EVALUATION OF POLYMER FILM BARRIER COATING INCORPORATING TWO DIFFERENT NANOPATICLE SIZE

By

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To my mom, dad, and brother

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LIST OF ABBREVIATIONS

APP	Atmospheric Pressure Plasma
BON	Biaxially Oriented Nylon
CEC	Cation Exchange Capacity
LLDPE	Linear Low Density Poly Ethylene
LMD	Low Molecular Weight
MMT	Montmorilonite
MW	Number-average Molecular Weight
OAC	Organic Ammonium Chloride
OPP	Oriented Poly Propylene
OTR	Oxygen Transmission Rate
PC	PVOH with Cloisite Na^+
PCL	PVOH with Cloisite Na^+ and Laponite JS
PCN	Polymer Clay Nanocomposite (barrier coating of one nanoparticle type)
PC2N	Polymer Clay 2 Nanocomposite (barrier coating of two types of nanoparticles)
PE	Poly Ethylene
PET	Polyethylene Terephthalate
PL	PVOH with Laponite JS
PVOH	Poly Vinyl Alcohol
Rp	Relative Permeability

NOMENCLATURE

A	Area of film (cm^2)
c1	gas concentration inside film
c2	gas concentration outside film
J	diffusive flux of gas through film ($cm^3/cm^2/s$)
L	film thickness
p_1	partial pressure of gas inside film
p_2	partial pressure of gas outside film
$\overline{P}$	gas permeability coefficient ($cc \cdot mil/cm^2/day$)
S	Henry's Law gas solubility coefficient
t	time
H	vertical length
h_1	d-spacing of clay 1
h_2	d-spacing of clay 2
d_a	d-spacing of clay 1 increases
L	lateral length
l_1	length of clay 1
l_2	length of clay 2
b_1	lateral distance between clay 1 platelets
b_2	lateral distance between clay 2 platelets
w_1	width of clay 1
w_2	width of clay 2
$Veff_1$	effective volume of clay 1
$Veff_2$	effective volume of clay 2
Φ	clay layers volume fraction

Φ_1	clay 1 layers volume fraction
Φ_2	clay 2 layers volume fraction

Abstract of Thesis Presented to the Graduate School
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Among a variety of barrier solutions in the packaging industry, polymer clay nanocomposites (PCN) coatings are attractive due to the potential to enhance barrier properties without modifying the base polymer. PCN barrier coatings require exfoliated microstructures of impermeable anisotropic fillers that can extend the tortuous path of permeating gas molecules. The fundamental expression for gas permeation was demonstrated with a variety of models based on Neilson's detour theory to design better barrier properties of PCN. Based on the physical detour path theory, a system using mixture of two particles with different aspect ratios was suggested to obtain higher barrier properties than with either particle alone by extending tortuous paths. The purpose of using two nanoparticle sizes was to attempt to achieve greater filler packing density and thus, greater tortuous path lengths resulting in greater barrier properties. In this study, a model of the proposed PC2N system and an equation to estimate relative permeability (Rp) of PC2N was developed. It was found that no barrier enhancement was achieved at constant volume fraction loadings. As a result it can be concluded that the final Rp of PC2N is governed by total volume fraction of filler. To estimate effects of orientation of nanoparticle platelets in PC2N system on Rp, the orientation parameter (s) and Rp equation

suggested by Bharadwaj were used. It was found that as volume fraction increased, particle orientation become less important. In order to investigate effects of PC2N coating on barrier properties, PC2N solutions were prepared and applied to substrates of known oxygen transmission rate. Results confirmed that barrier properties of PC2N were governed by total effective volume of filler particles, which are well dispersed in polymer matrix. It was found that PC2N coated films with a moderate barrier properties PCN offered benefits over in terms of coating weight and greater optical clarity.

CHAPTER 1
INTRODUCTION

Barrier Properties of Nanocomposites

Polymer Clay Nanocomposite (PCN) materials are some of the most attractive materials in the packaging industry because of its enhanced barrier property when compared to homopolymers or conventional microcomposites [1]. Traditionally, enhanced barrier properties of PCNs are achieved by dispersing impermeable anisotropic fillers such as 2:1 montmorilonite (MMT), which is an expandable dioctahedral smectite with a sufficient aspect ratio, directly into base polymers [2]. While specialized PCN polymers are commercially available, they tend to be highly proprietary and therefore such clays are expensive. Therefore, packaging polymer consumers would prefer to apply a PCN barrier coating system to unmodified polymer substrates.

The mechanism of gas permeation begins when gas molecules are adsorbed on the surface of a film. Subsequently, these molecules diffuse into the amorphous regions of polymer matrix, which have a lower packing density of polymer chains than crystalline regions. Higher packing densities of crystalline regions interrupt the vacancy hopping-based diffusion of gas molecules [3].

In homopolymers, increasing crystallinity or polymer thickness is the only way to enhance barrier properties. However, dispersion of impermeable nanofillers into the polymer matrix efficiently enhances the crystallinity of the polymer resulting in greater barrier properties.

The mechanism of gas permeation in Polymer Clay Nanocomposite (PCN) materials is similar to regular polymers. Thus, when gas molecules pass through a PCN film, clay platelets efficiently increase the diffusion path of gas molecules, as illustrated in Figure 1-1. Thus, longer detour lengths, and lower permeation values are attained by many and/or large platelets embedded in the polymer matrix.

Permeability

Permeation of a gas through a polymer film is a combination of diffusion and solubility. Gas will diffuses through a PCN film at a constant rate if a constant concentration gradient is maintained across the film. The diffusive flux, J, of a gas in a film is the amount (Q) passing through a surface of area (A) normal to the direction of flow during time (t), i.e.

$$J = \frac{Q}{At} \tag{1-1}$$

The diffusive flux of a gas through a film is directly proportional to the concentration gradient, $\frac{\partial C}{\partial L}$, across a surface of thickness (∂L) and is given by Fick's first law:

$$J = -D\frac{\partial C}{\partial L} \tag{1-2}$$

Where, J is the flux per unit area of permeant through the PCN, C is the concentration of the permeant, D is the diffusion coefficient for a particular gas diffusing through a particular film. D reflects the speed at which the permeant diffuses through the PCN.

As shown in Figure 1-2, when a steady state is attained, the flux is constant and Equation (1-2) can be integrated across the total thickness of the film length (L).

$$JL = -D(C_2 - C_1) \tag{1-3}$$

Rearranging the terms

$$J = \frac{D(C_1 - C_2)}{L} \tag{1-4}$$

Equation (1-4) can be rewritten by substituting for J using Equation (1-1).

$$Q = \frac{D(C_1 - C_2)At}{L} \tag{1-5}$$

At sufficiently low concentrations, Henry's law applies and C can be expressed as

$$C = Sp \tag{1-6}$$

Where S is the solubility coefficient, p is the partial pressure or permeant gas. By combining Equation (1-5) and Equation (1-6),

$$Q = \frac{DS(p_1 - p_2)At}{L} \tag{1-7}$$

DS is the permeability coefficient and is represented by the symbol P.

Which can be re-arranged to

$$\overline{P} = \frac{QL}{At(p_1 - p_2)} \tag{1-8}$$

Four assumptions were made in the derivation of permeability coefficient. First, diffusion is at steady state. Second, the concentration-distance relationship through the film is linear. Third, diffusion takes place in one direction only, and, fourth, both D and S are independent of concentration.

Morphology of Polymer Nanocomposites

Non-intercalated

Morphology of PCN can be classified as three typical structures including non-intercalated, intercalated and exfoliated [5]. When polymer cannot diffuse into the intergallery region between two platelets, a microcomposite consisting of micron sized agglomerated clumps of particles or "tactoids" is be obtained. This non-intercalated structure does not offer beneficial barrier properties. In contrast, the other two types of composites morphologies, which can be called as a nanocomposite, offer benefits to barrier properties.

