and delamination in PET nanocomposites.

The decomposition mechanisms and temperatures of organic clays used in this research, therefore, could be different, according to the chain lengths and the chemical groups of the clay modifiers.
Figure 3.1 Nanocomposite IV after extrusion of IV 0.74 dL/g PET and Cloisite 15A with different clay amounts (2, 3, 4, 5 wt%). ext.PET is IV after extrusion of pure PET.
Figure 3.2 Nanocomposite IV after extrusion of PET/10A, PET/15A, and PET/30B (IV 0.74 dL/g PET + 3 wt%, 5 wt% clays). ext.PET is IV after extrusion of pure PET.

[Nomenclature]; 10A3% is the mixture of PET and Cloisite 10A 3 wt%
15A3% is the mixture of PET and Cloisite 15A 3 wt%
30B3% is the mixture of PET and Cloisite 30B 3 wt%
3.1.1.2 Non-Newtonian behavior of nanocomposite at low shear viscosity

Another characteristic of PET nanocomposites is their non-Newtonian behavior in the relationships between melt viscosity and shear rate even in the low shear rate region. PET shows Newtonian behavior in the low shear rate region, so that melt viscosity at 10/sec can be used to express the molecular weight of PET like solution viscosity. The increase of clay amount caused non-Newtonian behavior in melt viscosity of nanocomposite, but the linearity between two values at 3 wt% clay was still obtained as shown in Figure 2.1 of the experimental part. One thing which is worth notice is that large amounts of clay (4, 5 wt%) nanocomposite showed pseudo-solid-like behavior, almost a linear relationship between shear viscosity and shear rate, while small amounts of clay (2, 3 wt%) nanocomposite showed shear thinning behavior, a gradual decrease of shear viscosity at high shear rate due to orientation, as given in Figure 3.3. Similar trends were observed in all three clay nanocomposites. Krishnamoorti and Silva [19,60] explained these phenomena as a yield stress. Some values of yield stress are needed to move the system in the cases of high contents of clay, whereas almost zero yield stress exists at low contents of clay. Divergence of shear viscosity at low shear rate is related to pseudo-solid-like behavior in high contents of clay nanocomposites. At high shear rate, the parallel orientation of clay layers or even tactoids to the flow direction makes melt viscosity of nanocomposites undergo shear thinning.

IV was obtained in this research by the conversion from melt viscosity at 10/sec shear rate into solution viscosity. There is the possibility that nanocomposite IV could be underestimated a little in the cases of 4 and 5 wt% clays, although the correlation curve between IV from solution and IV from melt viscosity was obtained with three pure PET samples and five nanocomposites containing 3 wt% clay.
Figure 3.3 Melt viscosity behaviors of nanocomposites at low shear rate with clay amounts

[Nomenclature]

* iv74; IV 0.74 dL/g PET

* 15A2% - Cloisite 15A clay 2 wt% was mixed with PET

* 15A5% - Cloisite 15A clay 5 wt% was mixed with PET
3.1.1.3 PET molecular weight effect on nanocomposite IV after extrusion

Compounding of PET and the clays was conducted with three IVs (0.74, 0.63, 0.48dL/g) of PET and three clays (Cloisite 10A, 15A, 30B) to produce PET nanocomposites with the twin screw extruder. The reason that three different IV PETs were used is to examine the effect of molecular weight on the degree of intercalation into the clay gallery. The concept that the shorter molecules of PET can penetrate the interlayer space of clay more easily than the longer molecules, is the base of this experiment.

Addition of 3 wt% clay caused an IV drop (Figure 3.4) as the former results. The higher IV of the PET resulted in the bigger IV drops of the nanocomposites. In addition to these results, PET/15A showed the least IV drop and PET/30B showed greatest IV drop regardless of initial PET IV. PET/30B clay has two hydroxyl groups in the modifier so that the introduction of these polar hydroxyl groups can enhance interaction with polar groups such as moisture in the air. This can accelerate further degradation of nanocomposites at high temperature. With enough thermal energy, such as provided by the high temperature of extrusion at 275 °C, moisture in the air can cause hydrolysis and oxygen can cause oxidative thermal degradation. The mechanism involved in IV drop after extrusion will be analyzed to determine the influence of thermal, hydrolytic, and oxidative degradation.
Figure 3.4 IV after extrusion of three IVs of PET (IV=0.74, 0.63, 0.48 dL/g) and three clays. Clay amount was fixed at 3 wt%. Circles are IVs of pure PET before extrusion.
3.1.2 Reasons for molecular weight reduction

3.1.2.1 Degradation

The reasons for molecular weight reduction of nanocomposites prepared by extrusion could include inappropriate drying (hydrolysis), oxidation, and thermal degradation [1,27,61,62]. These modes of degradation are known to occur near at 260~300 °C, the temperature range of PET melt processing or polymerization. These three types of degradations can all cause molecular weight reduction, but degradation proceeds in a different way. For example, hydrolytic degradation, the most rapid degradation among the three mechanisms, is known to increase the carboxyl and hydroxyl end group concentration as a result of backward reaction of esterification [1]. Hydrolysis can be affected by the amount of moisture, temperature, acidity, and type of catalysts [27,63].

Thermal degradation contains complex degradation schemes. Many researchers [64,65,66] have suggested several mechanisms, but there doesn’t seem to exist a unique mechanism. Common points in each degradation scheme are the formation of vinyl ester groups, acetaldehyde generation, and carboxyl end group formation during molecular weight reduction at high temperature even though these reactions occur at chain ends or at the ester linkages.

It is reported that oxygen accelerates the thermal degradation reaction so that discoloration, branched chains, gelation, and formation of several gaseous products can be detected more often than without oxygen when PET is exposed to high temperature [27,62]. It is believed that oxidative degradation of PET is involved in free radical mechanism, which can speed up the reaction rate.

To evaluate these three factors, thermal stability evaluations were performed under N₂ and air using a parallel plate rheometer and end group analysis.
Investigations on thermal stability were done with a parallel plate rheometer at 280 °C and under N₂ and air to elucidate the main degradation mechanism among hydrolysis, oxidation, and thermal degradation. Three effects (moisture, thermal, oxygen) were evaluated separately and two IV levels of nanocomposites were used to confirm reproducibility of the thermal stability method. Figures 3.5-3.8 show normalized melt viscosity changes for pure PET and the nanocomposites.

Figure 3.5 shows only thermal degradation effects on PET and PET nanocomposites in the range of IV 0.60 dL/g. In this case, oxygen was eliminated by the nitrogen flow in the rheometer chamber and moisture was excluded by both vacuum drying of samples and nitrogen flow in the rheometer chamber. The melt viscosity of PET was not thermally degraded, but was kept at an almost constant value for 20 minutes. All PET nanocomposites, however, showed drastic declines of melt viscosity, regardless of the sorts of clays used. Thermal stabilities of the nanocomposites under air showed similar trends with the results of nanocomposites heated under nitrogen, but the melt viscosity change was further decreased by 10% more than that under nitrogen. The melt viscosity of PET was also decreased by 30% under air so that acceleration of the thermal degradation rate by oxygen was confirmed by this experiment. The melt viscosity drop of PET heated under air was roughly half that of the nanocomposites heated under nitrogen.

The same experiments were done with higher IV PET and nanocomposites, within the 0.80 dL/g range of IV, as shown in Figure 3.7 and 3.8. The results under nitrogen and air showed similar trends with those results in the range of 0.60 dL/g IV. Thermal stability experiments indicate that PET nanocomposites are sensitive to temperature. Therefore, temperature and residence time could be the main factors to affect properties of PET nanocomposites.
Figure 3.5 Thermal stability of nanocomposites, which have near 0.60 dL/g IV, under N\textsubscript{2} at 280 °C for 20 minutes. Clay amount is fixed at 3 wt%. The number in parenthesis is IV and 3 is the clay amount; 10A3 is PET/10A nanocomposite, 15A3 is PET/15A nanocomposite, 30B3 is PET/30B nanocomposite
Figure 3.6 Thermal stability of nanocomposites, which have near 0.60 dL/g IV, under air at 280 °C for 20 minutes. Clay amount is fixed at 3 wt%. The number in parenthesis is IV and 3 is the clay amount; PET is WA314, 10A3 is PET/10A nanocomposite, 15A3 is PET/15A nanocomposite, 30B3 is PET/30B nanocomposite.
Figure 3.7 Thermal stability of nanocomposites, which have near 0.80 dL/g IV, under 
N₂ at 280 °C for 20 minutes. Clay amount is fixed at 3 wt%. The number 
in parenthesis is IV and 3 is the clay amount; 10A3 is PET/10A 
nanocomposite, 15A3 is PET/15A nanocomposite, 30B3 is PET/30B 
nanocomposite
Figure 3.8 Thermal stability of nanocomposites, which have near 0.80 dL/g IV, under air at 280 °C for 20 minutes. Clay amount is fixed at 3 wt%. The number in parenthesis is IV and 3 is the clay amount; 10A3 is PET/10A nanocomposite, 15A3 is PET/15A nanocomposite, 30B3 is PET/30B nanocomposite
3.1.2.2 End group analysis using FTIR

The carboxyl end group values of precursor (IV 0.63 dL/g PET) and SSP pellets (IV 0.74 dL/g PET) were measured as standard samples in the preliminary experiment using FTIR. The IV 0.63 dL/g precursor has 47 mmol/Kg PET as its carboxyl end group concentration whereas the IV 0.74 dL/g solid state polymerized material has 10 mmol/Kg PET as its carboxyl end group concentration. In general, the carboxyl end group value of the precursor is near 50 mmol/Kg PET and that of SSP pellets is near 15 mmol/Kg PET when we use the titration method.

3.1.2.2.1 End group concentration change of pure PET in the rheometer

Thermal degradation effect under nitrogen and air on IV 0.74 dL/g PET was evaluated using a rheometer at the condition of 280 °C and 10 rad/sec for 20 minutes. The carboxyl end group value under N₂ was increased from 10 to 18 mmole/Kg PET, while the hydroxyl end group value was slightly decreased (from 46 to 44 mmole/Kg PET). Those value changes can be explained by thermal degradation effects on PET. Oxidative thermal degradation effect was numerically expressed with the same experiment under air; Carboxyl end group value under air was drastically increased from 10 to 50 mmole/Kg PET and the hydroxyl end group value was also increased (46 to 62 mmole/Kg PET). With these results, we can distinguish thermal degradation from oxidative thermal degradation.

McMahon et al. [67] reported that the hydrolysis rate is 10,000 times faster than the thermal degradation rate, and 5,000 times faster than oxidative thermal degradation at the same temperature. Thermal stability of PET in the melt state is affected greatly by the sorts of metal compound [68], and carboxyl end groups can be increased even in the solid state according to drying temperature.
3.1.2.2.2 End group concentration change of PET nanocomposites after extrusion

Carboxyl end group values of PET/10A (compounding material of IV 0.74 dL/g PET and Cloisite 10A) and PET/15A (compounding material of IV 0.74 dL/g PET and Cloisite 15A) were 19 mmole/Kg PET on an average. This value was 9 mmol/Kg PET increases in carboxyl concentration due to addition of clays, when compared with that of IV 0.74 dL/g PET shown as in Figure 3.9. If hydrolysis is the main reason for molecular weight reduction, carboxyl end group value should be bigger than that of the precursor because IV ranges of nanocomposites were similar to that of the precursor. Solid state polymerization of precursor requires the consumption of carboxyl and hydroxyl end group concentration as the molecular weight increases. The major reaction of that process is the reaction between hydroxyl groups so that the difference of concentration of the hydroxyl group between before and after SSP reaction should be bigger than that of carboxyl end group. If hydrolysis is the main reason of molecular weight reduction, the same mole number of carboxyl and hydroxyl end group should be increased.

Hydroxyl group values of nanocomposites of PET/10A and PET/15A are increased by 14 mmole/Kg PET on an average. When we compare the increase of both end group concentrations (9 mmole/Kg PET increase in –COOH and 14 mmole/Kg PET increase in –OH), we can conclude that the main reason for molecular weight reduction is hydrolysis. If thermal degradation is the main reason, only -COOH concentration should be increased. If oxidative thermal degradation is the main reason, -COOH values should be much bigger (more than 2 times) than 19 mmole/Kg PET. The absorption rate of moisture of nanocomposite seems to be faster than that of PET due to clay even though vacuum drying was done. The clay particle has enormous surface area so this might accelerate moisture absorption rate during
melt mixing in the hopper.

Carboxyl and hydroxyl end group values of PET/30B (compounding material of IV 0.74 dL/g PET and Cloisite 30B) are bigger than those values of other nanocomposites. Presumably, this seems to be related to acceleration of degradation due to hydroxyl groups of modifier in Cloisite 30B.

The experimental results of this part can be summarized as follows:

* IV reduction of nanocomposites was more than 2 times greater than that of pure PET even though the drying condition was the same and the same extruder was used.

* Clay increased the rate of degradation of nanocomposites so that clay caused severe molecular weight reduction.

* Several degradation mechanisms could be involved in molecular weight reduction of nanocomposite. According to the increase of carboxyl and hydroxyl end group values, the hydrolysis was the main reason in melt intercalation.
Figure 3.9 Carboxyl end group analysis result of nanocomposites, precursor, and before and after sample of thermal stability test in the rheometer

[Nomenclature]

*7410A3; the mixture of IV 0.74 dL/g PET and Cloisite 10A at 3 wt%

*iv74-N2; the sample after thermal stability test of IV 0.74 dL/g PET under nitrogen at 280 °C
Figure 3.10 Hydroxyl end group analysis result of nanocomposites, precursor, and before and after sample of thermal stability test in rheometer

[Nomenclature]

*7410A3; the mixture of IV 0.74 dL/g PET and Cloisite 10A at 3 wt%

*iv74-N2; the sample after thermal stability test of IV 0.74 dL/g PET under nitrogen at 280 °C
3.1.3 SSP of nanocomposites

3.1.3.1 220 °C SSP result

The IV increase after SSP of IV 0.63 dL/g PET was 0.37 dL/g at 220 °C for 15 hrs under 700 liter/hr N₂ flow rate and 0.3 bar N₂ pressure. The same conditions were applied to do SSP of nanocomposites. IV differences between before and after SSP for 15hr at 220 °C gives SSP rates, as shown as in Figure 3.11. Addition of clays made the SSP rate more than 2 times slower than that of pure PET. Among three nanocomposites, the SSP rate of PET/30B nanocomposite was the fastest, and those of PET/10A and PET/15A nanocomposite were similar. Figure 3.12 shows the clay amount increase in PET/15A nanocomposite did not affect the SSP rate except for 5 wt% as given in Figure 3.12.

The possible reasons for the slow SSP rate of nanocomposites are two. First, clay particles are platelet structures which increase path length of volatile product. Ethylene glycol, a major gaseous product in the SSP reaction, becomes a vapor phase during the SSP reaction and the SSP reaction rate depends on the diffusion rate of ethylene glycol from the PET matrix. Platelets can cause the diffusion rate of ethylene glycol to be slower due to platelets’ own characteristic, to increase path length.

The second possible reason is the crystallinity increase due to the addition of clay (Figure 3.13). Clay can play the role of nuclei in crystallization so that an addition of clay can increase the crystallinity of the nanocomposite. The increase of crystallinity increases the path length of gaseous products, implying the decrease of the diffusion rate of the gaseous products. The increased crystallinity also requires higher activation energies in order for the SSP reaction to occur. The increased crystallinity, therefore, decreases SSP rate.
End group concentration, pallet size, and catalyst system could all be factors which can affect the SSP reaction [69,70]. End group concentrations of nanocomposites had better conditions for fast SSP rates but did not play a big role. Pallet size and catalyst system were the same, because the same PET was used (IV 0.74 dL/g PET) to prepare nanocomposites. This result meant that the effect of end group concentrations on SSP rate was smaller than that of platelet structure and crystallinity.

3.1.3.2 230 °C SSP result

SSP temperature was increased from 220 °C to 230 °C, because the SSP rate of nanocomposites was so slow that a long SSP time was needed to get 0.80 dL/g IV of nanocomposites after SSP, when IV 0.63 and 0.48 dL/g PET were used in melt mixing (Figure 3.14 and 3.15). SSP rate of PET/30B nanocomposites was the fastest and those of PET/10A and PET/15A nanocomposite were similar, which is the same trend with the result of 220 °C SSP. The presumable reason for the faster SSP rate of PET/30B nanocomposite is that Cloisite 30B has two hydroxyl groups in the modifier so that these groups accelerate the SSP rate.

The addition of clay reduced the SSP rate abruptly. To avoid this disadvantage, the increase of SSP temperature could be a supplemental way to enhance the SSP rate of nanocomposites. The crystallinity of nanocomposites was also increased compared with that of pure PET, as shown in Figure 3.13. Another way to improve the SSP rate is to select the clay which has functional groups to interact or react with functional groups of polymer, similar to that of Cloisite 30B.
Figure 3.11 IV after solid state polymerization at 220 °C for 15 hrs; rectangular shapes are IVs after extrusion of IV 0.74 dL/g PET and three clays. Circles are IVs after solid state polymerization of nanocomposites. The difference between the two is the SSP rate.
Figure 3.12 IV after solid state polymerization at 220 °C for 15 hrs; rectangular shapes are IVs after extrusion of IV 0.74 dL/g PET and 15A clay. Circles are IVs after solid state polymerization of nanocomposites. The difference between the two is the SSP rate.
Figure 3.13 Volume fraction crystallinity of nanocomposites after extrusion using the density gradient column when 0.74, 0.63, 0.48dL/g IV PET were compounded with Cloisite 10A, 15A and 30B

[Nomenclature of iv7415A2]

*iv74; IV 0.74 dL/g PET was used as matrix

*15A2; Cloisite 15A 2 wt%
Figure 3.14 IV after solid state polymerization at 230 °C for 15 hrs (IV 0.63 dL/g PET was used); Rectangular shapes are IVs after extrusion at 3 wt% clay addition. Circles are IVs after solid state polymerization of nanocomposites. The difference between the two is SSP the rate.
Figure 3.15 IV after solid state polymerization at 230°C for 5 hrs (IV 0.48 dL/g PET was used); Rectangular shapes are IVs after extrusion at 3wt% clay addition. Circles are IVs after solid state polymerization of nanocomposites. The difference between the two is the SSP rate. 30B nanocomposite has the fastest SSP rate.
3.1.4 Precursor density after crystallization

All precursors were crystallized at 150 °C for 1.5 hrs to measure the density of nanocomposites. An addition of clay increased the density of the nanocomposites, and the increase of clay amount tends to increase the density of the nanocomposites as shown in Figure 3.16. The densities of Cloisite 10A, 15A, and 30B are 1.90, 1.66, and 1.98 g/cc respectively. The densities of IV 0.63 and 0.48 dL/g PET are 1.374 and 1.377 g/cc. An addition of high density clay into low density PET, therefore, increased the density of mixtures. Cloisite 30B has the largest value of density and clay 15A has the smallest density. The results of densities of nanocomposites follow this order. The lower IV of PET has the bigger density so that the density of nanocomposites, compounded with the lowest IV of PET and Cloisite 30B, has the biggest density of nanocomposite.
Figure 3.16 Density of nanocomposites after extrusion when 0.74, 0.63, 0.48dL/g IV PET were compounded with Cloisite 10A, 15A and 30B.

[Nomenclature of iv7410A3]

*iv74; IV 0.74 dL/g PET was used as matrix

*10A3; Cloisite 10A 3 wt%
3.1.5 Thermal characteristics of nanocomposites prepared by melt intercalation

The glass transition temperature (Tg), crystallization temperature when heating from room temperature (Tc1), crystallization temperature when cooling from 300 °C (Tc2), and melting temperature (Tm) were measured from dynamic DSC scan. The effect of clay on thermal characteristics was examined.

Tg values obtained for nanocomposites were shown in Figure 3.17. It is observed that Tg of all nanocomposites were decreased by 2~3 °C compared with Tg of pure PET. Three different IV PETs showed the same trend. This trend is related to molecular reduction after extrusion. Glass transition temperature of PET increased with an increase of molecular weight, while copolymerization and moisture absorption cause a decrease of Tg [27].

Melt mixing of PET with clay changed the crystallization temperatures of nanocomposites drastically (Figure 3.18 and 3.19). Tc1 of nanocomposites decreased by 35 °C, and Tc2 values increased by 25 °C on an average. Both values meant faster crystallization rate of nanocomposites compared with those of pure PET. Crystallization rate is strongly sensitive to an existence of nuclei, and affected by molecular weight although the degree of effect is not as big as the effect of nuclei on crystallization rate. The effect of molecular weight on Tc1 was a 5 °C difference when the IV difference was 0.01 dL/g in the case of PET. Ebengou [71] reported that the nucleation process governs the crystallization kinetics. Heterogeneous nucleation occurs in polymer system and impurities can act as active nucleation sites. Abrupt changes in Tc1 and Tc2 of nanocomposites shows the strong dependency of crystallization rate on nuclei, clay particles. Clay particle, therefore, caused rapid
crystallization in both cases of cold crystallization and melt crystallization because clay particles make it easy to form nuclei for crystal. If a sample has low Tc1, crystallization can occur easily when we perform thermoforming, whereas a sample has high Tc2, we can get a haze in injection molded part.

Melting temperatures of nanocomposites did not show big changes from that of PET as shown in Figure 3.20. The biggest difference of Tm between two materials was 1.5 °C, when pure PET IV was 0.74 dL/g. This implies that the melting point does not strongly depend on a nuclei in the range of this research. Jabarin [72] reported the dependency of melting point of PET on several variables. Melting point of PET depends mainly on heat setting temperature of polymer. This is related to the degree of perfection of the crystals. Higher crystallization temperature or SSP temperature results in higher melting temperatures. In this research, crystallization and SSP temperature was the same so that melting temperatures of nanocomposites were similar.
Figure 3.17 Glass transition temperature (Tg) of nanocomposites, prepared by melt intercalation when three IVs of PET were melt mixed with 3 wt% clay of Cloisite 10A, 15A, and 30B.
Figure 3.18 Crystallization temperature of nanocomposites heated from 40 °C (Tc1) in 2\textsuperscript{nd} scan. Three IVs of PET were melt mixed with 3 wt% clay of Cloisite 10A, 15A, and 30B in twin screw extruder to prepare nanocomposites.
Figure 3.19 Crystallization temperature of nanocomposites cooled from 300 °C (Tc2).

Three IVs of PET were melt mixed with 3 wt% clay of Cloisite 10A, 15A, and 30B in twin screw extruder to prepare nanocomposites.
Figure 3.20 Melting temperature (Tm) of nanocomposites. Three IVs of PET were melt mixed with 3 wt% clay of Cloisite 10A, 15A, and 30B in twin screw extruder to prepare nanocomposites.
3.1.6 Nanostructure analysis by XRD

3.1.6.1 The basal spacing of nanocomposites

The basal spacing of clays was measured to compare the results from the clay manufacturer. The measured values, as shown in Figure 3.21, were 20.5 Å (Cloisite 10A), 32.7 Å (Cloisite 15A), and 19.3 Å (Cloisite 30B), whereas the values supplied by the clay manufacturer were 19.2 Å (Cloisite 10A), 31.5 Å (Cloisite 15A), and 18.5 Å (Cloisite 30B) respectively. These values had a little difference: my results have ~1 Å bigger value than the value supplied by the company.

One characteristic of peak shape of the clay in XRD is a broadness, which means the basal spacing of clays doesn’t have the same value but have a distribution of values. This broadness can make the analysis of nanocomposites, the mixture of clay and polymer, difficult, because the intensity of the peaks could be so weak due to several reasons such as low contents of clay, inhomogeneous mixing, and dubious affinity of clay with polymer. It may be hard to distinguish the peak and a baseline of XRD, especially at low angles and low contents of clay.

3.1.6.2 Basal spacing with clay type and amounts (PET IV was 0.74 dL/g)

Three organic clays, which have different characteristics, were selected to investigate the effect of various hydrophobicity and polar interactions of clay modifiers on nanostructure in intercalation method.

Figure 3.22 shows that the basal spacing of PET/10A and PET/30B nanocomposites becomes bigger after extrusion, indicating the PET was intercalated into the interlayer of organic clays, and an increase of clay amount from 3 wt% to 5 wt% tends to increase the basal spacing of nanocomposites. The basal spacing of PET/15A nanocomposite did not change and the increase of 15A clay amount did not
change the basal spacing of nanocomposites, meaning no intercalation occurred. The increases of the basal spacing of PET/10A and PET/30B were 11.8 and 12.6 Å at 3 wt% clay addition. From these results, we can say that Cloisite 10A and Cloisite 30B have an affinity with PET, while Cloisite 15A doesn’t have any affinity with PET. These results can be related the characteristics of clays shown as in Table 1 of the introduction part.

Lebaron et al. [73] reported the surface polarities of polymer and organic clay should be matched when polymer and clay are fully wet to intercalate the interlayer space. Polar interaction [74] is also critical for the formation of intercalation or exfoliation of nanostructure, especially when nanocomposites are prepared by a melt intercalation method. Cloisite 15A contained the biggest interlayer spacing, allowing easier intercalation of the PET molecules, but there were no changes in basal spacing after extrusion. Cloisite 15A is strongly hydrophobic, polarity between PET and Cloisite 15A was not matched, and there was no polar interaction. These reasons caused Cloisite 15A dispersed poorly in a PET matrix and failed to expand the interlayer spacing.

Cloisite 30B materials possessed two hydroxyl groups in their modifier, which make it possible to interact strongly with hydroxyl and carboxyl group in PET molecules, promoting the intercalation of PET molecules into clay gallery. Hydrophobicity of Cloisite 30B is rather similar to natural clay than hydrophobicity of Cloisite 15A, shown as in Figure 1.7 of the introduction. Figure 3.23 shows the peak intensity of three nanocomposites. The peak locations were similar, but the intensity of PET/Cloisite 30B was the weakest among three nanocomposites, implying Cloisite 30B holds the best affinity with PET chains. However, this result does not mean exfoliation structure, which shows no peak in XRD graph. It is presumed that the
mixing time of PET and Cloisite 30B in an extruder, 3~5 minutes, was not enough to
give PET chains to penetrate the gallery fully, or the polymer size is too big to
penetrate the gallery completely.

Cloisite 10A is expected to hold moderate compatibility and better
hydrophobicity than 15A due to substitution of a hydrogenated tallow group by a
benzene ring structure. The absence of strong polar groups makes the interaction
between the modifier and montmorillonite layers weak. Nanostructure of PET/Cloisite
10A is between the results of PET/Cloisite 15A and PET/Cloisite 30B, meaning the
affinity of Cloisite 10A is the medium range of those two with PET.

According to above results, characteristics of the various modifiers in clay can
cause different affinity with PET molecules resulting in various nanostructures. The
melt intercalation method was not sufficient to form exfoliated nanostructures, unless
the modifier contains perfect structure to give PET molecules affinity with respect to
polarity, hydrophobicity, and interactivity.
Figure 3.21 XRD measurement result of Cloisite 10A, 15A and 30B. X-ray measurement range was from $1.6^\circ$ ($55 \, \text{Å}$) to $7^\circ$ ($12.6\, \text{Å}$).
Figure 3.22 Basal spacing changes with clay type and amounts when three clays were melt mixed with 0.74 dL/g IV PET

[Naumenclature]

*7410A3; IV 0.74 dL/g PET was mixed with 10A clay 3 wt%
Figure 3.23 XRD measurement result of PET/Cloisite 10A, PET/ Cloisite 15A and PET/ Cloisite 30B. X-ray measurement range was from 1.6° to 7°.

Figure 3.23 XRD measurement result of PET/Cloisite 10A, PET/ Cloisite 15A and PET/ Cloisite 30B. X-ray measurement range was from 1.6° to 7°.
3.1.6.3 PET IV effect on nanostructure

Same experiments were done with several different IV PET resins in order to evaluate the effects of mobility of the PET chains. The shorter chain can penetrate the interlayer of the clay platelets more easily. IVs of pure PET were 0.48, 0.63, and 0.74 dL/g. Figure 3.24 showed the effects of these pure PET molecules. The basal spacing of the nanocomposites, however, was not changed much. PET IV of 0.48 dL/g had the largest basal spacing but the difference between 0.48 and 0.74 dL/g was small that we can conclude that the effect of molecular weight on nanostructure in the melt intercalation method was almost none within these ranges of IVs. The number average molecular weight of IV 0.60 dL/g PET is 19,900 and that of IV 0.80 dL/g PET is 29,000 [72].

3.1.6.4 SSP effect on nanostructure

Twelve samples, all the samples resulting from the melt intercalation method, were analyzed to evaluate solid state polymerization effects on nanostructure. The basal spacing expansion could be expected during the SSP reaction if some of the PET chain ends were located in the gallery of clay platelets through melt mixing. Figure 3.25 showed the basal spacing changes from before and after the SSP reaction. The dotted line was basal spacing before the SSP reaction and solid line was basal spacing after the SSP reaction. According to this result, the basal spacing seemed to be reduced after SSP in most cases except the case of PET IV 0.48/30B 3 wt% (4830B3) and PET IV 0.74/15A 2 wt% (7415A2).

XRD spectrums showed, however, that new peaks at low angle were generated in the cases of PET/Cloisite 10A and PET/Cloisite 30B (Figure 3.26). XRD has limitations for measuring the peaks located at lower angles than 1.6°. We could,
nevertheless, see the fact that the location of a new peak was less than 1.6°, meaning basal spacing was bigger than 55 Å. This result implied that the basal spacing of melt extrusion nanocomposite was expanded during the SSP reaction in these two cases. From this result, it was proved that SSP reaction had positive effect on basal spacing expansion in PET nanocomposites. This expansion, however, did not occur in all the clay platelets, as we could observe in Figure 3.25. Some of their basal spacings were getting smaller a little during SSP reaction. The fact of peak movement to a higher angle, which meant basal spacing was reduced, seemed to be related to the possibility of thermal degradation during SSP reaction. Nanocomposites were heated for 15 hrs at 220 or 230 °C during SSP, so that this might cause degradation of the organic modifier of clay. This will be evaluated more thoroughly in in situ polymerization, where nanocomposites get more heat during melt polymerization. The small peak at 5.6° (15~16 Å) indicates that some part of clay moved to natural MMT peak basal spacing (~12 Å).