Intercalated / Exfoliated

When several polymer chains are inserted into the intergallery space between particles resulting in fixed, but enlarged interlayer spacing, intercalated morphology is achieved. Fully

exfoliated structures (particles fully dispersed in polymer) are the ideal morphology at small filler loadings to obtain superior barrier properties. Completely separated and dispersed fillers in the polymer matrix results in random arrangement of particles in polymer, which is called an exfoliated structure.

These three typical structures are shown in Figure 1-3. However, various morphologies exist in the real PCN system and a general microstructure of a real exfoliated PCN material can be described as a mixture of intercalated and exfoliated structure with higher degree of exfoliated regions. A specific desired structure of PCN can be tailored by controlling in several ways. Selection of materials for PCN requires some careful consideration. For instance, a natural MMT is a hydrophilic and compatible with polar polymers such as polyvinyl alcohol (PVOH). However, interlayer distances are not sufficient to allow PVOH chains to diffuse into platelet between particles, therefore particle surface modification are sometimes required using organic modifiers. Their modifications typically involve cation exchange reaction.

In general, grafted organic modifiers act as an agent for increasing interlayer space. It is necessary to matching polarity between polymer matrix and a modifier to have more favorable interactions. Processing methods also have significant effects on morphology of the final PCN. Key processing parameters include shear stress, time, and temperature. These parameters must be optimized in order to achieve exfoliation.

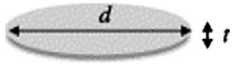
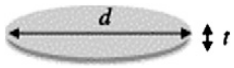
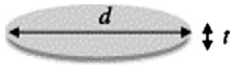
Models

Various models have been proposed to predict barrier properties of platelet filled nanocomposites. These models are usually based on random, parallel platelets perpendicular to the permeation direction. As shown in Table 1-1, these models are sorted by filler type. Through

these models, relative permeability (Rp) may be predicted. A common aspect of these models is the prediction of decreasing Rp with increasing volume fraction of filler.

Factors critical to modeling PCN barrier properties are (1) PCN thickness, (2) longer detour length by intercalated or/and exfoliated morphology, (3) optimum processing control, and (4) consideration of compatibility between polymer and clay.

Table 1-1. Models for predicting barrier properties of platelet filled nanocomposites (adapted from Ref. [6], copyright by Elsevier)

Model	Filler type	Particle geometry	Formulas
Nielsen [7]	Ribbon[a]		$(P0/P)(1-\phi) = 1+\alpha\phi/2$
Cussler [8] (Regular array)	Ribbon[a]		$(P0/P)(1-\phi) = 1+(\alpha\phi)^2/4$
(Random array)	Ribbon[a]		$(P0/P)(1-\phi) = (1+\alpha\phi/3)2$
Gusev and Lusti [9]	Disk[b]		$(P0/P)(1-\phi) = \exp[(\alpha\phi/3.47)0.71]$
Fredrickson and Bicerano [10]	Disk[b]		$(P_0/P)(1-\phi) = 4(1+x+0.1245x2)/(2+x))^2$ where $x= \alpha\phi/2\ln(\alpha/2)$
Bharadwaj [11]	Disk[b]		$(P_0/P)(1-\phi) = 1+0.667\alpha\phi(S+(1/2))$ where S = orientation factor (from -1/2 to 1)

[a] For ribbons, length is infinite, width, w; thickness, t; aspect ratio, $\alpha = w/t$.
[b] For disks, circular shape of diameter d and thickness t; aspect ratio, $\alpha=d/t$

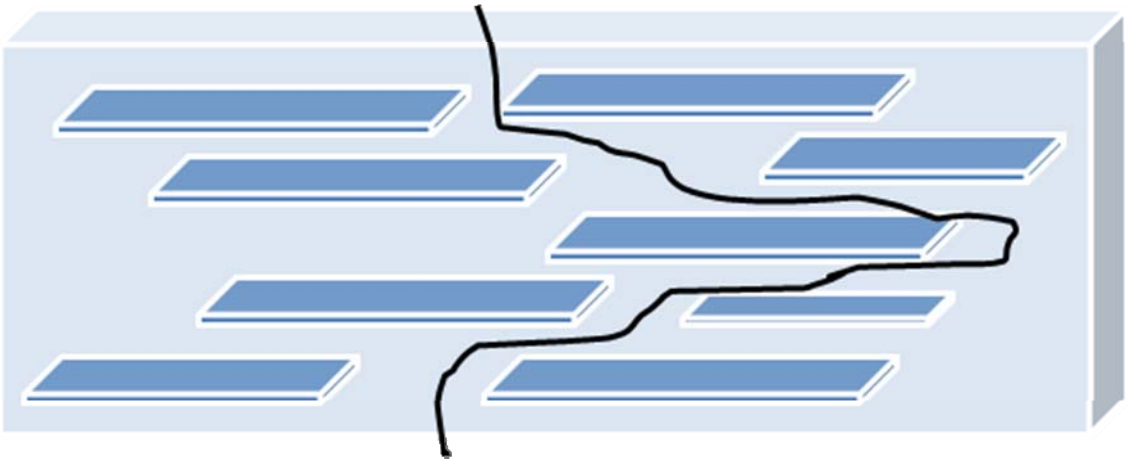


Figure 1-1. Barrier to permeation imposed by nanoparticles imbedded in a polymeric matrix.

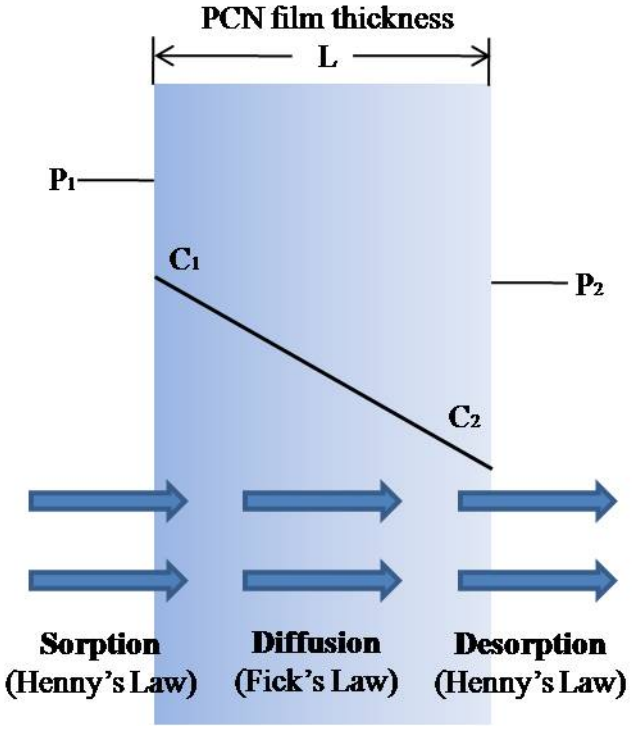


Figure 1-2. Permeability model for gas transfer through a polymer

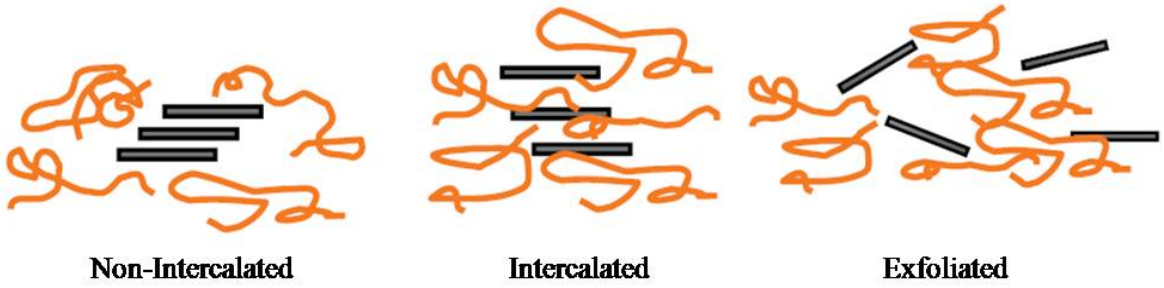


Figure 1-3. Illustration of different states of dispersion of organ clays in polymers

CHAPTER 2
DESIGN OF POLYMER CLAY 2 NANOCOMPOSITE (PC2N)

Introduction

Preparation of an effective PCN requires consideration of the microstructure of clay platelets. Typically, published research has shown one type of nano-particle is used to create PCNs [12]. However, it believed that a mixture of two particles with different sizes and aspect ratios may provide greater tortuous paths and therefore, greater barrier properties than PCNs produced from just one particle variety. Hence, PCN produced with two particle types is referred to as "PC2N." Figure 2-1 shows the concept of enhancing particle packing density using two types of nano-particles [21]. A structure as shown in Figure 2-1 should have the same effect as increasing total volume fraction of particles, which would enhance barrier properties of the PCN.