Figure 3.26 showed that the peak shape of SSP of IV 0.48 dL/g PET/Cloisite 30B was different from that of other XRD shapes obtained for SSP nanocomposites. The peak intensity grows continuously from 4.5 ° to 1.6°. This was the best nanostructure obtained with the melt intercalation method, proving that the best affinity of Cloisite 30B with PET molecules, and the lowest IV PET could result in a better nanostructure. The nanostructure we could get in melt blending method, therefore, was the intercalated one because of the existence of peaks.

All PET/15A nanocomposites did not show the new peak at low angle (near 1.6°) after the SSP reaction, as shown in Figure 2.27. This explains that the affinity of Cloisite 15A clay is worse than Cloisite 10A or Cloisite 30B clays with PET. No peak at low angle was observed in any of the nanocomposites before the SSP reaction of
samples prepared with the melt intercalation method.

Figure 3.24 PET IV effect on nanostructure. PET IVs were 0.48, 0.63, and 0.74 dL/g.

The basal spacing of clays was written below their names.
Figure 3.25 The SSP effect on the basal spacing of nanocomposites. Solid line is the basal spacing after the SSP reaction and dotted line is the basal spacing before the SSP reaction. First three data are the basal spacing of three clays
New peaks observed in XRD (3 wt% clay)

a) PET/10A nanocomposites

b) PET/30B nanocomposites

Figure 3.26 A new peak generation at low angle in XRD after SSP reaction in the cases of PET/10A and PET/30B nanocomposites (3 wt% clay). X-ray measurement range was from 1.6° to 7°
Without new peak in XRD (3 wt% clay)

**a) PET/15A nanocomposites**

**b) Basal spacing before the SSP reaction in three nanocomposites when IV 0.48 dL/g PET was used**

Figure 3.27 X-ray patterns of nanocomposites without new peaks at low angle after the SSP reaction in the case of PET/15A nanocomposites, and the mixture of IV 0.48 dL/g PET and three clays.
3.2 In situ polymerization in PET conditions

3.2.1 Melt polymerization behavior

Three clays were individually added into each of two polyester melt polymerization processes, designated as ES clay addition or PC clay addition. In the case of the ES clay addition, the clay was added at the early stage of the esterification reaction. For the PC clay addition, the clay was added at the early stage of the polycondensation reaction. This was done in order to study the effect of the clay on the melt polymerization process and also to determine the properties of nanocomposites prepared by an in situ polymerization method. For this work, clays were added into the standard melt polymerization conditions of PET.

3.2.1.1 Esterification reaction

Esterification time was measured from the time when heating started to the time when esterification was finished. The termination of the esterification reaction was decided with the temperature of top part of the distillator, the transparency of BHET, and the amount of water accumulated as a product. It took 345 minutes for pure PET to finish the esterification reaction. Esterification time was reduced to 300 minutes when Cloisite 10A and 30B were added, and to 330 minutes with Cloisite 15A. This accelerated esterification reaction could be related to metal impurities in the clay. Several metal compounds [27] such as titanium, sodium, potassium, and manganese, etc. can accelerate the esterification reaction. A suggested mechanism is that metal cation causes solvation with alcohol and then the alcoholete anions attack the carboxyl group to promote esterification. All three clays contain many metallic and organic compounds as shown in Table 2 of the experimental section. Another possibility is the reaction at relatively high temperature, compared with the PET.
polymerization conditions. If the nanocomposite oligomer has a lower melting temperature due to some reason, the reaction at PET conditions becomes higher relatively for nanocomposite.

3.2.1.2 Polycondensation reaction

The polycondensation reaction was stopped at a constant, but a different torque value in each process. This value was 0.71 kw in the case of ES clay addition and 0.78 kw in the case of PC clay addition, indicating that the attainable molecular weight was different in the two polymerization processes due to different residence time in the reactor. The total residence time of ES clay addition in the reactor was ~410 minutes, whereas that of PC clay addition in the reactor was ~90 minutes, implying that a different level of thermal degradation could occur according to the processes. The torque value of each process was decided using the maximum torque of the 30B nanocomposite. Cloisite 30B has the poorest thermal stability among the three clays, as shown in IV drop after extrusion, so that the torque value of the 30B nanocomposite was leveled off first during polycondensation reaction.

Figure 3.28 showed polycondensation (PC) time and precursor IV of ES clay addition. IV values were not consistent even though the torque value was the same. It took about fifteen minutes to pull out the strand from the reactor, so that thermal degradation could happen during this part of the process. Different thermal degradation rates of the clays caused IV differences in the precursors, especially the 10A and 30B nanocomposites showed lower IV values than those of 15A nanocomposites. This implied that 10A and 30B nanocomposites had poor thermal stability in comparison to the 15A nanocomposites. The 15A nanocomposite and pure PET showed similar IV. These results seemed to be related to the size of modifier in
organic clay. 15A clay had two hydrogenated tallow which were bulky and long chains so that longer chain could resist to temperature better than the smaller size of chemical group such as methyl group.

The same trend was observed in PC clay addition as shown in Figure 3.29. Polycondensation temperature was lowered by 10 °C at the early stage of polycondensation to reduce the amount of foam in the case of 15A nanocomposite. For this reason the 15A nanocomposites had the longest PC time.

One of the difficulties in melt polymerization with clay was foam generation. The esterification reactor was 90 % full in ES clay addition process. The polycondensation reactor was more than 100 % full of foam in PC clay addition process when PET nanocomposites were melt polymerized at PET polymerization conditions. Foam sometimes went with the vaporized ethylene glycol to the condenser, and clogged the pipeline inside of the condenser, valves, pressure regulator, and nitrogen input lines. It was difficult to melt polymerize nanocomposite according to the melt polymerization conditions of PET. Reduction of foam generation was a serious issue in the melt polymerization of nanocomposites.
Figure 3.28 Polycondensation (PC) time and precursor IV in ES clay addition process

Figure 3.28 Polycondensation (PC) time and precursor IV in ES clay addition process
Figure 3.29 Polycondensation (PC) time and precursor IV in PC clay addition process
3.2.1.3 Reactor contamination due to foam generation

After finishing polymerization, the inside of the reactor was examined. Several parts were contaminated with the traces of clays in the case of ES clay addition, but not severely. The upper parts of the polycondensation reactor and condenser were severely contaminated with the mixture of clay and BHET in the case of PC clay addition (Figure 3.30). Severe contamination was from foam generation by clays, when the clay was added into the polycondensation reactor. The foam generation interrupted and delayed the polycondensation reaction.

Figure 3.30 Reactor contamination after melt polymerization of nanocomposites
3.2.2 Thermal properties of nanocomposites melt polymerized at PET conditions

3.2.2.1 Glass transition temperature (Tg) and melting temperature (Tm) on 2nd scan

Glass transition temperature (Tg) and melting temperature (Tm) were measured at 10 °C/min heating from 40 °C to 300 °C after quenching the sample from the melt at 300 °C for 5 minutes. Figure 3.31 shows that Tg values of all nanocomposites were lowered compared with the Tg of pure PET, melt polymerized at the same conditions. This trend was consistent in precursors and SSP pellets, and in the cases of both ES clay addition and PC clay addition. Tg becomes lower as a polymer chain contains more flexible parts and/or a polymer contains more free volume [75]. The addition of clay, therefore, increased the contents of flexible parts. The 30B nanocomposite had the lowest Tg and the 15A nanocomposite had the highest Tg among the three nanocomposites. After the SSP reaction of nanocomposite precursors at 230 °C for 15 hrs, Tg values were increased, keeping the order of Tg among three nanocomposites.

Tm is decreased as a polymer chain has more irregular parts. The Tm values of all nanocomposites were 9-20 °C lower than that of pure PET in precursor and SSP pellets, and in both polymerization processes (ES clay addition and PC clay addition). This result tells us that addition of clay changed PET chain regularity during melt polymerization. The 30B nanocomposite has the lowest Tm and the 15A nanocomposite has the highest Tm among the three clays. This is the same trend as with changes in Tg. Melt intercalation nanocomposites, which were compounded with twin screw extruder, did not show these big changes in Tg and Tm as given in Figure 3.17 and 3.20. The change of thermal properties in melt intercalation nanocomposites was related to IV drop after extrusion. In the case of in situ polymerization, thermal property changes, however, are related to the generation of more flexible structures.
during melt polymerization.

Figure 3.31 Tg of ES clay addition and PC clay addition nanocomposites

[Nomenclature]

* PET,ES is PET polymerized with ES reaction and PC reaction
* PET,PC is PET polymerized only with PC reaction using BHET
* 10A (15A,30B),ES is 10A (15A,30B) nanocomposite from ES clay addition process
* 10A (15A,30B),PC is 10A (15A,30B) nanocomposite from PC clay addition process
Figure 3.32 Tm of ES clay addition and PC clay addition nanocomposites

[Nomenclature]

* PET,ES is PET polymerized with ES reaction and PC reaction
* PET,PC is PET polymerized only with PC reaction using BHET
* 10A (15A,30B),ES is 10A (15A,30B) nanocomposite from ES clay addition process
* 10A (15A,30B),PC is 10A (15A,30B) nanocomposite from PC clay addition process
3.2.2.2 Copolymer content analysis by H NMR

The Tm of PET polymerized from the esterification reaction was 252 ℃ in the case of the precursor, while 30B nanocomposite precursor prepared by ES clay addition had a Tm of 232 ℃. The difference of Tm was so big that copolymer content was examined by NMR. Figure 3.33 illustrated copolymer content of PET precursor, polymerized from the esterification reaction, and 30B nanocomposite precursors prepared by ES clay addition. The two precursors had 5.3 mole/acid (~3 wt%) and 12.7 mole/acid (~7 wt%) diethylene glycol. Lee at el. [76] reported that Tm was depressed by 1.96 °C/DEG mole and Tg was depressed by 0.74 °C/DEG mole when heating rate was 5 °C/min. According to this result, Tm of the 30B nanocomposite precursor prepared by ES clay addition should be near 234 ℃ (my data was 232 ℃) and Tg should be near 67 ℃ (my data was 68 ℃). The difference between two values could be related to the difference in heating rate (5 °C/min vs. 10 °C/min), sample preparation, and molecular weight (IV). According to this result, the generation of DEG during melt polymerization caused the decrease in Tm and Tg of nanocomposites.

DEG is the side reaction product generated at the end of the esterification reaction and/or in the early stage of the polycondensation reaction [27]. Several factors can cause DEG generation during melt polymerization. High EG contents, high reaction temperature, metal compounds (kinds and amounts) all have critical effects on DEG generation during melt polymerization. The only difference between pure PET and nanocomposites was the addition of clay. Clay contains many inorganic impurities as shown in Table 1 of the experimental section. Inorganic impurities such as titanium, potassium, and manganese compound, can act as catalysts which accelerate DEG formation [27].
Figure 3.33 H NMR results of PET,ES and 30B nanocomposite prepared by ES clay addition
3.2.2.3 Crystallization rate from cold state and melt state

Tc1 is the crystallization temperature obtained when a sample is heated from the cold state after being quenched from the melt state. The lower the Tc1 is, the faster the crystallization occurs when heated from room temperature. Tc2 is the crystallization temperature when a sample is cooled from the melt state. The higher the Tc2 is, the faster the crystallization is when cooled from a high temperature. Clay particles can act as nucleating agents and the addition of clay into PET also increases DEG contents.

Figure 3.34 schematically illustrates nucleating agents and DEG effects on crystallization rates heated from the glassy state and when cooled from the melt. The addition of nucleating agent [77,78] and an increase of DEG content [79,80,81] cause a decrease in Tc1, making the crystallization rate faster, when a sample is heated from room temperature, as shown in Figure 3.34. In the case of Tc2, the effect of nucleating agent and the effect of DEG are showing different directions. The addition of nucleating agents increases Tc2, but the increase of DEG content increases Tc2. Therefore final Tc2 value will be decided with the degree of the effect of each factor (Figure 3.34 b).

All nanocomposites contained clay and the DEG content of nanocomposites was higher than that of pure PET. As the effect of nucleating agent and DEG had the same direction in the case of Tc1 (lower Tc1), Tc1 became lower than that of PET. In the case of Tc2, however, both effects had opposite directions. The results showed faster crystallization (higher Tc2) except for ES 30B nanocomposite (nanocomposite prepared by ES clay addition). The ES 30B nanocomposite contained the highest DEG content (12.7 mole/acid) so that DEG effect was almost equivalent to the effect of nucleating effect, meaning the same Tc2 value with that of PET (Figure 3.35).
a) Tc1 and Tc2 in DSC chart  
b) Nucleating agent and DEG effect on half-time of crystallization

Figure 3.34 Schematic diagram of crystallization rate. a) Tc1 and Tc2 in DSC chart, b) Nucleating agent and DEG effects on half-time of crystallization for isothermal crystallization; Thick solid line is that of pure PET, thin solid line is DEG effect on Tc1 and Tc2, dotted line is nucleating agent effect on Tc1 and Tc2
Figure 3.35 Nanocomposites Tc1 and Tc2. a) Tc1 of precursors and SSP pellets of nanocomposites and PET, b) Tc2 of precursors and SSP pellets of nanocomposites and PET
3.2.3 SSP of nanocomposites prepared by in situ polymerization

Solid state polymerization was performed in order to overcome low molecular weight of nanocomposites after melt polymerization. The SSP conditions were the same as those used with the conditions of melt intercalation; SSP at 230 °C for 15 hrs and 700 liter/hr N₂ flow rate and 0.3 bar N₂ pressure. The SSP rate was not as fast as that of melt intercalation nanocomposites. The SSP IV values of nanocomposites (precursor IV; ~0.40 dL/g) made by in situ polymerization were lower than those of nanocomposites made by melt intercalation (compare Figure 3.15 and Figure 3.36). It required 9 more hours of SSP for in situ polymerized materials than for melt intercalated one to increase precursor IV up to higher than 0.80 dL/g.

The slower SSP rates could be related to several factors such as decreased diffusion rate and increased crystallinity. Unbalanced end group concentration or better nanostructure can reduce SSP rate.
Figure 3.36 Solid state polymerization rate of nanocomposites at 230 °C. a) nanocomposites prepared by ES clay addition, b) nanocomposites prepared by PC clay addition.
3.2.4 End group analysis with FTIR

Figure 3.37 illustrates the FTIR spectra of PET made by melt polymerization and the 30B nanocomposite made by ES clay addition. An important characteristic of the nanocomposite is that the level of carboxyl end groups was drastically increased, while that of the hydroxyl end groups was drastically decreased. Figures 3.38 and 3.39 show significant differences in –COOH and –OH end group concentrations compared with those of pure PET. These drastic changes of the two end groups were not detected in nanocomposites prepared by the melt intercalation method (Figure 3.9 and 3.10).

Thermal degradation of PET causes IV reduction, discoloration, increasing levels of acetaldehyde, decreasing hydroxyl end group concentrations, and increasing concentrations of carboxyl end groups and vinyl ester groups [1]. Several schemes were suggested for thermal degradation. In Figure 3.40 some of them can be used to understand the reasons for the considerable changes in carboxyl and hydroxyl end group concentrations of nanocomposites prepared by melt polymerization. Carboxyl end groups are generated as a thermal degradation product, and hydroxyl end group is consumed to form acetaldehyde or DEG as shown in Figure 3.40. If metallic compounds in clay accelerate these degradation reactions, big differences in the two end group concentrations could be explained. The residence time in the twin extruder was 3~5 minutes, but that of melt polymerization was 2~9 hrs. Thermal degradation, due to the long residence time at high temperature, could increase the carboxyl end group concentrations and decrease the hydroxyl end group concentrations.

The peak at 3630 cm\(^{-1}\) was from the clay as shown in Figure 2.4 in the experiment section, and all three nanocomposites had the peak even after the deuteration of nanocomposites.
Figure 3.37 FTIR spectra of PET made by melt polymerization and the 30B nanocomposite made by ES clay addition
a) ES clay addition nanocomposites

b) PC clay addition nanocomposites

Figure 3.38 -COOH end group concentration of precursor and 230 °C-15hrs SSP pellet. a) ES clay addition nanocomposites, b) PC clay addition nanocomposites
Figure 3.39 -OH end group concentration of precursor and 230 °C-15hrs SSP pellet.

a) ES clay addition nanocomposites

b) PC clay addition nanocomposites

a) ES clay addition nanocomposites, b) PC clay addition nanocomposites
Figure 3.40 Schemes of thermal degradation of pure PET [1]. Dotted line circle is carboxyl end group generation and solid line circle is hydroxyl end group consumption.
3.2.5 Nanostructure analysis with XRD

3.2.5.1 Basal spacing of ES clay addition nanocomposites

Basal spacing was measured to examine nanostructure of nanocomposites, made by in situ polymerization. Figure 3.41 shows that the 10A nanocomposite precursor didn’t have any peaks at low angle, where a small peak was observed at 2.7° in PET/Cloisite 10A nanocomposite prepared by the melt intercalation method (Figure 3.22). The 15A nanocomposite precursor had a peak near at 2.7°, similar to the result of PET/Cloisite 15A nanocomposite prepared by melt intercalation method (Figure 3.27), but the intensity was reduced in the precursor produced by the in situ polymerization method, which implies some parts of a regular structure disappeared during in situ polymerization. The 30B nanocomposite precursor had a small peak near at 1.6°, similar to the result of SSP of IV 0.74 dL/g PET/Cloisite 30B nanocomposite prepared by melt intercalation method (Figure 3.26), and had a big peak at 5.8°, meaning the biggest amount of thermally degraded clay.

All samples prepared by melt polymerization contained a peak near 5.6° and the sample with 30B clay has the highest intensity at that angle. Nanocomposites formed by the melt intercalation method also had that peak, but intensities were not strong. Barber et al. [82] reported that the peak near at 5.6° was related to pristine clay, which was an agglomeration of untreated clay. According to the above results and the reference article [82], the intensity near at 5.6° could be related to the amount of pristine clay or clay agglomeration after thermal degradation. Cloisite 30B appeared to be the most thermally sensitive material; therefore, the amount of this thermally degraded clay was the largest among three clays.

One particular thing was that 15A nanocomposites did not show as strong
intensity as those exhibited in the melt intercalation method, as shown in Figure 3.41. The 15A clay might have an affinity with PET in the case of in situ polymerization due to the mobility of the monomer, but this affinity was not enough to eliminate the peak at 2.7° completely.

Figure 3.41 Basal spacing of ES clay addition nanocomposites. Basal spacing of nanocomposites precursor. X-ray measurement range was from 1.6° to 7°
a) XRD result of nanocomposite precursors

b) XRD result of nanocomposites after SSP reaction at 230 °C for 15 hrs

Figure 3.42 Basal spacing of PC clay addition nanocomposites. Basal spacing of nanocomposites precursor and after SSP reaction at 230 °C for 15hrs.
3.2.5.2 Basal spacing of PC clay addition nanocomposites

XRD pattern of the 30B nanocomposite had almost no peak at 2.7° and a faint peak at 5.8° in the precursor. After the SSP reaction, this trace almost disappeared as shown in Figure 3.42, which meant the 30B nanocomposite became an almost exfoliated nanostructure. Good affinity of Cloisite 30B with PET and the short residence time in the reactor made nanostructure almost exfoliated. The 10A nanocomposite still had a peak in the both cases of precursor and after SSP reaction. This was related to less affinity with BHET than that of 30B clay. Cloisite 10A, therefore, needed more mixing time with ethylene glycol to have better affinity with the PET chains. The 15A nanocomposite showed strong intensity in the precursor, but this intensity was reduced after the SSP reaction. Some of regular structure of Cloisite 15A seemed to be destructed by SSP reaction. The peak intensity in the precursor indicated that the affinity of Cloisite 15A with PET was the worst among the three clays. After the SSP reaction, all nanocomposites contained a new peak at 1.6°, meaning an intercalating space bigger than 55 Å was formed during SSP reaction.

The intensity near at 5.8° was much less than that of all nanocomposites prepared by ES clay addition. This meant that thermal degradation in the case of PC clay addition was less than that in ES clay addition due to shorter residence times (7 hrs vs. 2 hrs).

According to XRD results of ES clay addition and PC clay addition nanocomposites, each clay had a different optimum process and this depended on characteristics of clays. The optimum process could be summarized as shown below;
Optimum process for each clay according to XRD result

*30B clay - PC clay addition

The polymerization during the shorter residence time (PC clay addition) made the better nanostructure, that was almost exfoliated. The nanostructure was better than that obtained by melt intercalation.

*10A clay - ES clay addition

The PC clay addition nanocomposite had a stronger XRD peak than the peak obtained for ES clay addition. Shorter residence time didn’t improve the nanostructure.

*15A clay - ES clay addition and a compatibilizer

15A nanocomposite always showed the peak in XRD regardless of polymerization processes, but the ES clay addition method showed a smaller peak than the peak in PC clay addition. This means that Cloisite 15A needs a compatibilizer to get more affinity of clay with PET and ES clay addition is better than PC clay addition.

XRD results proved that the in situ polymerization method was more favorable to develop exfoliated nanostructure than the melt intercalation method, although several difficulties existed and quality problems remained. Better nanostructure and properties could be expected after the improvement of melt polymerization conditions. This research will focus on Cloisite 30B nanocomposite development, using PC clay addition, because that clay showed the best affinity with PET. Until now, nanocomposite structures were investigated only with XRD, but this method has limitation at low angle. TEM will be used as a complimentary technique to get detailed information about nanostructure.
3.3 Improvement of melt polymerization process

It was difficult to melt polymerize PET nanocomposites due to foam generation, both in the esterification reaction and the polycondensation reaction. Furthermore, there was no proper clay for PET nanocomposite, which can resist high temperature exposure. XRD results showed that the nanostructure prepared by melt polymerization is better than that formed by melt intercalation. The foam generation issue, therefore, will be one of the key issues that must be solved in order to develop PET nanocomposite by in situ polymerization. Reduction of foam amounts and DEG contents will be the main objectives in this section.

3.3.1 Foam amount reduction

3.3.1.1 Aluminium dish experiment

To understand the reason why foam was generated so severely, an aluminium dish experiment was done in a small scale, with 14 combinations of variables. (BHET, 2 clays. mixture of TPA and EG, catalyst, phosphoric acid, silicone oil, antifoam H-10, water) This experiment started after BHET was completely melted on the hot plate at 210 °C because melted BHET makes the mixture of TPA and EG liquid phases, and then the esterification reaction is performed homogeneously as the commercial plant does. It was difficult to determine the antifoam agent, which could be used at high temperatures. Dow chemical company suggested H-10 for a surfactant in petrochemical applications. Phosphoric acid and silicone oil were candidates for another type of surfactant. The name of materials and purpose were summarized in Table 3.1.

Figure 3.43 illustrated the amount of foam after the sample temperature reached 210~220 °C. Experiment of #1,2,11,12 had fast foam generation and large amounts of
foam within 7 minutes. The common components of the above four experiments were BHET, organic clay, and TPA/EG (or sb). The mixing of BHET and TPA/EG or the mixing of BHET and sb at 220°C can induce the reaction so that bubbles were observed as that result. The addition of clay caused foam generation as we can see #1 and #4 experiments. The detailed information (Table 3.2) about foam generation is summarized as shown below;

a. BHET and TPA/EG (or sb) were reacted to make finite size of bubble.

b. Addition of organic clay increased the viscosity of finite bubbles, which came from evaporation of H₂O as a product of esterification reaction, and caused the foam generation.

c. A catalyst accelerated the foam generation rate. Sb or TPA/EG can act as catalyst for BHET reaction.

d. Natural clay did not increase the viscosity of finite size of bubbles.

e. Water delayed foam generation a little.

f. Antifoam agent (H-10) reduced the foam amount but the color became brown.

g. Addition of phosphoric acid or silicone oil accelerated foam generation.

<table>
<thead>
<tr>
<th>Material name</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>BHET (oligomer after the esterification reaction)</td>
<td>To make the mixture of TPA and EG a liquid phase</td>
</tr>
<tr>
<td>TPA and EG</td>
<td>Monomers of PET</td>
</tr>
<tr>
<td>Organic clay or natural clay</td>
<td>Material for nanocomposite</td>
</tr>
<tr>
<td>Catalyst (sb)</td>
<td>To accelerate the polymerization</td>
</tr>
<tr>
<td>Phosphoric acid, silicone oil, water</td>
<td>To reduce viscosity of foam</td>
</tr>
<tr>
<td>Antifoam H-10</td>
<td>To reduce foam amount</td>
</tr>
</tbody>
</table>

Table 3.1 Material names and purpose used in aluminium dish experiment
Figure 3.43 Picture of aluminium dish experiment, 2 minutes and 7 minutes later.

Detailed explanations for each dish number are in Table 3.1
Table 3.2 Detailed results of aluminium dish experiment

<table>
<thead>
<tr>
<th>No</th>
<th>BHET</th>
<th>Clay</th>
<th>TPA/EG</th>
<th>Sb</th>
<th>Other additive</th>
<th>result</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td></td>
<td>Fast(4), foams#1</td>
</tr>
<tr>
<td>2</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td></td>
<td>Fast(4), foams</td>
</tr>
<tr>
<td>3</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td>water</td>
<td>Medial(3), foams</td>
</tr>
<tr>
<td>4</td>
<td>O</td>
<td></td>
<td>O</td>
<td></td>
<td></td>
<td>No foam, small bubbles</td>
</tr>
<tr>
<td>5</td>
<td>O</td>
<td></td>
<td>O</td>
<td></td>
<td></td>
<td>No foam, small bubbles</td>
</tr>
<tr>
<td>6</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td>Natural clay</td>
<td>No foam, small bubbles</td>
</tr>
<tr>
<td>7</td>
<td>O</td>
<td></td>
<td>O</td>
<td></td>
<td></td>
<td>No foam</td>
</tr>
<tr>
<td>8</td>
<td>O</td>
<td>O</td>
<td></td>
<td></td>
<td></td>
<td>No foam</td>
</tr>
<tr>
<td>9</td>
<td>O</td>
<td>O</td>
<td></td>
<td></td>
<td></td>
<td>No foam</td>
</tr>
<tr>
<td>10</td>
<td>O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>No foam</td>
</tr>
<tr>
<td>11</td>
<td>O</td>
<td>O</td>
<td></td>
<td></td>
<td>Phosphoric acid</td>
<td>Very fast(5), overflow of foam</td>
</tr>
<tr>
<td>12</td>
<td>O</td>
<td>O</td>
<td></td>
<td></td>
<td>Silicone oil</td>
<td>Very fast(5), overflow of foam</td>
</tr>
<tr>
<td>13</td>
<td>O</td>
<td></td>
<td></td>
<td></td>
<td>EG</td>
<td>No foam</td>
</tr>
<tr>
<td>14</td>
<td>O</td>
<td>O</td>
<td></td>
<td></td>
<td>Antifoam agent, H-10</td>
<td>Not fast(3), 70% full, brown color</td>
</tr>
</tbody>
</table>

#1; very fast(5), very slow(1)
3.3.1.2 Experiment in the reactor

The reason for foam generation was revealed, but there was no additive to reduce the foam amount. In the reactor, processing variables were examined to determine proper melt polymerization conditions for nanocomposite, in which melt polymerization is possible with organic clay. Half of the experiments were stopped, during this experiment due to full of foam in the reactor. Table 3.3 indicates the idea when melt polymerization with organic clay is possible.

Table 3.3 Foam reduction experimental result of ES clay addition of 10A clay, polycondensation temperature was 280 °C

<table>
<thead>
<tr>
<th></th>
<th>E/T=1.5</th>
<th>E/T=1.35</th>
<th>E/T=1.25</th>
<th>E/T=1.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>ES reaction</td>
<td>OK</td>
<td>OK</td>
<td>OK</td>
<td>Fail</td>
</tr>
<tr>
<td>Foam amount</td>
<td>&lt;30%</td>
<td>80%</td>
<td>40%</td>
<td>50%</td>
</tr>
<tr>
<td>ES max. T(°C)</td>
<td>239</td>
<td>242</td>
<td>239</td>
<td>241</td>
</tr>
<tr>
<td>Pressure (Kgf/cm²)</td>
<td>1.3</td>
<td>0.7</td>
<td>1.4</td>
<td>1.2</td>
</tr>
<tr>
<td>PC reaction</td>
<td>OK</td>
<td>Fail</td>
<td>OK</td>
<td>Fail</td>
</tr>
<tr>
<td>Resin Tm(°C)</td>
<td>237</td>
<td>-</td>
<td>241</td>
<td>-</td>
</tr>
</tbody>
</table>

It was clear from above experiments that foam generation was sensitive to esterification temperature, esterification pressure, and E/T (ethylene glycol/terephthalic acid mole ratio). To melt polymerize 10A nanocomposite without significant foam generation, the esterification temperature should be lower than 240 °C, high esterification pressure is required (>1.2 kgf/cm²), and E/T should be bigger than 1.25 (min. E/T=1.25. Unreacted organic clay caused the foam generation at high temperature and surplus EG lowered Tm due to increased DEG content). At
E/T=1.2, esterification was successful under high ES pressure (1.4 kgf/cm²) and low ES temperature (240 °C), but foam generation made the polycondensation reaction impossible. Finally, E/T=1.25 conditions were set as a control condition for Cloisite 10A nanocomposite.

In PC clay addition process, 5 minutes mixing of melted BHET and Cloisite 30B, under nitrogen charging without N₂ pressure, was performed at 255 °C. After 5 minutes, vacuum pump started for polycondensation at 280 °C. This condition caused severe foam generation. To reduce the amount of foam, conditions were changed; the mixture of melted BHET and clay was pressurized (0.2 kgf/cm² N₂) for 15 minutes at 240°C to make homogeneous mixing, and then vacuum pump started. This condition, a control condition for Cloisite 30B nanocomposite, made the melt polymerization possible with reduced foam amount.