A model was developed to predict Rp of PCN consisting of two types of clay particles having different aspect ratios. The Rp of the PC2N can be calculated using the following equation (2-1),

$$R_P = \frac{2H_1(1-\phi_T)}{\left(L_1 + L_2\left(\frac{\phi_2}{v_{eff\,2}}\right)\right) + 2H_1} \tag{2-1}$$

Where, H and L are vertical length (h1+w1) and lateral length (l1+b1) occupied by clay 1, respectively, h1, w1, l1, b1, Φ2, Veff2 are d-spacing, width, lateral distance between two particles, volume fraction of filler and effective volume of a clay particle. Subscripts 1, 2 and t represent clay particles having larger and smaller aspect ratio and both, respectively [21]. Where, effective volume can be calculated using Equation (2-2) and (2-3).

$$v_{eff\,1} = (l_1 + b_1)^2 (h_1 + w_1) \tag{2-2}$$

$$v_{eff\,2} = (l_2 + b_2)^2 (h_2 + w_2) \tag{2-3}$$

Based on this model for PC2N systems, barrier property prediction may be made.

Consideration of PC2N Barrier Property

Volume Fraction

When two different types of clays are dispersed in a polymer matrix, the size effect of two particles has to be known. High barrier properties may be achieved by designing the maximum detour length in the microstructure of composite materials.

Effects of relative size of the smaller nanoparticle (clay2)

Figure 2-2 shows effects of relative size of clay 2 on Rp of PC2N. The relative size of clay 2 appears to offer no effect on decreasing permeability. Figure 2-2 predicts constant Rp values at each volume fraction of clay 2. Higher aspect ratio of clay 2 promises a longer tortuous path, but this requires a lower quantity of clay 2 possibly resulting in a compensation effect. Therefore, total distance, d' in the system is similar for all aspect ratio of clay 2. However, as clay 2 volume fraction increases, Rp decreases due to increased number of platelets of clay 2 in the same effective volume created by clay 1 particles. From this relationship, it can be deduced that volume fraction of clay 2 is more a significant factor than size of platelets at fixed volume fraction of clay 1; this should result in a composite with better barrier properties.

Effects of d-spacing of larger clay particle (clay 1)

Another critical factor in the process of making PC2N is the choice of alkyl ammonium ions. Ion exchange of cations (Na^{2+} or Ca^{2+}) in the intergallery region of natural clays by alkyl ammonium ions leads to expansion of this region as well as modification from hydrophilic to organophilic, thus enabling diffusion of polymer chains. The number of carbons in alkyl ammonium and the layer charge of the clay particle will determine the arrangement of alkyl ammonium chains in the intergallery region. Diffusion of polymer chains will be determined by shear forces and molecular weight of polymer [13].

Therefore, d-spacing between clay platelets vary depending on parameters that can be controlled during processing. In the PC2N system, d-spacing of clay 1 affects Rp as shown in Figure 2-3. The larger the d-spacing of clay 1 at constant volume fractions of two clays, the higher the Rp value. This phenomenon may be caused by a lower number of clay 1 platelets per unit volume as increased d-spacing of clay 1 leads to more sparse distribution of clay 1, corresponding to decreased tortuosity. There would be no increment in d_a contributed by clay 2 particles in fixed volume fraction of clay 2. Effects of increased volume fraction of clay 2 on Rp has the same tendency as the one shown in Figure 2-2. That is, detour length increased by insertion of clay 2 into the intergallery region has constant value when the volume fraction of clay 2 is fixed. D-spacing can be increased by cation exchange and shear processing, but it is also possible to increase d-spacing by insertion of clay 2 between clay platelets 1.

Effects of arrangements of smaller (clay 2) particles

The preceding expected Rp values are based on the assumption that there are no local changes in d-spacing of clay 2 (h_2) as d-spacing of clay 1 (h_1) generated during the insertion process can result in a deviation from the general barrier properties. However, the case that some increment of Δh can occur as shown in Figure 2-4, should be considered. This increase in d-spacing would occur by insertion of exfoliated clay 2 in the polymer matrix into the intergallery region with the aid of cation exchange reactions and shear processes. Thus $h_1^{'}$ is required to be substituted for h_1 to estimate Rp of this material and $h_1^{'}$ can be defined as shown in Equation (2-4).

$$h_1^{'} = l(w_2 + h_2) - h_2 + 2h_{12} \tag{2-4}$$

Figure 2-5 illustrates how the arrangement of clay 2 particles affects d-spacing of clay 1 corresponding to its Rp. When a constant number of platelets of clay 2 at a fixed volume fraction

are dispersed in the intergallery of clay 1, more layers are formed, therefore reducing the number of clay platelets in each layer. This means that although d-spacing can be increased by creating more layers, the possibility that a diffusant encounters a platelet when passing by a layer would be lower. As a result, effects of increased tortuous path cannot exceed a critical Rp by compensation effects of d_a of clays as d-spacing of clay 1 increases. The initial dramatic decrease in Rp when $h_1^{'}$ approaches to 0 suggest that d_a plays a key role by forming a densely packed arrangement in the reduction of permeability. Therefore, densification of platelets with higher volume fraction may be the ideal approach to achieve a superior barrier material. However, when the spacing between clay platelets including a lateral distance is not enough for a diffusant to bypass, good barrier properties cannot be obtained. In other words, the state of aggregation of particles can have significant effect on permeability resulting in increased Rp at higher volume fraction. Therefore, an understanding of the aggregation is required for all types of nanocomposites materials since this not only affects barrier properties, but also other physical properties. In this work, the state of aggregation of clay 1 particles is investigated by varying the width of clay 1 from 0 to 1000 nm in Equation (2-1).

Effects of state of aggregation on relative permeability (Rp) of PC2N system

As shown in Figure 2-6, a higher degree of aggregation results in higher Rp because aggregates of particles that are not separated from the stacked agglomerate lower N_1, shorten the detour length and even reduce the possibility of successful insertion of clay 2. This figure also shows that as volume fraction of clay 2 increases, the gap between Rp of initial point at w_1 of 1 nm and one obtained at w_1 of 1000 nm is decreased. Increased volume fraction of clay 2 will result in increased d_a due to insertion or dispersion in polymer matrices comparing to lower volume fraction as shown Figure 2-7. If the assumption that d-spacing of clay 1 is determined

only by a cation exchange reaction and shear forces, Rp will depend on d-spacing of clay 1 at fixed ratio of clays. This dependence is shown in Figure 2-8. As the volume fraction of clay 1 increases, Rp of all d-spacing conditions will converge to 0 at the volume fraction of 0.9. The dense arrangement of clay 1 results in lower Rp and therefore, there would be no change in the effect of d_a caused by clay 2 once its volume fraction is set.

Orientation

Previous studies on barrier properties based on tortuosity or diffusion detour theory have focused on the aspect ratio of clay platelets [14-15] and volume fraction of filler [16-18]. Existing barrier models are based on the one common assumption that all clay platelets are dispersed in an orientation that is normal to the diffusant. However, the 3-dimensional displacement of clay platelets in the actual exfoliated PC2N system will cause some deviation from theoretical permeability. Bharadwaj reported the effect of orientation of clay platelets on Rp of PCN [17]. Based on this work, effects of orientation of clay platelets on Rp of PC2N can be estimated as shown in Figure 2-9. This figure shows that enhanced relative permeability (Rp) is achieved when orientation parameter (S) approaches 1. Low Rp can be obtained by increasing aspect ratio of clay platelets as described in Figure 2-9.

Bharadwaj et al. (2002) predicted a following equation, which considers orientation in predicting Rp [17].

$$\frac{P}{P_0} = \frac{1-\phi}{1+\frac{L}{2W}\phi\left(\frac{2}{3}\right)\left(S+\frac{1}{2}\right)} \tag{2-5}$$

Equation (2-6) was derived from equation (2-5), for use with PC2N.

$$\frac{P}{P_0} = \frac{1-(\phi_L+\phi_C)}{1+\left(\frac{L_1}{2W_1}\phi_1+\frac{L_2}{2W_2}\phi_2\right)\left(\frac{2}{3}\right)\left(S+\frac{1}{2}\right)} \tag{2-6}$$

Figures 2-10, 2-11, and 2-12 are plotted by Equation (2-5) and (2-6). All Rp values were calculated using actual size data of Cloisite Na^+, and Laponite JS. Both clays have similar tendency that Rp is increased as orientation angle of clay platelets increasing. However, Cloisite Na^+ has slightly lower Rp due to its larger aspect ratio.

Effects of orientation of polymer chains on barrier properties of a polymer were examined by Somlai et al. (2005) [19]. The relationship between orientation of polymer chains and permeability is not well reported in their work.

It is well known that processes that oriented polymer films tend to enhance strength and barrier properties. It is believed that greater molecular alignment causes an increase in crystallinity and therefore, barrier properties. When orientation is performed on polymer films with clay nanoparticles it is likely that the particle alignment is enhanced as well.

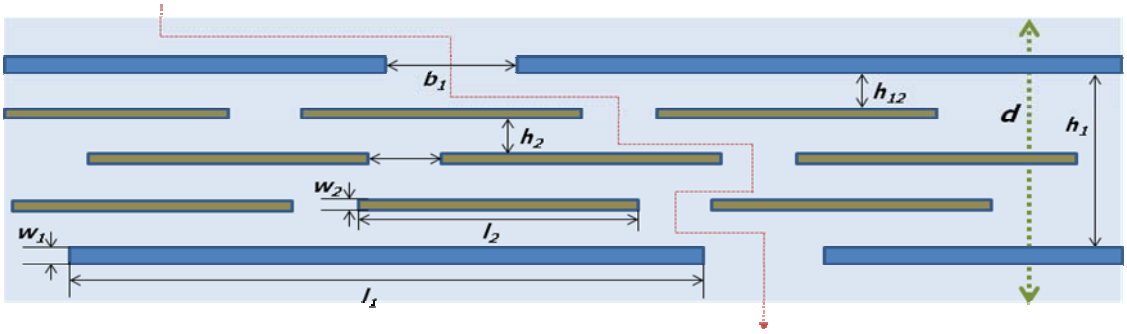


Figure 2-1. A predicting schematic of PC2N system.

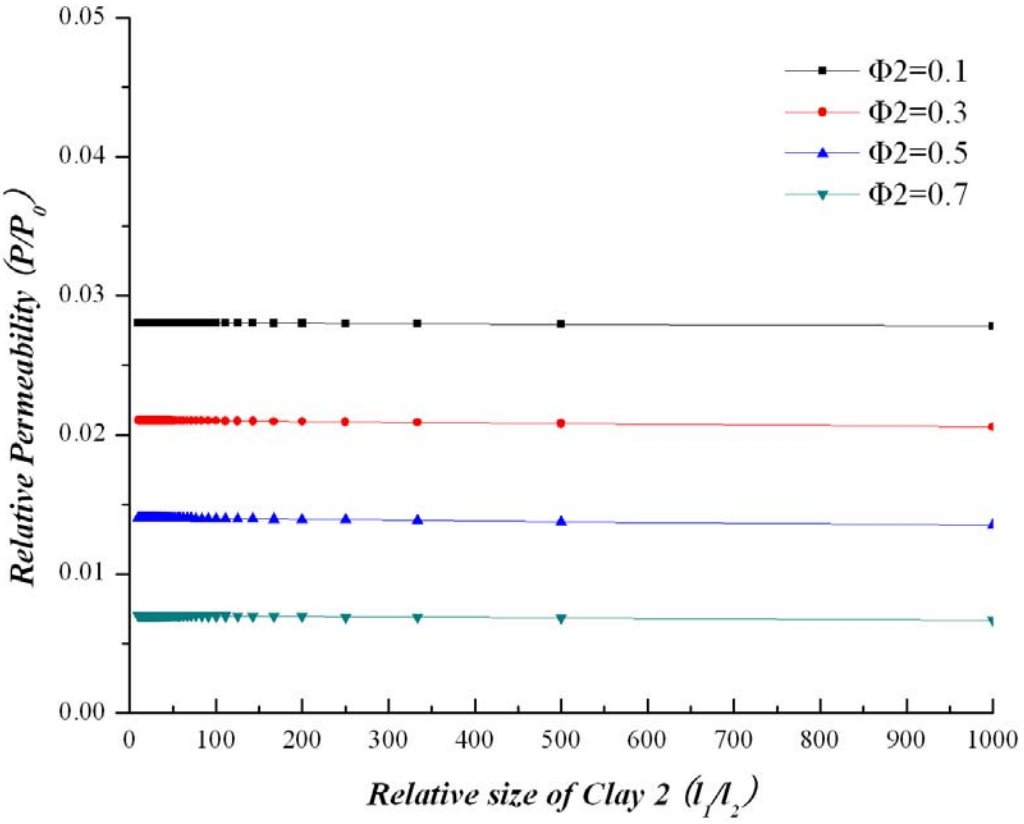


Figure 2-2. Effects of relative size of clay 2 on relative permeability of PC2N: obtained by equation (2-1) (l_1=100 nm, l_2=0.1 ~ 10 nm, w_1=w_2=1 nm, b_1=10 nm, b_2=l_2/10, h_1=1 nm, h_2=0.001 nm, 1=0.1)

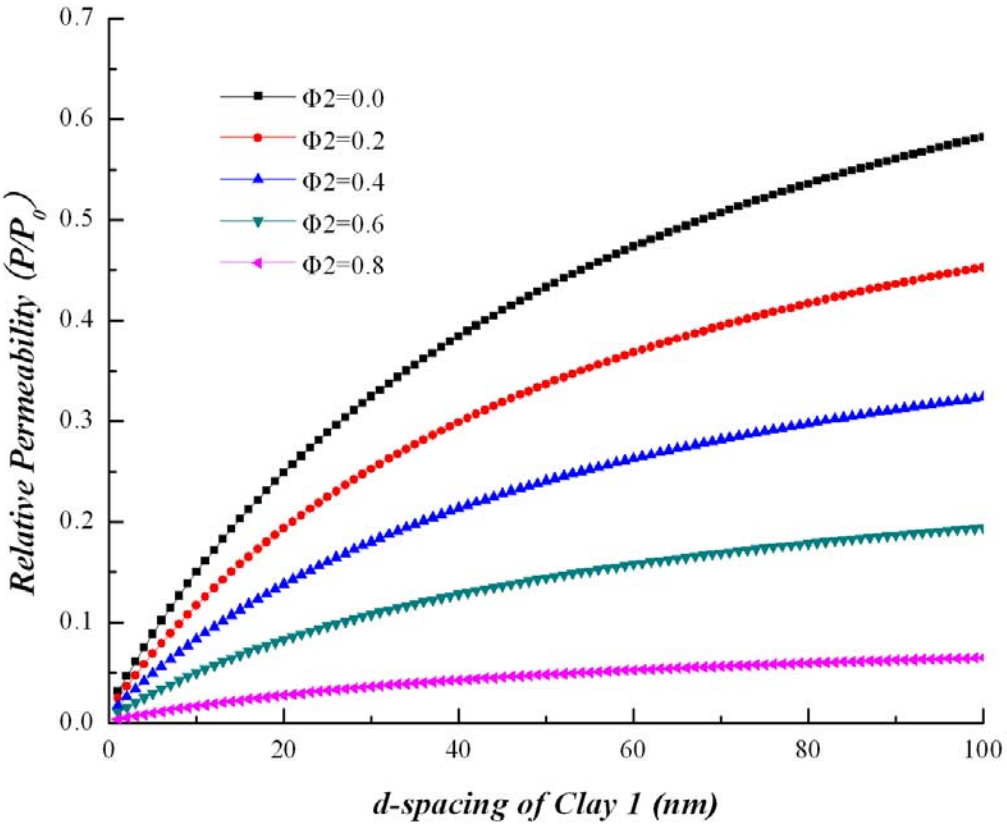


Figure 2-3. Effects of d-spacing of clay 1 on relative permeability of PC2N: obtained by equation (2-1) (l_1=100 nm, l_2=5 nm, w_1=w_2=1 nm, b_1= l_1/10, b_2=l_2/10, h_1=1 ~ 100 nm, h_2=0.001 nm, ϕ_1=0.1)