*Standard amount of additive; All polymer contained these amounts of additives.

<ES reactor> for oligomer  →  <PC reactor> for polymer

TMAH 100ppm

antimony oxide (Sb 250ppm), cobalt acetate (Co 30ppm),
phosphoric acid (P 20ppm)

The relationships between reaction variables and material properties (end groups, melting point) have been further investigated in order to determine the optimum melt polymerization conditions for Cloisite 10A and 30B.
In an effort to reduce formation of DEG additional TMAH was added to ES reactor or PC reactor. Triphenyl phosphate (TPP) was added to PC reactor instead of Phosphoric acid to reduce DEG content and carboxyl concentration. Irganox 1010 or Irganox HP2225 was used in ES reaction or PC reaction to improve color of nanocomposite. Polycondensation temperature was decreased to reduce DEG content and carboxyl concentration. Catalyst amount was increased to reduce the residence time in the PC reactor. Reaction variables are summarized in Table 3.4.

<table>
<thead>
<tr>
<th>Name</th>
<th>Usage &amp; purpose</th>
<th>Reactor, Amounts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetramethylammonium hydroxide (TMAH)</td>
<td>DEG suppressor To reduce DEG</td>
<td>ES, 100ppm</td>
</tr>
<tr>
<td>Tetramethylammonium hydroxide (TMAH)</td>
<td>DEG suppressor To reduce DEG</td>
<td>PC, 100ppm</td>
</tr>
<tr>
<td>Triphenyl phosphate (TPP)</td>
<td>Metal stabilizer To reduce DEG and -COOH</td>
<td>PC, P 20ppm</td>
</tr>
<tr>
<td>Irganox 1010</td>
<td>Antioxidant To prevent oxydation</td>
<td>ES, 1000ppm for 10A clay</td>
</tr>
<tr>
<td>Irganox HP2225</td>
<td>Antioxidant To prevent oxydation</td>
<td>ES, 1000ppm for 10A clay</td>
</tr>
<tr>
<td>Irganox 1010</td>
<td>Antioxidant To prevent oxydation</td>
<td>PC, 500ppm for 30B clay</td>
</tr>
<tr>
<td>Polycondensation Temperature</td>
<td>To reduce thermal degradation</td>
<td>PC, 10℃ down</td>
</tr>
<tr>
<td>Antimony trioxide</td>
<td>Catalyst To reduce reaction time</td>
<td>PC, 30% increase</td>
</tr>
</tbody>
</table>

Table 3.4 Variables, usage & purpose, and amount for improvement of nanocomposite properties. These additives were added more into standard amount of additives.
3.3.2. Variables effect on nanocomposite melting temperature

3.3.2.1 E/T and additives effect on Tm; 10A nanocomposite (ES clay addition)

EG/TPA (TPA amount was fixed at 1Kg per batch) mole ratio and additive effect on melting point were evaluated at 280 °C. Melting point was related to DEG content, which was the proof of side reaction or degradation. A 4.7 °C of Tm was increased as E/T ratio decreased from 1.5 to 1.25. Free EG, which does not participate in the esterification reaction, can be converted into DEG at the end of the esterification reaction or at the early stage of the polycondensation reaction [27]. The melting point of the nanocomposite will increase as E/T ratio decreases. The ratio of E/T=1.25, however, seems to be a minimum ratio, which makes polymerization possible. Polycondensation did not occur at E/T=1.2, even though esterification was successfully done (Figure 3.44 and Table 3.5).

Nanocomposites, melt polymerized under PET conditions, show low IV and dark brown color, due to degradation during melt polymerization. An antioxidant [83], which was expected to reduce degradation or improve color if oxygen, trapped in clay particles, caused degradation. There, however, was no improvement in Tm with an addition of antioxidant (Irganox 1010, Irganox HP2225) as shown in Figure 3.45 and Table 3.6.
Figure 3.44 E/T effect on Tm in 10A nanocomposite (ES clay addition) at 280 °C polycondensation

Table 3.5 E/T effect on PC-h, IV, and Tm in 10A nanocomposite (ES clay addition) at 280 °C polycondensation

<table>
<thead>
<tr>
<th></th>
<th>E/T=1.2</th>
<th>E/T=1.253</th>
<th>E/T=1.35</th>
<th>E/T=1.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC-h (min)</td>
<td>No reaction</td>
<td>95</td>
<td>85</td>
<td>78</td>
</tr>
<tr>
<td>IV (dL/g)</td>
<td>-</td>
<td>0.43</td>
<td>0.44</td>
<td>0.41</td>
</tr>
<tr>
<td>Tm (°C)</td>
<td>-</td>
<td>241.8</td>
<td>240.8</td>
<td>237.1</td>
</tr>
</tbody>
</table>
Figure 3.45 Antioxidants effect on Tm in 10A nanocomposite (ES clay addition) at 280 °C polycondensation

Table 3.6 Antioxidants effect on PC-h, IV, and Tm in 10A nanocomposite (ES clay addition) at 280 °C polycondensation

<table>
<thead>
<tr>
<th></th>
<th>control (E/T=1.253)</th>
<th>Irganox 1010 (1000ppm)</th>
<th>Irganox HP225 (1000ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC-h (min)</td>
<td>95</td>
<td>100</td>
<td>90</td>
</tr>
<tr>
<td>IV(dL/g)</td>
<td>0.43</td>
<td>0.42</td>
<td>0.43</td>
</tr>
<tr>
<td>Tm (°C)</td>
<td>241.8</td>
<td>241.8</td>
<td>237.9</td>
</tr>
</tbody>
</table>
3.3.2.2 E/T and PC temperature effect on Tm; 30B nanocomposite (PC clay addition) at 270 °C polycondensation

Melting point of 30B nanocomposite increased by 8.9 °C as polycondensation temperature was reduced from 280 °C to 270 °C. The melting point of 30B nanocomposite raised by 2.6 °C as E/T was decreased from 1.5 to 1.2 (Figure 3.46 and Table 3.7). The polycondensation reaction did not occur up to an IV of 0.44 dL/g at E/T=1.11, due to lack of ethylene glycol, and the maximum attainable IV with Cloisite 30B was 0.41 dL/g. At the same E/T, the attainable IV of pure PET was higher than 0.59 dL/g. The minimum E/T ratio for nanocomposite is a little higher than that of pure PET. Minimum E/T of Cloisite 10A for ES clay addition was 1.25, and that of Cloisite 30B for PC clay addition was 1.2. That of pure PET in both cases was 1.11. According to this result, clay requires some additional amount of ethylene glycol for melt polymerization. When ethylene glycol amount was less than the minimum amount, melt polymerization did not occur, due to severe foam generation.

3.3.2.3 Additive effect on Tm; Cloisite 30B nanocomposite (PC clay addition) at 270 °C polycondensation

TMAH was known as a DEG suppressor so that 100 ppm was added into the ES reaction or PC reaction. Chang et al. [84] reported that TPP was the most effective metal stabilizer to reduce DEG and –COOH content as a stabilizer compared with trimethyl phosphate, Irganox1010, Irganox 1222, and tetraethylammonium hydroxide. Antimony catalyst amount was increased by 30% to reduce the residence time in the PC reactor, because short residence time can reduce the amount of DEG [27].

Four additives were evaluated but a little improvement in Tm (~1.3 °C) was obtained as shown in Figure 3.47 and Table 3.8. The effect of additives on properties
were evaluated at E/T was 1.2.

Figure 3.46 PC temperature and E/T effect on Tm of 30B nanocomposite (PC clay addition) at 270 °C polycondensation

Table 3.7 PC temperature and E/T effect on PC-h, IV, and Tm of 30B nanocomposite (PC clay addition) at 270 °C polycondensation

<table>
<thead>
<tr>
<th></th>
<th>E/T=1.11</th>
<th>E/T=1.2</th>
<th>E/T=1.3</th>
<th>E/T=1.5</th>
<th>E/T=1.5 (280°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC-h (min)</td>
<td>119</td>
<td>112</td>
<td>98</td>
<td>103</td>
<td>80</td>
</tr>
<tr>
<td>IV (dL/g)</td>
<td>0.41</td>
<td>0.45</td>
<td>0.46</td>
<td>0.46</td>
<td>0.47</td>
</tr>
<tr>
<td>Tm (°C)</td>
<td>248.5</td>
<td>244.1</td>
<td>244.7</td>
<td>241.8</td>
<td>232.9</td>
</tr>
</tbody>
</table>
Figure 3.47 Additive effect on $T_m$ of 30B nanocomposite (PC clay addition) at 270 °C polycondensation

Table 3.8 Additive effect on PC-h, IV, and $T_m$ of 30B nanocomposite (PC clay addition) at 270 °C polycondensation, E/T was 1.2 when additive effect was evaluated

<table>
<thead>
<tr>
<th></th>
<th>control</th>
<th>TPP</th>
<th>Irganox1010 (500ppm)</th>
<th>TMAH (PC)</th>
<th>Sb 30% up</th>
<th>TMAH (ES)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC-h (min)</td>
<td>97</td>
<td>97</td>
<td>88</td>
<td>97</td>
<td>80</td>
<td>100</td>
</tr>
<tr>
<td>IV (dL/g)</td>
<td>0.43</td>
<td>0.44</td>
<td>0.44</td>
<td>0.45</td>
<td>0.44</td>
<td>0.45</td>
</tr>
<tr>
<td>$T_m$ (°C)</td>
<td>242.8</td>
<td>244.0</td>
<td>244.2</td>
<td>244.0</td>
<td>244.2</td>
<td>243.8</td>
</tr>
</tbody>
</table>
3.3.3. End group analysis (FTIR)

3.3.3.1 10A nanocomposites; E/T and antioxidant effect at 280 °C polycondensation

To accelerate the SSP rate, the ratio of -COOH/-OH should be near 0.7 in the case of PET [30], but that of nanocomposite had near 5 when nanocomposite was melt polymerized at E/T=1.5 and 280 °C polycondensation.

There was no improvement (increase in –OH and/or decrease in –COOH compared with E/T 1.5 in Figure 3.48) in the both end groups, when E/T was decreased from 1.5 to 1.25 and two antioxidants were added, as shown in Figure 3.48.

3.3.3.2 30B nanocomposites; E/T and PC temperature effect at 270 °C polycondensation

A decrease in polycondensation temperature from 280 to 270 °C at E/T=1.5 increased hydroxyl end group concentration, but there was no change in carboxyl end group concentration (Figure 3.49). This result might be caused by counterbalancing the decrease in temperature with the increase in residence time. When the polycondensation temperature was decreased from 280 to 270 °C, the residence time was increased by 23 min (80 min →103 min). Another possibility of higher content in hydroxyl end group of E/T=1.5 at 270 °C than that of E/T=1.5 at 280 °C, is that less EG was consumed to form DEG. A nanocomposite of E/T=1.5 at 280 °C has 232.9 °C as the melting temperature, while a nanocomposite of E/T=1.5 at 270 °C has 241.8 °C (Figure 3.46 and Table 3.5).

E/T=1.3 showed the best ratio of –COOH/-OH (2.5, which is closest to 0.7 of PET) so that E/T=1.3 could be the optimum ratio among experimental ranges (E/T=1.11–1.5) with respect to both end group concentrations. E/T=1.11 had negative
effect on the both end groups concentration due to lack of EG as shown in Figure 3.49.

3.3.3.3 30B nanocomposites; Additive effect at 270 °C polycondensation

Figure 3.50 showed that sb 30% up result had the best result on both end groups (decrease of –COOH and increase of –OH concentration). TPP, TMAH addition (ES, PC), and antioxidant also gave improvement in results. The decision about which variable will be selected to improve both end groups depends on the nanostructure result.

Figure 3.48 E/T and antioxidant effect on carboxyl and hydroxyl end groups in 10A nanocomposite (ES clay addition at 280 °C), [ ] is the ratio of –COOH/-OH

Figure 3.48 E/T and antioxidant effect on carboxyl and hydroxyl end groups in 10A nanocomposite (ES clay addition at 280 °C), [ ] is the ratio of –COOH/-OH
Figure 3.49 E/T and PC temperature effect on both end groups in 30B nanocomposite (PC clay addition at 270 °C), [ ] is the ratio of –COOH/-OH

Figure 3.50 Additive effect on both end groups in 30B nanocomposite (PC clay addition at 270 °C), E/T=1.2 except E/T1.5(280 °C),[ ] is the ratio of –COOH/-OH
3.3.4 SSP of nanocomposites

3.3.4.1 10A nanocomposites; E/T and antioxidant effect at 280 °C polycondensation

Solid state polymerization was done to increase molecular weight of precursor. The SSP conditions were at 230°C, 15 hrs, N₂ 0.3 bar and 700 liter/hr N₂ flow rate. Crystallization conditions of precursor were 150°C and 2hr. The difference between precursor IV and 15hrs SSP IV indicated SSP rate shown as in Figure 3.51. There was no significant difference in the SSP rate when E/T and additives were changed.

3.3.4.2 30B nanocomposites; E/T and PC temperature effect at 270 °C polycondensation

The increase of E/T from 1.11 to 1.5 at 270 °C increased the SSP rate although this trend was flattened from ET=1.3 to 1.5, as shown in Figure 3.52. All SSP rates were faster than E/T=1.5 at 280 °C even though precursor IVs were almost the same except for E/T=1.11. These results could be interpreted like this; E/T=1.11 was lack of EG so that precursor IV was low and –COOH/-OH was not proper to give rapid SSP reactions. The ratio of E/T=1.5 at 280°C resulted in more degradation than others so that –COOH/-OH ratio was deviated so much from an optimum ratio. The trend of the SSP rate and the trend of end group concentrations have a similarity. The decrease in the PC temperature from 280 °C to 270 °C accelerated the SSP rate due to better –COOH/-OH ratio, caused by less thermal degradation. In this part, -COOH/-OH ratio was the main factor in the SSP rate among precursor IV, -COOH/-OH ratio, and Tm (DEG contents).
3.3.4.3 30B nanocomposites; Additive effect at 270 °C polycondensation

Figure 3.53 and Figure 3.50 showed the same trend, meaning end group concentrations were the important factor in the SSP rate. Precursor IV was similar, in the range of 0.43 - 0.45 dL/g. Residence time in PC reactor affected the SSP rate so that Sb 30% increase nanocomposite showed the fastest SSP rate, which is related to catalyst amount increase and better –COOH/-OH ratio.

Figure 3.51 Solid state polymerization rate of 10A nanocomposites; E/T and antioxidant effect
Figure 3.52 Solid state polymerization rate of 30B nanocomposites; E/T and PC temperature effect

Figure 3.53 Solid state polymerization rate of 30B nanocomposites; additives effect
3.3.5 Nanostructure analysis

3.3.5.1 Precursor XRD of 10A nanocomposites; E/T and antioxidant effect at 280 °C polycondensation

A nanocomposite was thought to exhibit the exfoliated nanostructure when there was no peak in the XRD spectrum as can be seen in Figure 3.54. Precursor XRD result of E/T=1.35 nanocomposite showed an exfoliated structure, with small amount of clay agglomeration due to thermal degradation. The other three samples also showed a similar trend, but they contained clear peaks near at 5.8°. E/T=1.35 nanocomposite, therefore, appeared to have the most exfoliated nanostructure among four samples.

3.3.5.2 Precursor XRD of 30B nanocomposites; E/T and PC temperature effect at 270°C polycondensation

Figure 3.55 showed that the E/T=1.2 nanocomposite was almost flat, implying the presence of exfoliated structure with a small amount of clay agglomeration. The other results were similar to that of the 10A nanocomposite. When the XRD results of 30B nanocomposites were compared with those of 10A nanocomposites, the amount of agglomeration was smaller in the case of the 30B nanocomposites as shown in Figure 3.54 and Figure 3.55. From this, it was known that the peak near at 5.8° was related to the residence time and polycondensation temperature. The 10A nanocomposites had about an 8 hrs residence time and 280 °C polycondensation, whereas the 30B nanocomposites had about a 2 hrs residence time and 270 °C polycondensation. 30B nanocomposites, therefore, had less clay agglomeration due to less thermal degradation than 10A nanocomposites.
3.3.5.3 Precursor X ray of 30B nanocomposites; Additive effect at 270 °C polycondensation

E/T=1.2 (without additive) had the best nanostructure (Figure 3.56). When additives were added, XRD spectra showed strong peak. Sb 30% up and TPP added nanocomposites had very strong peak near at 2θ=2.7°, which means those nanostructure were intercalated. In addition to this, additives increased the amount of clay agglomeration.

Figure 3.54 Precursor XRD result of 10A clay nanocomposites. X-ray measurement range was from 1.6° to 7°
Figure 3.55 Precursor XRD result of 30B nanocomposites (E/T effect, 270 °C PC reaction).

Figure 3.56 Precursor XRD result of 30B clay nanocomposites (additive effect, 270 °C PC reaction). X-ray measurement range was from 1.6° to 7°.
3.3.5.4 XRD of 10A nanocomposites after SSP reaction (ES clay addition at 280 °C polycondensation)

After the SSP reaction, the XRD results showed some changes in shape (Figure 3.57). The 10A clay nanocomposite with E/T=1.25, Irganox HP2225 showed better XRD result after SSP. The other three samples contained a new peak at low angle after the SSP reaction.

3.3.5.5 XRD of 30B nanocomposites after SSP reaction (PC clay addition at 270 °C polycondensation)

All samples of 30B nanocomposites given in Figure 3.58 showed similar results to those of the precursors (Figure 3.55).

Figure 3.59 had an interesting XRD results. All samples had similar nanostructure, no clear peak or almost flat behavior, even though some of them had a clear peak in the precursor. Two clearly intercalated nanostructures became an exfoliated structure after the SSP reaction. These were catalyst (sb) 30% increased nanocomposite and TPP added nanocomposites as a metal stabilizer. Addition of these additives might help some chain ends stay inside of interlayer spacing, and then the SSP reaction must have expanded the basal spacing. Sb 30% increased nanocomposite was further examined with TEM. E/T=1.2 also showed the best result (the most flat) after the SSP reaction. These two nanocomposites were examined by TEM to get detailed information for nanostructure.
Figure 3.57 XRD of 10A nanocomposites after SSP (E/T and additive effect, ES clay addition at 280 °C polycondensation)

Figure 3.58 XRD of 30B nanocomposites after SSP (E/T effect, 270 °C PC reaction)
Figure 3.59 XRD of 30B nanocomposites after SSP (additive effect, 270 °C PC reaction)
3.3.5.6 Nanostructure analysis by TEM

Three samples, analyzed by XRD, were selected to confirm the nanostructure by TEM; E/T=1.2 30B nanocomposite precursor, which was the best nanostructure by XRD. Precursor and SSP pellet of sb 30% increased 30B nanocomposite, which were intercalated and almost exfoliated nanostructure respectively (a big difference in XRD before and after SSP). TEM results could elucidate more detailed nanostructure of these materials.

Figure 3.60 showed that E/T=1.2 30B nanocomposite precursor contained many single or double platelets (dark single or double line, which was exfoliated structure), a few several platelets with expanded basal spacing (stack of several dark lines, which was intercalated structure), and dark block (lump of dark lines, which was clay agglomeration). We could, therefore, concluded that the nanostructure of E/T=1.2 30B nanocomposite was mostly or partially exfoliated with a small amount of intercalated and clay agglomeration.

Figure 3.61 illustrated that the precursor of sb 30% increased 30B nanocomposite was intercalated nanostructure, which was the same result with the result of XRD (Figure 3.56). After the SSP reaction, the distance between platelets became far from each other, and then several triplet, doublet could be observed even though the number of single platelet was not as many as shown in Figure 3.60. One thing interested was the number of platelets before melt polymerization. The number of platelets was more than 30 according to Figure 3.61b). After melt polymerization, those numbers of clay platelets were separated into single platelets or double platelets due to good affinity with PET in the case of 30B nanocomposite.

From the above evaluations, it was known that several factors could give
different results in thermal properties, end group contents, SSP rate, and nanostructures. The most important point in this research was whether a nanocomposite had an exfoliated nanostructure or not, because the purpose of this research was to develop PET nanocomposite, which contained exfoliated nanostructure.

According to XRD and TEM results, E/T=1.2 30B nanocomposite had the most exfoliated nanostructure. Moreover, this nanocomposite showed good results in thermal properties, SSP rate, and end group contents, even though those were always not the best in every property. E/T=1.2 30B nanocomposite from in situ polymerization and PET/15A nanocomposite from melt intercalation method were selected to evaluate the property dependency on nanostructure in the next chapter.

Figure 3.60 TEM picture of E/T=1.2 30B nanocomposite precursor, the scale was 50 nm
a) Precursor of sb 30% increased 30B nanocomposite. The scale was 20 nm

b) SSP pellets of sb 30% increased 30B nanocomposite. The scale was 20 nm

Figure 3.61 TEM picture of sb 30% up 30B nanocomposite; a) precursor, b) SSP pellets
3.4 Comparison of two nanocomposites

In this section, two nanocomposites, produced through different preparation methods, will be compared to investigate property dependency on nanostructure. Evaluation will include examinations of nanostructure by XRD and TEM, as well as characteristics of physical properties, thermal properties, and oxygen permeabilities of sheet and films. The first material to be evaluated is the PET/15A nanocomposite. This material was prepared through a twin screw extrusion of 3 wt% Cloisite 15A clay and IV 0.74 dL/g PET. After melt blending the material was solid state polymerized to achieve 0.80 dL/g. It was then, single screw extruded to form a sheet. The second material to be evaluated is the 30B nanocomposite produced through in situ polymerization. For production of this material 3 wt% clay was added into the polycondensation reaction and polymerized at 270 °C. The SSP reaction and single screw extrusion was done in the same way as for the previously described PET/15A nanocomposite. Investigation of factors to affect above results is described in the following sections.

3.4.1 Nanostructure analysis

3.4.1.1 Nanostructure analysis by XRD

The XRD result shown in Figure 3.62 indicated that PET/15A sheet had 33 Å basal spacing (2θ=2.6 °) and 30B sheet was almost flat. The peak locations of Cloisite 15A and 30B clay were 2.6 ° and 4.6 ° (19 Å basal spacing). All nanocomposites prepared by in situ polymerization or melt intercalation had the peak near at 5.6°, even though the intensities were different. The peak near at 5.6° results from thermal degradation of clay [82]. PET/15A sheet was compounded with 15A clay and IV 0.74dL/g PET in a twin screw extruder at 275 °C. The residence time was only 3-5
minutes, nevertheless, PET/15A sheet had the peak near 5.6°, indicating thermally degraded clay. The XRD spectrum of Cloisite 15A and Cloisite 30B clays did not show any peak near 5.6°. This implied that all clays used in this research contained thermally sensitive parts, which would degrade at PET processing or polymerization temperature. The 30B nanocomposite contained a similar peak, but the intensity was weak, meaning very small amounts of degradation product were present. From the above analysis, it could be summarized that the PET/15A nanocomposite had a tactoid nanostructure, because there was no change in the basal spacing between clay and the mixture after melt mixing. In the case of 30B nanocomposite, XRD result indicated that the clay was almost an exfoliated nanostructure, since there was no clear peak in the XRD pattern.

![XRD results of PET/15A sheet and 30B sheet. X-ray measurement range was from 1.6° (55 Å) to 7° (12.6 Å)](image)

Figure 3.62 XRD results of PET/15A sheet and 30B sheet. X-ray measurement range was from 1.6° (55 Å) to 7° (12.6 Å)
3.4.1.2 Nanostructure analysis by TEM using microtome

To further evaluate the nanostructure analyzed by XRD, the two materials were cut into very thin slices with a microtome in preparation for characterization with TEM. Figure 3.63 showed TEM pictures of PET/15A and 30B nanocomposite sheets at the scale of 20 nm. The PET/15A nanocomposite consisted of ~30 layers of platelets and the basal spacing was 2~3 nm (20~30 Å) in the TEM picture. The 30B nanocomposite showed many single platelets, but also contained other nanostructures. Some parts contained intercalated structures and other parts had clay agglomerations. The portions of exfoliated materials, however, were greater than the sum of the intercalated and clay agglomeration portions. When we compared the results of XRD and those of TEM for PET/15A nanocomposite and 30B nanocomposite, similar information was got.

The orientation of clay platelet was different between the PET/15A and 30B nanocomposites. The 15A clay platelets were aligned in one direction, but the orientations of platelets of the 30B nanocomposite were random. This difference of nanostructure and the orientation of platelets could cause differences in tensile and oxygen permeability in PET/15A and 30B nanocomposite sheets. There was no force to align clay platelets to one direction in sheet forming, but the stretching process (such as bottle blowing) could align clay platelets in the stretching directions. The stretching process, therefore, could change physical and gas barrier properties of nanocomposite materials.
a. PET/15A nanocomposite (clay 3 wt%), precursor

b. 30B nanocomposite (clay 3 wt%), precursor

Figure 3.63 TEM pictures of PET/15A and 30B nanocomposite using microtome (the scale is 20nm)
3.4.2 Tensile properties of two cases

3.4.2.1 Sheet properties

Addition of clay into a PET matrix improved the tensile properties of resultant sheet. Figure 3.64 and Table 3.9 showed that the tensile modulus of PET nanocomposites was improved by 7~11% with the addition of 3 wt% clay, while the tensile strength was not improved. Four months later, the same measurement was performed. The trend was similar to before, but the absolute values decreased especially in tensile modulus (Figure 3.65). This was due to the plasticizer effect of moisture in the PET matrix [72]. All the sheet samples were kept in constant temperature and constant relative humidity (25°C and 50% R.H.). Absorption of moisture for four months could decrease tensile properties of sheets [72]. Exfoliated 30B nanocomposite sheet has higher tensile modulus and strength than that of 33 Å basal spacing PET/15Å nanocomposite sheet or PET without clay. We can presume the degree of improvement could be different according to nanostructure. The addition of hard clay particles makes the polymer matrix stiffer and increases the resistance of the material to stress.

Ke et al. [34] reported that the modulus was improved by 2.5 times that of pure PET showing 23% decrease in strength at 3 wt% clay in in-situ polymerization method. The specimen was 1~2 mm film with compression molding of precursor PET. Barber et al. [51] improved tensile modulus by 30% at 5 wt% clay in twin screw extrusion. Injection molding was used to prepare tensile specimen.

The improvement obtained in this research was not as significant as reported in the two articles. The possible reasons are the difference in interfacial interaction force between the clay and PET, dispersion of clay, thermal stability of the clay, and degree of orientation of clay platelets.
Figure 3.64 Tensile properties of three sheets, three days after sheet extrusion

IV (dL/g) of PET sheet (0.73), PET/15A sheet (0.74), 30S sheet (0.73)

Table 3.9 Modulus and strength values of three sheets. SD is standard deviation

<table>
<thead>
<tr>
<th></th>
<th>Modulus (MPa)</th>
<th>Modulus- SD</th>
<th>Strength (MPa)</th>
<th>Strength- SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET sheet</td>
<td>930</td>
<td>54</td>
<td>54</td>
<td>3</td>
</tr>
<tr>
<td>PET/15A sheet</td>
<td>998</td>
<td>61</td>
<td>53.3</td>
<td>2</td>
</tr>
<tr>
<td>30B sheet</td>
<td>1033</td>
<td>79</td>
<td>56</td>
<td>3</td>
</tr>
</tbody>
</table>
Figure 3.65 Tensile properties of sheets after four months conditioning under 25 °C and 50% RH
3.4.2.2 Stretched film properties with various stretching ratio

Tensile modulus was measured using the samples prepared at various stretching ratios (2x2, 3x3, 3.5x3.5) as shown in Figure 3.66. PET film showed increases in modulus from near 3x3 stretching ratio, where PET film shows the start of self limiting behavior [73] due to orientation. The modulus increased steeply at 3.5x3.5 stretching ratio. The PET/15A nanocomposite film showed similar behavior with PET film but the modulus at 3.5x3.5 was slightly smaller than that of the PET film. On the other hand, the modulus of the 30B nanocomposite film slightly decreased down to 3x3 stretching ratio, and then increased a little at 3.5x3.5 stretching ratio. The 30B nanocomposite film showed the largest modulus in a unstretched sheet but PET film showed the largest value at 3.5x3.5 stretching ratio. The 30B nanocomposite sheet results seem to be related to microstructure change in the nanocomposite during stretching. Changes in tensile strength exhibited similar trends to those of tensile modulus, as seen in Figure 3.67.

Chang et al. [8,46] reported that tensile modulus of unstretched nanocomposite fiber was increased by 1.8 times that of unstretched pure PET fiber at 3 wt % clay. This improvement was not maintained after stretching. They suggested that debonding could occur and voids in the nanocomposite were formed during high stretching. These phenomena should reduce the tensile properties due to imperfect inclusion/matrix interface and weak resistance to large stress.

To research this phenomenon, oxygen permeability was examined, and several properties, including density, thermal properties, and polarized microscope were measured to confirm or disprove the existence of voids in the films.
Figure 3.66 Tensile modulus changes with stretch ratios in film. Error bar shows standard deviation.

Figure 3.67 Tensile strength changes with stretch ratios in film. Error bar shows standard deviation.
3.4.3 Oxygen permeability

3.4.3.1 Sheet

Addition of clay brought about 2 results in oxygen permeability. PET/15A nanocomposite (tactoid nanostructure) did not reduce oxygen permeability, while 30B nanocomposite (almost exfoliated nanostructure) decreased permeability by 29% in a sheet, compared with that of PET sheets as shown in Figure 3.68. To better understand the performance of PET/15A and 30B nanocomposite, which were prepared in this research, theoretical permeability values were calculated for each case.