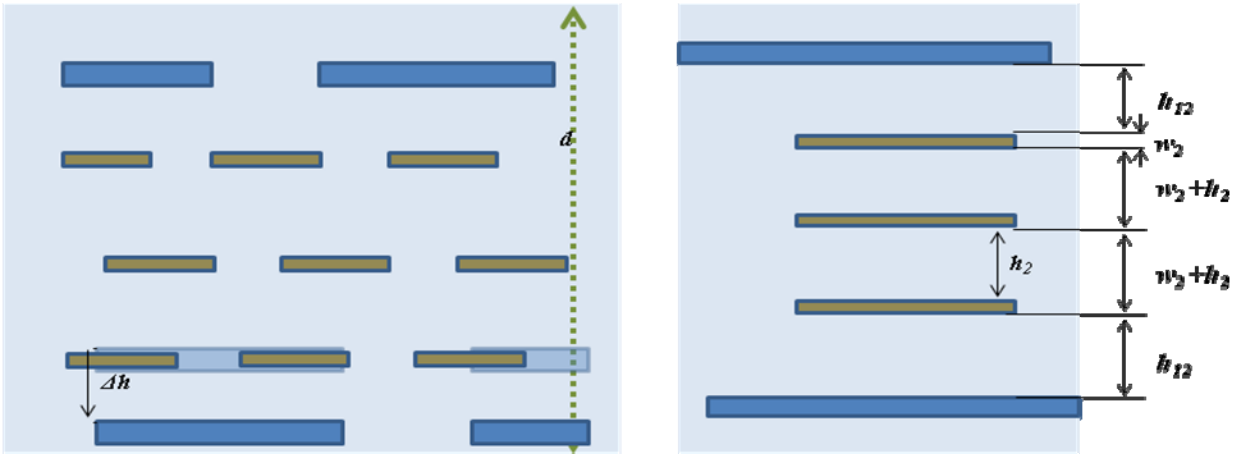


Figure 2-4. Schematic diagram showing effects of changes in d-spacing

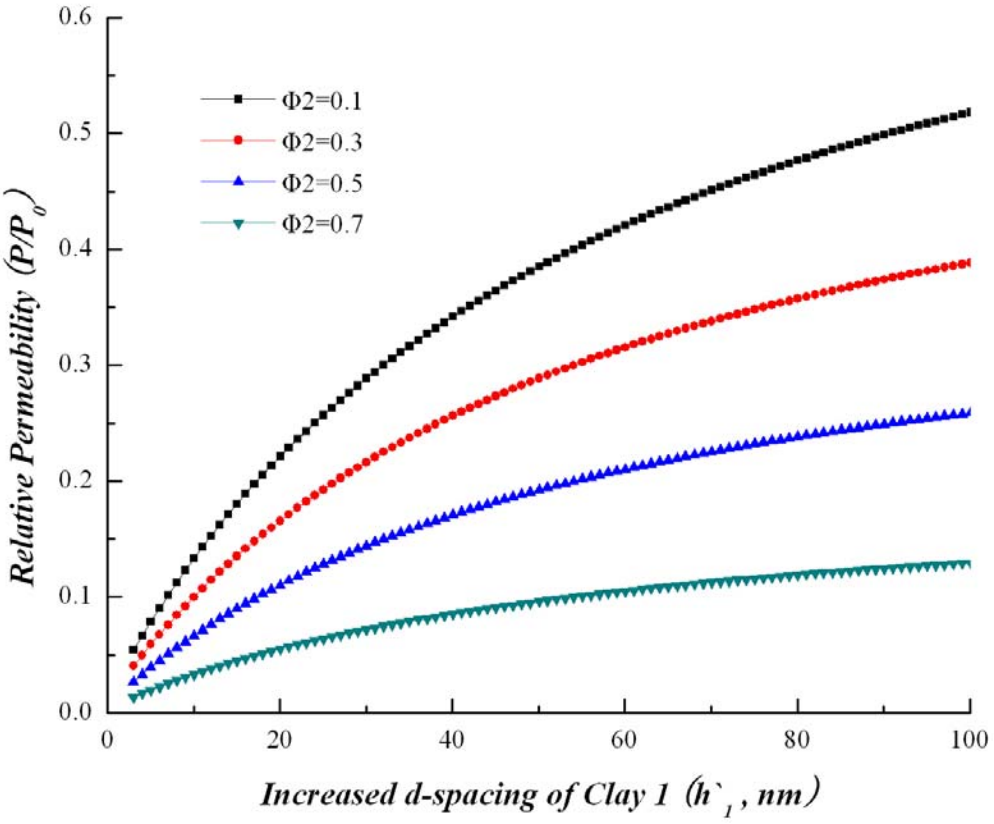


Figure 2-5. Effects of increased d-spacing of clay 1 on relative permeability of PC2N obtained by equation (2-1) (l_1= 100 nm, l_2= 5 nm, w_1=w_2=1 nm, b_1= l_1/10, b_2=l_2/10, Φ_1=0.1)

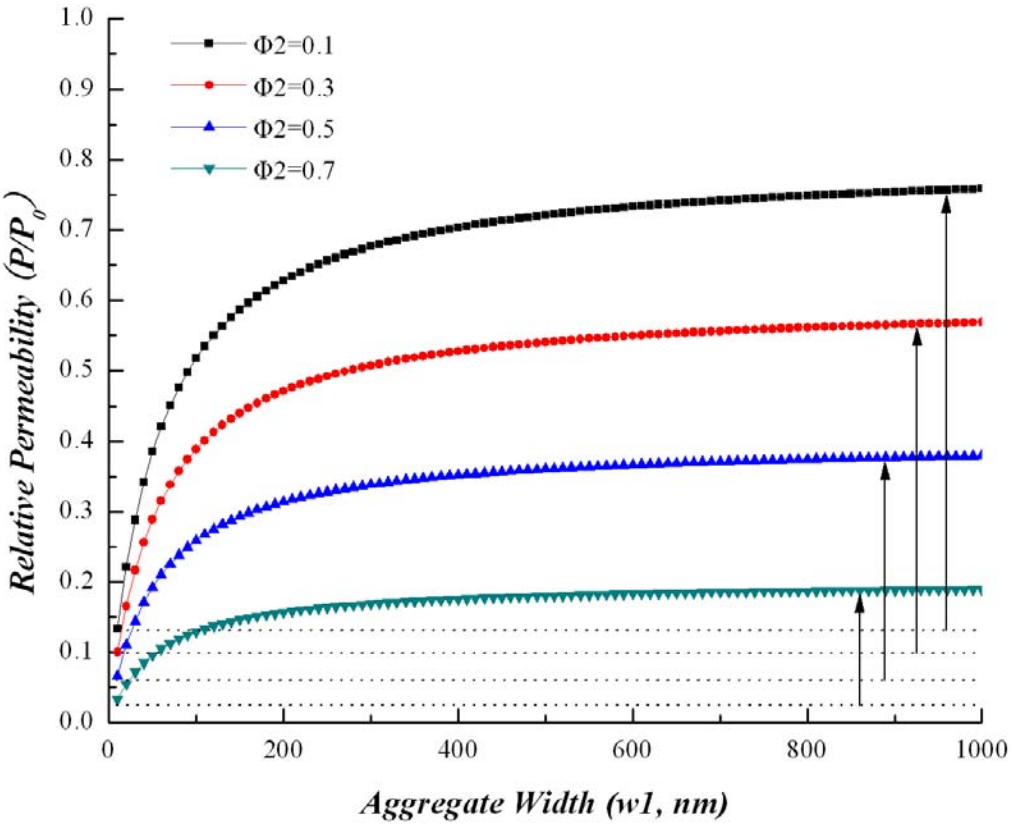


Figure 2-6. Effects of the state of aggregation of clay 1 on relative permeability of PC2N: obtained by equation (2-1) (l_1= 100 nm, l_2= 5 nm, w_2 = 1 nm, b_1= l_1/10, b_2=l_2/10, h_1= 1 nm, h_2= 0.001 nm, Φ_1=0.1)