![Figure 3.68 Oxygen permeability of PET, PET/15A nanocomposite, and 30B nanocomposite sheet](image-url)
Southern Clay Products Inc. provided the information that the aspect ratio of three clays was 75-100 but the aspect ratio of 75 was the most. Volume fraction of clay to polymer was calculated from the residual of clay ash (reported in the end of this section). The volume fraction of the clay in PET/15A nanocomposite was 0.022 (the density of Cloisite 15A clay was 1.66 g/cc) and that in 30B nanocomposite was 0.018 (the density of Cloisite 30B was 1.98 g/cc). The theoretical permeability of 30B nanocomposite can be calculated from the above data according to:

\[ \tau \approx 1 + \left( \frac{L}{2W} \right) \phi \]  

(equation 10)

where, \( \tau \)=tortuosity, \( L \)=length, \( W \)=width, \( L/W \)=aspect ratio, \( \phi \)=volume fraction of filler

\[ \tau \approx 1 + \left( \frac{75}{2} \right) 0.018 = 1.7 \]  

(equation 11)

\( \rightarrow \) 70% increase in tortuosity

\[ P_{\text{nanocomposite}} = \frac{(1-\phi)P_{\text{matrix}}}{1+\alpha\phi/2} \]  

(equation 12)

Where, \( P_{\text{nanocomposite}} \); the permeability of the resulting nanocomposite

\( P_{\text{matrix}} \); the permeability of matrix

\( \phi \); the volume fraction of platelets

\( \alpha \); the aspect ratio of the platelets
\[
P_{\text{PET}} = 12.9 \text{ cc(STP)} \cdot \text{mil/(100 sq.in • day • atm)} \text{ (from the measurement)}
\]

\[
P_{\text{nanocomposite}} = (1-0.018) \cdot \frac{12.9}{(1+75 \cdot 0.018/2)} \tag{equation 13}
\]

\[
= 7.6 \text{ cc(STP)} \cdot \text{mil/(100 sq.in • day • atm)}
\]

\[
\therefore \frac{7.6}{12.9} = 0.71 \text{ (29% improvement, compared with } P_{\text{PET}}) \]

The theoretical permeability of 30B nanocomposite sheet was 41% improvement, compared with that of pure PET sheet due to 70% increase in tortuosity. (the aspect ratio of 100 gives 48% improvement)

There was 12% difference in permeability improvement between the theoretical value and the experiment result. Two possibilities could be suggested about this difference. The first one is that the clay was not perfectly exfoliated in the matrix. Some parts of 30B nanocomposite contained intercalated structure and some parts contained clay agglomeration, due to thermal degradation. These could reduce tortuosity and makes the permeability a higher value than the theoretical value. The second possibility is that 100% of the clay was not oriented parallel to the surface of the sheet. Some parts of clay were aligned in that fashion but others had different orientations (Figure 3.61b), since there was no strong force to orient the clay particles parallel to the sheet surface. Stretching the sheet can cause the clay platelets to be oriented parallel to the surface of film.
PET/15A nanocomposite was not an exfoliated nanostructure, therefore tortuosity would be expected to be much smaller than that of an exfoliated structure. If we assume clay 15A has 30 layers on an average, tortuosity and permeability can be calculated like this;

\[ \tau \approx 1 + \left( \frac{75}{60} \right) 0.022 = 1.03 \]  \hspace{1cm} \text{(equation 14)}

\[ P_{\text{nanocomposite}} = (1-0.022) \times 12.9/(1+75/30\times0.022/2) \]  \hspace{1cm} \text{(equation 15)}

\[ = 12.3 \text{ cc (STP) \cdot mil/(100 sq. in \cdot day \cdot atm)} \]

The PET/15A nanocomposite, therefore, would not be expected to significantly improve permeability, due to only a 3% increase in tortuosity.
3.4.3.2 Stretched film with various stretch ratios

As a PET sheet is extended, PET chain starts to align after a specific extension ratio has been exceed, resulting in a high degree of orientation in the direction of stretching. This orientation of PET causes strain-induced crystallization [85]. Oxygen permeability is influenced by the crystallinity of polymer because the diffusion of oxygen is affected by more tortuous path through polymer due to increased crystallinity, so that stretching causes the decrease of oxygen permeability [72,86]. Oxygen permeability of PET and PET/15A nanocomposite showed a similar behavior in the relationship between permeability and stretching ratio. The oxygen permeability of 30B nanocomposite, however, did not. The oxygen permeability improvement of 30B nanocomposite in a sheet was not maintained at high stretch ratios (3.5x3.5) (Figure 3.69).

All three sheets were transparent in the form of sheet after extrusion as shown Figure 3.70. The transparencies of the films decreased except that of pure PET, as they were highly stretched and, the surfaces of the nanocomposites became rough. These phenomena means there was a possibility of phase separation between PET and the clay particles. The adhesive forces of the PET chains to the clay surface are weaker than the stretching force. If phase separation did not occur, the 30B nanocomposite film (3.5x3.5) might have better oxygen permeability than PET film (3.5x3.5), since clay platelets were aligned along with the stretching direction and more strain induced crystallization to occur due to the nucleation effect of clay particles.

The 2x2 films of nanocomposite lost a little transparency, but the 2x2 PET film was transparent. At a stretch ratio of 3x3, films of nanocomposite were translucent, while PET film was still transparent. Phase separation might be occurring from 2x2
stretch ratios in the case of nanocomposites.

The surface of nanocomposites was rough due to lots of tiny spots and spheres, while that of PET film was smooth even at a 3.5x3.5 stretch ratio. The rough surfaces could be caused by micro voids and/or thermally degraded materials. If micro voids were generated during stretching, the densities of nanocomposites might be affected due to the light density of air.

Figure 3.69 O₂ permeabilities of PET (wa314), PET/15A nanocomposite, and 30B nanocomposite film with various stretch ratios. Stretch ratio of sheet is 1x1.
Figure 3.70 Pictures of sheets and films of PET (WA314), PET/15A and 30B nanocomposite
3.4.4 Factors to affect properties

3.4.4.1 Density of sheet and film

Densities of 30B, 15A, and PET sheet were 1.349, 1.338 and 1.321 g/cc respectively. The increase of nanocomposite density value was caused by the addition of heavier clay particle into the PET matrix. The densities of clay 15A and 30B are 1.66 and 1.98 g/cc [13]. The density of amorphous homopolymer PET is 1.333 g/cc so that the density of amorphous copolymer PET will have a lower value than the density of homopolymer, proportional to comonomer content, if isophthalic acid was used as a comonomer. One more factor, which increases density of nanocomposite sheet, is that the addition of clay can increase the crystallization rate from the melt state when the sheet was formed in the cooling roll of the single screw extruder. Small amounts of nuclei or crystals can increase the density of the nanocomposites.

Figure 3.71 shows that sheet densities were increased a little at 2x2 stretch ratios. At 3.5x3.5 stretch ratio, large increases in density occurred in the case of PET, but the density increase of two nanocomposites films was not as significant. The nanocomposite consists of 97 wt% of PET and 3 wt% of clay. If the interface between PET and clay is firmly connected, the increase of nanocomposite density might follow the trend in that of PET density when highly stretched (3.5x3.5). Here, microstructure changes in the two nanocomposite films can be inferred from these smaller increases of the density during stretching. The material, which has less dense than PET, can decrease the density of nanocomposite films. Clay particles are heavier than PET, and don’t have stronger interfacial force with PET molecules than tensile force. Micro void can, therefore, be the candidate of this less increase in the densities of 3.5x3.5 nanocomposite films.
Figure 3.71 Density change with stretch ratios
3.4.4.2 Impurities in nanocomposites

3.4.4.2.1 Microscopy of sheet

a) PET sheet (50x1.25) b) PET/15A sheet (50x1.25)

c) 30B sheet (50x1.25) d) scale (50x1.25), 1 scale=10μm

Figure 3.72 Impurities in PET, PET/15A, and 30B nanocomposite sheet

PET sheet contained no impurity in a sheet, while a PET/15A nanocomposite sheet had some impurities and a 30B nanocomposite sheet contained many impurities as shown in Figure 3.72. These impurities could be from thermal degradation of clay modifier during the melt polymerization. Several spherical particles in 30B nanocomposite sheet were larger than 10 μm.

3.4.4.2.2 Microscopy of 3.5x3.5 stretched film
Figure 3.73 Microscopy of PET/15A and 30B nanocomposite stretched film; nonpolarized, polarized, and polarized pictures after heat set at 80°C for 30 min at 50x1.25 magnification
Figure 3.73 a) and b) showed 3.5x3.5 stretched films had many fine spherical particles. These spherical particles could be microvoids, spherulites, thermally degraded materials, or gels. These can affect the density of 3.5x3.5 stretched film of PET/15A and 30B nanocomposites.

In the polarized microscopy photo, PET/15A nanocomposite film c) showed darkness, which means there was no part which could pass the polarized light. If the material had spherulites in it, which had a different refractive index, polarized picture might show some brightness. Small particles in PET/15A nanocomposite film were not spherulites. In 30B nanocomposite film, polarized light were penetrated through analyzer, which mean the film contained a different refractive index materials. After 80°C heat setting of the 30B nanocomposite films for 30 minutes, the picture showed darkness, implying no spherulite. This phenomenon could be interpreted like this; When we added rigid clay into polymer then stretched, most of stress could be accumulated at the surface of clay, because matrix PET and clay particles were strong enough to resist tensile force up to 3.5x3.5 stretch ratio but the interface force between clay and PET was not strong. That stress (very high level stress) at the interface caused a strange phenomenon in the polarized light analysis. After heat setting, most stress might be disappeared so that polarized picture after heating became dark due to the disappearance of stress. Spherical shapes in 30B film (3.5x3.5) were not spherulites but that could be microvoids, containing very high level stress. Among spherical particles, some could be gels and some could be burned materials.
3.4.4.3 Thermal properties of nanocomposites sheet and film

Figure 3.74 showed DSC scan of PET, PET/15A nanocomposite, and 30B nanocomposite sheets at the first scanning. There was no big difference in heat of crystallization (designated “A”) and heat of melting (designated “B”) in all three samples, implying all sheets were initially almost amorphous materials. One difference was that the cold crystallization peak (Tc1) of PET was higher than two nanocomposites. The addition of clay increased the crystallization rate.

DSC of 3.5×3.5 stretched films was done to determine whether the spherical particles in the microscopy picture were crystalline materials or not. If they were crystalline materials, a glass transition peak of nanocomposites would be smaller than that of PET, because the amount of spherical particles would reduce the amorphous faction of the material. In solid state polymerized PET, only a very small glass transition is detected because of high crystallinity. Another expectation was that the crystallization peak of 3.5×3.5 stretched films of 30B nanocomposite might be the smallest, when heated from room temperature at the first scanning with the same reason.

Two stretched films (PET and PET/15 nanocomposite) showed insignificant glass transition temperatures but the transition was more apparent for the 30B nanocomposite film (Figure 3.75). The difference between area B (the heat of melting) and area A (the heat of crystallization) in 3.3×3.5 stretched PET film proved the existence of crystalline material caused by strain-induced crystallization [1]. This phenomenon was seen in the density increase of 3.3×3.5 stretched PET film in Figure 3.71. When we investigate crystallization peak (Figure 3.75), the crystallization peak area of PET film was the smallest among three films, and 30B nanocomposite film showed the bigger area of two crystallization peaks than that of others. From these
results, we can expect that spherical particles in stretched film are not crystalline material such as spherulites. If they were spherulites, the crystallization peak area of 30B nanocomposites should be the smallest than those of other two films, because the density of 30B nanocomposite film had the biggest value (Figure 3.71) and the number of spherical particle was the largest.

Figure 3.74 DSC results of sheets. 1st scan of three sheets
Figure 3.75 DSC result of 3.5x3.5 stretched films. 1\textsuperscript{st} scan of three films
3.4.4.4 Reproducibility

3.4.4.4.1 The residual clay contents

The levels of clay present in nanocomposites was examined after burning sheets at 900 °C for 1 hr. First 4 rows of Table 3.10 showed the reproducibility of ash content analysis for pure PET and 30B nanocomposite. WA314 didn’t have any clay in it so that there was no residual after burning PET. 54 th was the 30B clay nanocomposite, melt polymerized by the PC clay addition process. The clay residual amount was 2.7 wt% and the difference between two values was 0.07wt%. The range of residual amount of clay was 2.66~2.95 wt% in Table 3.8 so 93% of clay was left in the nanocomposite on an average when the added clay amount was 3 wt%. The residual amount of clay was 2.83 wt% in PET/15A nanocomposite sheet and was 2.74 wt% in 30B nanocomposite sheet. These values were used to calculate theoretical values of the permeability of nanocomposites.

Table 3.10 Ash content of PET/15A and 30B nanocomposites

<table>
<thead>
<tr>
<th>Material name or batch number</th>
<th>Clay amount (wt%)</th>
<th>Clay residual (wt%)</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>WA 314</td>
<td>0</td>
<td>0.00</td>
<td>Pure PET, reproducibility</td>
</tr>
<tr>
<td>WA 314</td>
<td>0</td>
<td>-0.03</td>
<td>“</td>
</tr>
<tr>
<td>54 th</td>
<td>3</td>
<td>2.73</td>
<td>30B nanocomposite in the reactor, reproducibility</td>
</tr>
<tr>
<td>54 th</td>
<td>3</td>
<td>2.66</td>
<td>“</td>
</tr>
<tr>
<td>26 th</td>
<td>3</td>
<td>2.82</td>
<td>30B nanocomposite in the reactor</td>
</tr>
<tr>
<td>27 th</td>
<td>3</td>
<td>2.95</td>
<td>10A nanocomposite in the reactor</td>
</tr>
<tr>
<td>28 th</td>
<td>3</td>
<td>2.74</td>
<td>15A nanocomposite in the reactor</td>
</tr>
<tr>
<td>PET/15A sheet</td>
<td>3</td>
<td>2.83</td>
<td>PET/15A nanocomposite in the extruder</td>
</tr>
<tr>
<td>30B sheet</td>
<td>3</td>
<td>2.74</td>
<td>30B nanocomposite in the reactor</td>
</tr>
</tbody>
</table>
3.4.4.2 Polymerization processes

Polycondensation time (PC-h) had reproducibility within 10% of each value and the other values had less than 10% differences, regardless of clay addition point (ES or PC clay addition). After finishing melt polymerization and solid state polymerization, the difference of IV at the same formulation was less than 0.02 dL/g (Table 3.11).