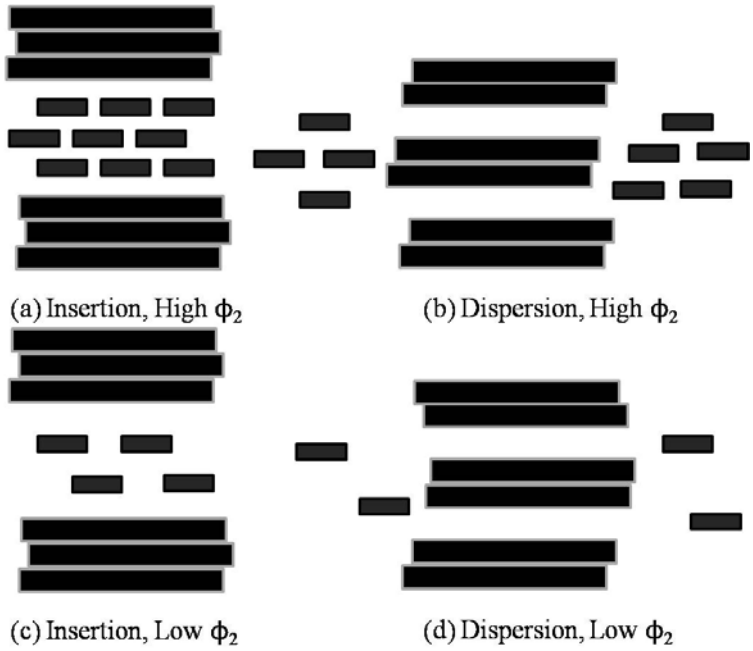


Figure 2-7. Arrangement of clay 2 particles in PC2N system: (a) Insertion of high volume fraction of clay 2 particles into intergallery regions of clay 1, (b) Dispersion of high volume fraction of clay 2 in a polymer matrix, (c) Insertion of a low volume fraction and (d) Dispersion of a low volume fraction.

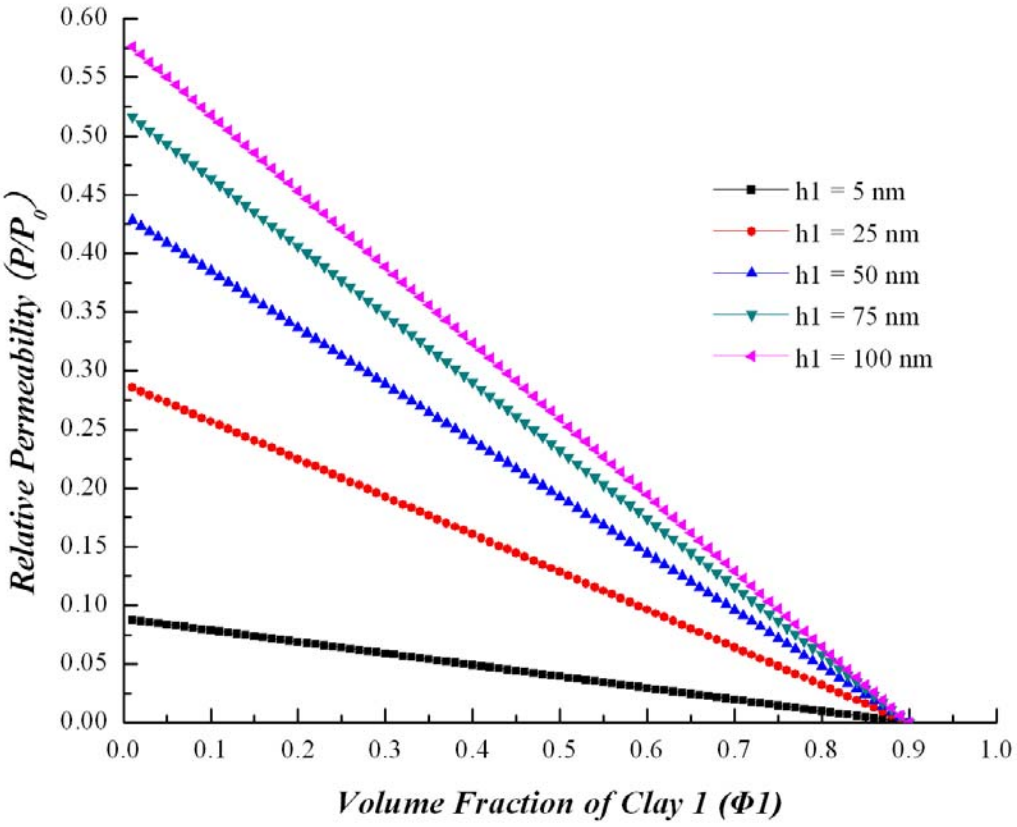


Figure 2-8. Effects of the volume fraction of clay 1 on relative permeability of PC2N obtained by equation (2-1) (l_1= 100 nm, l_2= 5 nm, $w_1 = w_2$ = 1 nm, $b_1 = l_1/10$, $b_2 = l_2/10$, h_2= 0.001 nm, Φ_2= 0.1, Φ_2=0.01 ~ 1)

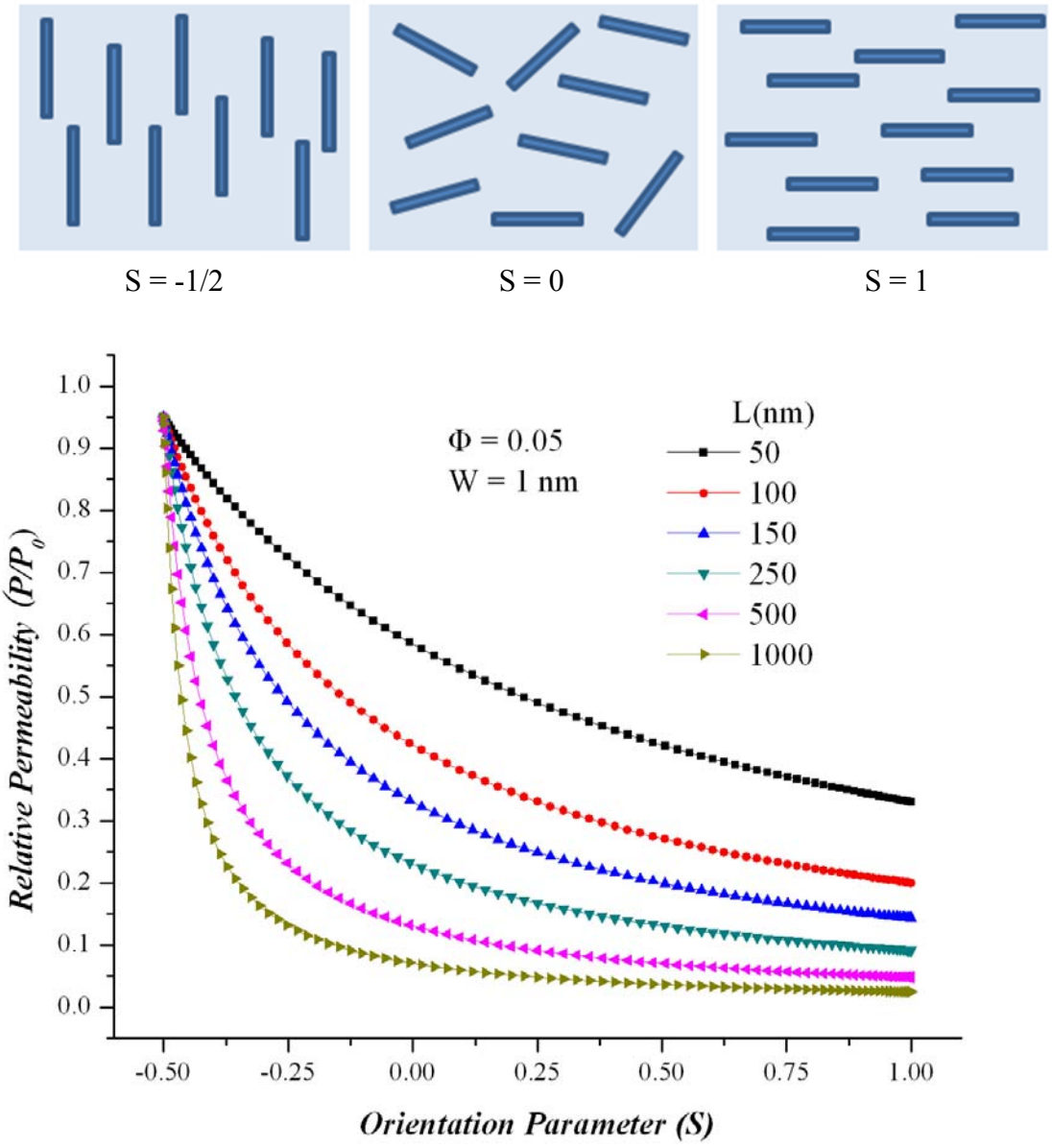


Figure 2-9. Effects of particle orientation on relative permeability in exfoliated nanocomposites

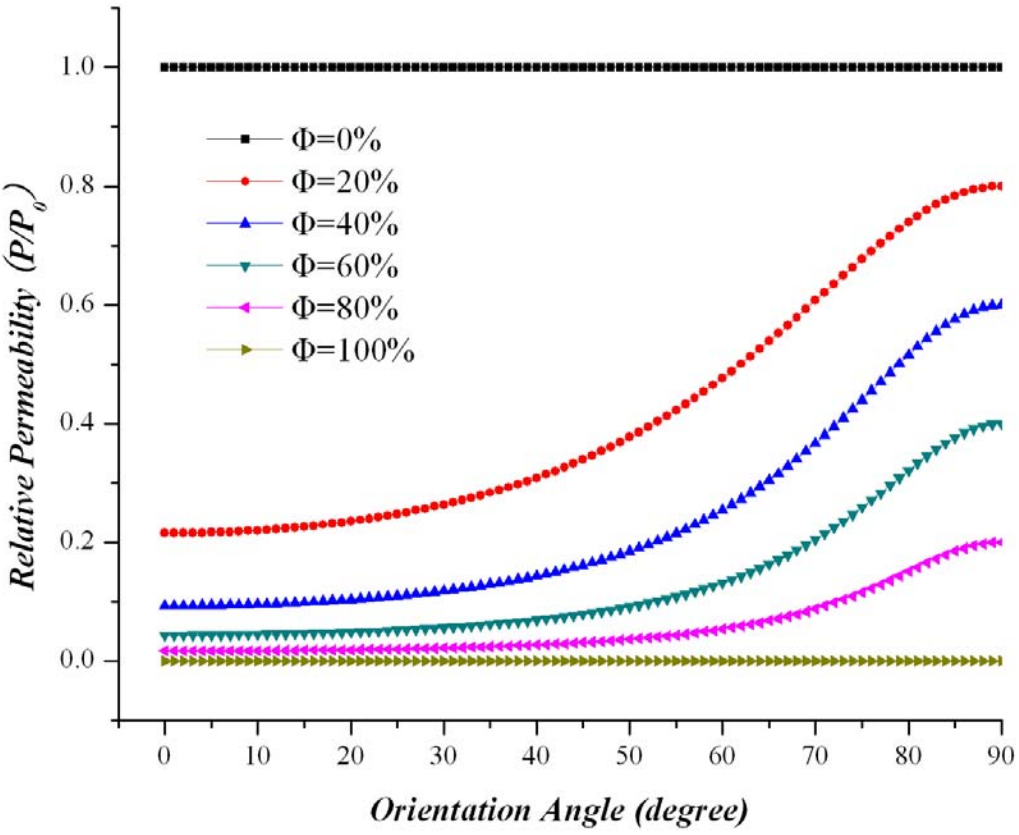


Figure 2-10. Effects of orientation angle (degree) and volume fraction (Φ) on relative permeability of Laponite JS

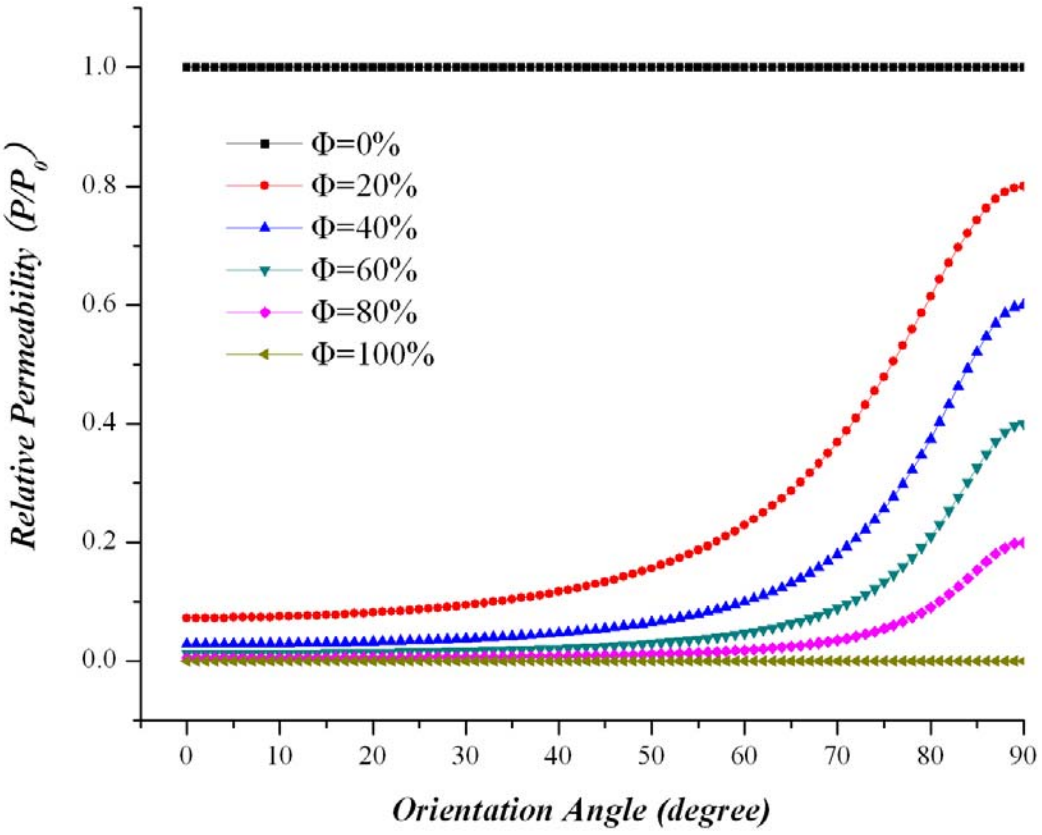


Figure 2-11. Effects of orientation angle (degree) and volume fraction (Φ) on relative permeability of Cloisite Na^+