Table 3.11 Polycondensation reaction and solid state polymerization data

<table>
<thead>
<tr>
<th>Batch number</th>
<th>PC-h (min)</th>
<th>Torque (kw)</th>
<th>Melt IV (dL/g)</th>
<th>PC Temp. (°C)</th>
<th>SSP IV (dL/g) at 230°C</th>
<th>remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>21 th</td>
<td>110</td>
<td>0.72</td>
<td>0.40</td>
<td>280</td>
<td>0.90</td>
<td>ES clay addition, 24hr SSP</td>
</tr>
<tr>
<td>30 th</td>
<td>120</td>
<td>0.71</td>
<td>0.38</td>
<td>280</td>
<td>0.89</td>
<td>“</td>
</tr>
<tr>
<td>53 th</td>
<td>108</td>
<td>0.75</td>
<td>0.44</td>
<td>270</td>
<td>0.84</td>
<td>PC clay addition, 15hr SSP</td>
</tr>
<tr>
<td>69 th</td>
<td>97</td>
<td>0.75</td>
<td>0.43</td>
<td>270</td>
<td>0.82</td>
<td>“</td>
</tr>
</tbody>
</table>
3.4.4.4.3 XRD

Figure 3.76 X-ray results of 2 sets of the same formulation

Two sets of x-ray results showed the same trend and the same peak position: 21st and 30th batch (280 °C PC clay addition), 53rd and 69th batch (270 °C PC clay addition). XRD results also showed good reproducibility for the same formulation.
3.5 Further improvement

CHMD addition, 6 wt% clay addition, low IV at 267 °C polycondensation

Hydrophilicity of two hydroxyl groups in ethylene glycol (EG) made the mixture of montmorillonite and EG well mixed, and formed a gel as shown in Figure 3.77. XRD proved the expansion of basal spacing of the mixture (Figure 3.78). Cyclohexane dimethanol (CHDM) contains two hydroxyl groups like EG, and the size of CHDM is bigger than that of EG. In addition to these characteristics, CHDM has three dimensional structures, a mixture of chair and boat isomer. If CHDM molecules can penetrate the gallery of the clay, the better nanostructure can be obtained than that prepared with EG.

Figure 3.77 A mixture of EG and clay

Cloisite 30B 35g ; powder
Cloisite 30B 35g+100g EG ; gel

Three weight percent of clay was added in this research as a control. The increase of clay amount can reduce oxygen permeability according to tortuous model. The addition of three weight percent Cloisite 30B reduced 41% permeability theoretically, and 29 % reduction was acquired in actual experiment. Six weight percent addition of Cloisite 30B at standard melt polymerization with PC clay
addition method is expected to get further improvement in gas barrier property.

Organic clays were sensitive to temperature and residence time in the reactor. XRD results implied short residence time and/or low temperature would reduce the amount of clay agglomerations in nanocomposites. The effect of residence time in the reactor on nanostructure as a preliminary experiment was evaluated using PC clay addition method with Cloisite 30B and E/T=1.2 BHET. To actualize that aim, melt polymerization was suspended at three torque values to prepare samples during reaction (Table 3.12). Figure 3.79 illustrated that the basal spacing of nanocomposite already reached to the constant value at low molecular weight in 30B nanocomposite. To reduce the degree of thermal degradation during melt polymerization, low molecular weight nanocomposite was melt polymerized at the lowest melt polymerization temperature (267°C).
Figure 3.78 Basal spacing of a mixture of EG and Cloisite 30B, a mixture of CHDM and Cloisite 30B
Figure 3.79 Basal spacing of nanocomposite prepared with various polycondensation time

Table 3.12 properties of nanocomposites suspended at various polycondensation time

<table>
<thead>
<tr>
<th></th>
<th>Torque (Kw)</th>
<th>PC-h (min)</th>
<th>IV (dL/g)</th>
<th>rpm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Start</td>
<td>0.39</td>
<td>0</td>
<td>-</td>
<td>90</td>
</tr>
<tr>
<td>1\textsuperscript{st} sample</td>
<td>0.43</td>
<td>60</td>
<td>0.15</td>
<td>90</td>
</tr>
<tr>
<td>2\textsuperscript{nd} sample</td>
<td>0.66</td>
<td>90</td>
<td>0.40</td>
<td>90</td>
</tr>
<tr>
<td>3\textsuperscript{rd} sample</td>
<td>0.88</td>
<td>135</td>
<td>0.50</td>
<td>45</td>
</tr>
</tbody>
</table>
An addition of CHDM showed a trend that PC-h was reduced as the amount of CHDM was increased. CHDM addition decreased the melting point of nanocomposites due to the increase of irregularity in structure so that this can cause to deteriorate gas permeability. Figure 3.77 showed CHDM 3 wt% contained more clay agglomeration compared with E/T=1.2 270 ℃. This could make barrier property worse. Color after SSP reaction showed the increase of Col-b (yellowness) in 3 wt% and 5 wt% addition (Table 3.13).

Characteristics of 6 wt% clay addition were similar to those of a control 270 ℃ except for color-L and permeability. Color-L was decreased by 7 due to increase of clay amount, and the permeability had 63% improvement. The theoretical value of improvement was 59% (permeability in Table 3.11 should be 41). XRD showed 6 wt% clay nanocomposite contained a peak near 3.0° and more clay agglomerations compared with that of a control (Figure 3.80). These could cause much less improvement in permeability than theoretical value.

Low IV nanocomposite (0.38 dL/g), which was melt polymerized at 267 ℃, improved color-L and color-b of nanocomposite.

Table 3.13 Properties of 30B nanocomposites for further improvement

<table>
<thead>
<tr>
<th></th>
<th>CHDM 3wt%</th>
<th>CHDM 5wt%</th>
<th>6wt% clay</th>
<th>Low IV at 267°C</th>
<th>Control 270°C</th>
<th>280°C</th>
<th>PET wa314</th>
</tr>
</thead>
<tbody>
<tr>
<td>Torque (Kw)</td>
<td>0.75</td>
<td>0.75</td>
<td>0.74</td>
<td>0.65</td>
<td>0.75</td>
<td>0.72</td>
<td>-</td>
</tr>
<tr>
<td>PC-h (min)</td>
<td>110</td>
<td>105</td>
<td>100</td>
<td>85</td>
<td>112</td>
<td>110</td>
<td>-</td>
</tr>
<tr>
<td>IV (dL/g)</td>
<td>0.49</td>
<td>0.47</td>
<td>0.47</td>
<td>0.38</td>
<td>0.45</td>
<td>0.40</td>
<td>-</td>
</tr>
<tr>
<td>Tm (℃)</td>
<td>230</td>
<td>223</td>
<td>242</td>
<td>242</td>
<td>244</td>
<td>232</td>
<td>-</td>
</tr>
<tr>
<td>SSP Col-L</td>
<td>45</td>
<td>45</td>
<td>43</td>
<td>55</td>
<td>50</td>
<td>47</td>
<td>86</td>
</tr>
<tr>
<td>SSP Col-b</td>
<td>10</td>
<td>10</td>
<td>7</td>
<td>7</td>
<td>8</td>
<td>8</td>
<td>-2</td>
</tr>
<tr>
<td>Permeability*</td>
<td>105</td>
<td>-</td>
<td>63</td>
<td>-</td>
<td>71</td>
<td>-</td>
<td>100</td>
</tr>
</tbody>
</table>

*; the permeability of WA314 sheet was set to 100%
Figure 3.80 Basal spacing of nanocomposites prepared with CHDM, 6 wt% clay and 
E/T=1.2 270 °C. Circles meant intercalated nanostructure or more clay 
agglomerations than E/T=1.2 270 °C
Chapter IV.

Conclusions and recommendations

4.1 Conclusions

4.1.1 Melt Intercalation

Three molecular weights of PET were melt compounded with three clays at 275 °C using a twin screw extruder. Mobility effect of a PET chain and affinity effect of clay modifier on nanostructure were monitored to characterize the nanocomposite produced by melt intercalation.

Addition of clay resulted in a large molecular weight reduction of PET nanocomposite even though all materials were dried overnight. PET/Cloisite 30B showed the greatest molecular weight reduction while PET/Cloisite 15A had the least molecular weight reduction, implying the modifier of clay can affect the degradation rate of nanocomposites. This trend was the same when three IVs of PET (0.74, 0.63, 0.48dL/g) was used. Thermal stability experiment showed that the thermal degradation rate of nanocomposite was faster than that of PET. FTIR results, however, proved hydrolysis was the main reason of molecular weight reduction during extrusion, which has 3–5 minutes residence time. The SSP rate was decreased by more than 2 times than that of PET. This came from the platelet structure of clay particles, increasing the path length of volatile gas phase. Crystallization rates, when heated from room temperature and when cooled from melt state, were accelerated due to the addition of clay particles. The basal spacing in PET/Cloisite 10A and
PET/Cloisite 30B nanocomposites after melt extrusion was increased, indicating intercalated nanostructure. After solid state polymerization, nanocomposites containing Cloisite 10A and Cloisite 30B showed another peak at low angle in XRD, illustrating that some parts of clay contained the bigger basal spacing than 55 Å, although all samples prepared by melt intercalation method did not show exfoliated nanostructure. The most hydrophobic modifier with the biggest basal spacing, Cloisite 15A, did not show any affinity with PET even after solid state polymerization. According to the above results, the melt intercalation method cannot produce the exfoliated nanostructure with three clays and the molecular weight effect (IV range is from 0.74 to 0.48 dL/g) on nanostructure was small. The modifier effect of clay on nanostructures was greater than that of molecular weight.

4.1.2 In situ polymerization in PET conditions

Clays were added in the early stage of esterification reaction, residence time of ~9 hrs, or in the early stage of polycondensation reaction, the residence time of ~2 hrs, at PET melt polymerization conditions. Former process was named as ES clay addition, and the latter was named as PC clay addition. PET was polymerized with two processes for the comparison of properties as a control.

Esterification reactions were accelerated by ~10% due to the addition of clay but polycondensation reactions were difficult to perform due to severe foam generation. The attainable IV in melt polymerization was lower than that of PET because of thermal degradation. Nanocomposites prepared by polycondensation (PC) clay addition method had 0.07 dL/g higher IV than nanocomposites prepared by esterification (ES) clay addition method due to shorter residence time. Tg and Tm of nanocomposites was decreased due to high contents of flexible parts, and the biggest
drop in melting point was $20\,^\circ\mathrm{C}$ in 30B nanocomposite. NMR showed that the flexible part in PET nanocomposite was diethylene glycol (DEG), and some mechanisms of several PET degradation reaction could explain the generation of DEG. Crystallization rates of nanocomposites were affected by both clay particles as nuclei and DEG contents as a copolymer. The SSP rate of nanocomposite prepared by melt polymerization was slower than that of melt intercalation nanocomposites. End group analysis results illustrated that carboxyl end group concentration was drastically increased and hydroxyl group concentration was extremely reduced. Unbalanced ratio of the both end group concentrations caused the reduction of the SSP rate of in situ polymerized nanocomposites compared with those of melt intercalation nanocomposites, and these large changes in the both end group concentrations were caused by the long residence time in the reactor. XRD results showed that in situ polymerization method can produce almost exfoliated nanostructure even though the amount of clay agglomerations was higher than that of melt intercalation nanocomposites. The 30B nanocomposite showed the more exfoliated nanostructure due to the same structure of hydroxyl group in PET and the modifier of clays, while hydrophobicity of Cloisite 15A caused the worst affinity with PET. PC clay addition method contained less contents of thermally degraded clay than ES clay addition method.

4.1.3 Improvement of melt polymerization process

Aluminium dish experiment revealed that BHET and TPA/EG slurry were reacted to make finite size of bubble. Addition of organic clay increased the viscosity of that system, and then finite size bubbles grew to the top of dish. In the reactor experiment, it was found that foam generation was sensitive to esterification
temperature, esterification pressure, and the mole ratio of terephthalic acid and ethylene glycol (E/T). These variables had their own optimum points to reduce the amount of foam. EG/TPA mole ratio, DEG suppressor, metal stabilizer, antioxidant, PC temperature, PC residence time were evaluated to find out the relationship between variables and properties (melting point, carboxyl and hydroxyl end group concentration, SSP rate, nanostructure). Nanostructure was the most important property among them. The best nanocomposite was obtained when Cloisite 30B and BHET of E/T=1.2 without additive were polymerized at 270 ℃ using PC clay addition method. XRD and TEM showed that the above conditions produced the exfoliated nanocomposite with a little amount of clay agglomeration. The melting temperature of the nanocomposite was improved by 11 ℃ (former one had 233 ℃ of Tm) and the SSP rate was increased due to the better ratio of carboxyl and hydroxyl concentrations. 30% catalyst (sb) increased nanocomposite contained the best performance in all properties but nanostructure was not better than 30B nanocomposite of E/T=1.2 without additive.

4.1.4 Comparison of two nanocomposites

To evaluate the relationship of nanostructures and properties, nanocomposites prepared by two different methods were selected. First one is PET/15A nanocomposite, which was the melt mixture of IV 0.74 dL/g PET and Cloisite 15A, and second one is 30B nanocomposite, which was melt polymerized at 270 ℃ by the PC clay addition method with E/T=1.2 BHET. XRD and TEM analysis results proved that the former nanocomposite was tactoid, no change in the basal spacing due to lack of affinity between PET and clay, and the latter one was exfoliated nanocomposite with a little amount of clay agglomeration, no peak in XRD due to good affinity
between two. The exfoliate nanocomposite had 11% improvement in tensile modulus and no improvement in tensile strength compared with those of PET. After stretching, this improvement was disappeared. The exfoliated nanocomposite had 29% reduced oxygen permability at 3wt % clay than that of PET, but stretching vanished this improvement. Tactoid structure did not show any improvement in permeability as we expected in theoretical calculation. Results of density, microscopy, and DSC implied that stretching process caused third component generation in nanocomposite films such as micro voids, which were lighter than PET, spherical shape, and not crystalline material.

4.1.5 Further improvement

To improve nanocomposite properties further, CHDM addition, clay amount increase, and less thermal degradation was evaluated. Characteristics of these nanocomposites were compared with respect to melt polymerization time, nanostructure, permeability, and color. The increase of clay amount from 3 wt% to 6 wt% improved the permeability by 37%, whereas the theoretical value of improvement was 59%. XRD showed 6 wt% clay nanocomposite contained a faint peak (intercalated) and more clay agglomerations compared with that of a control. This could cause less improvement in permeability than theoretical value. The clay of 6 wt% was too much to keep an effective performance regarding the permeability. There will be the optimum content of clays between 3 and 6 wt% at which the clay doesn’t agglomerate. Low IV nanocomposite (0.38 dL/g), which was melt polymerized at 267 °C, improved color-L and color-b of nanocomposite. This result illustrated that if we have more thermally stable organic clay, the color of nanocomposites will be better than that of the nanocomposite
produced in this research. An addition of CHDM made worse color and worse oxygen permeability of nanocomposites than those of a control nanocomposite. CHDM, therefore, was not a good monomer candidate for better nanocomposites.

4.2 Recommendations

Although we performed a wide range of experiments with various variables, there should be future investigations for more comprehensive understanding of PET nanocomposites.

- Research for organic clays which have high temperature resistance up to PET polymerization temperature, better affinity with PET, reactivity with end groups of PET monomers, flexibility for stretching, and expandability with ethylene glycol.
- The most important characteristic of a nanoparticle is the high aspect ratio. If the aspect ratio of the nanoparticle is about 1,000, a 95% improved barrier property could be achieved, meaning 20 times better barrier property than the matrix polymer.
- Study for purification of clay. Inorganic and organic impurities cause the acceleration of thermal degradation, discoloration, and deterioration of properties of nanocomposite.
- Compatibilizer study. To get better affinity with PET, a compatibilizer such as ionomer could be used.
Chapter V.

Acknowledgement

I would like to express thanks to PET consortium members who have supported all the researches and discussion on our results at Polymer Institute, University of Toledo.
Chapter VI.

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