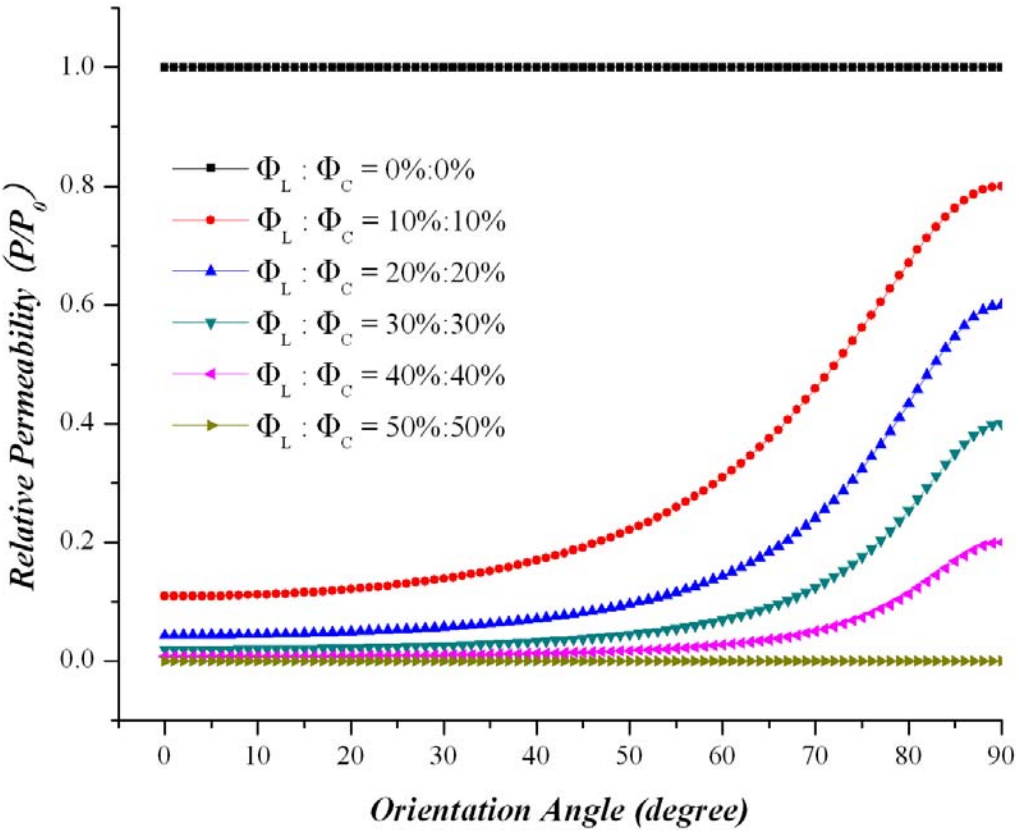


Figure 2-12. Effects of orientation angle (degree) and volume fraction (Φ) on relative permeability of mixture composed of Laponite JS and Cloisite Na^+

CHAPTER 3
INCORPORATION OF NANOPATICLE MIXTURES TO ENHANCE BARRIER PROPERTIES OF POLYMER FILMS

Introduction

Long shelf-life foods require high barrier packaging. Traditional approaches to producing high barrier materials involve multi-layer laminate films. Each layer of a multi-layer film contributes to overall properties of the structure. Multi-layer food packaging structures used by the United States military typical contain an aluminum foil layer. The foil layer provides high barrier properties. However, foils are prone to pinholes, which create quality control issues. Also, processes involving foils prevent use of microwaves. Therefore, a high-barrier film without foil is desired.

Polymer clay nanocomposites (PCN) are attractive in packaging applications due primarily to enhanced barrier properties [20]. Improvements to barrier properties with low concentrations of clay nano scale particles have been reported by many research groups [16,18]. Several models have been suggested to predict gas barrier properties in polymers and PCN materials. According to Nielsen's model (1967) [7], barrier properties of PCN can be changed by the microstructure of particle-polymer matrix as well as the aspect ratio of particles. Nielsen proposed that the mechanism of enhanced barrier was increased diffusion path. Other models to estimate the relative permeability (Rp) of composite materials are based on this detour path model. Therefore, the microstructure of clay particles is the crucial factor which determines the barrier properties of a composite material.

Three particle-polymer microstructures are generally recognized that are related to degree of dispersion of particles in polymer. These are referred to as non-intercalated, intercalated and exfoliated and may be loosely interpreted as poorly dispersed with irregularly spaced aggregates,

dispersed with regularly spaced aggregates, and completely dispersed particles, respectively. Exfoliated structures provide superior gas barrier properties when compared to the other two structures.

Incorporation of inorganic particles into polymers is difficult due to high temperatures, high viscosities and polarity incompatibilities between particles and polymer. Therefore, commercial PCN materials tend to involve proprietary processing technologies and command high prices. Work by Kwak et al. (2009) [24] explored the possibility of developing an aqueous based PCN that could be applied as a coating or paint and then dried in place to achieve a high barrier coating on inexpensive, commodity base materials.

Development of candidate PCN coating solutions requires consideration of particle-polymer compatibility, particle dimensions (aspect ratio) and coating adhesion onto base polymers. Properties of PCN materials depend on properties of particles including layer charge, water adsorption capacity, cation exchange capacity (CEC), aspect ratio, viscosity of the final composite system, and the arrangement of cation exchange ions in the intergallery region between negatively charged particle layers. Spacing between two clay platelets can be enlarged by via cation exchange. Once the intergallery region is opened, exfoliation of clay platelets in the polymer matrix usually can be achieved with high shear processing [13].

For any coating to be effective, it must bind well to the substrate. Even if a PCN coating were used within a multilayer film structure good adhesion would be required to achieve high barrier. Adhesion is enhanced through increased surface area and increased concentrations of polar functional groups on surfaces. Various techniques have been proposed to modify the surface of polymeric materials such as corona discharge [22], plasma [23] and chemical modification. Atmospheric plasma treatment is becoming popular due relative treatment

uniformity and the ability to modify gas mixtures to suit applications. Plasma is created by applying energy to a gas to produce excited species and ions. Polymer film surfaces are activated by plasma treatment though chemical reaction with and etching. Optimization of conditions for effective plasma treatment was done previously by Kwak et al. [24].

Therefore, the purpose of this work is to (1) develop a model to predict relative permeability, Rp, of nano-composite incorporating two different particles (Laponite JS and Cloisite NA^+ - referred to as PC2N), (2) prepare PC2N solutions and apply to substrates of known oxygen transmission rate in order to experimentally measure Rp, and (3) produce multilayer barrier films using PC2N applications that provide promise as a replacement for foil in high-barrier, multi-layer films.

Materials and Methods

Materials

PCN and PC2N solutions were made with a synthetic layered silicate, Laponite JS and a natural montmorillonites, Cloisite Na^+ **(**Southern Clay Products, Louisville, KY). PVOH was supplied by Scientific Polymer Product, Inc. The specific informations of materials used for the preparation of composite films are listed in Table 3-1.

Organic ammonium chloride (OAC), [2-(Acryloyloxy)ethyl]-trimethyl ammonium chloride was used for intergallery modification. A multi-layered film consisting of oriented polypropylene (OPP) and linear low-density polyethylene (LLDPE) (Master Packaging Inc., Tampa, FL) was used as a substrate for coating.

Preparation of PCN and PC2N Solutions

Two PCN solutions containing Laponite JS or Cloisite Na^+ respectively were prepared using the same method. At first, OAC buffer solution which amount is compare to 1 wt% of clay

was added into a corresponding amount of deionized water at 40°C and pH 10 were premixed for 2-3 minutes with a magnetic stirrer. Each clay powder was added each beaker gradually to prevent aggregation. Prepared clay solutions were placed at room temperature for about 1 day to allow for cation-exchange in order to increase inter-particle distances. 8 wt% polymer stock solutions were prepared by dissolving PVOH in deionized water at 80°C and stirring with magnetic stirrer for 6 - 8 hours. Prepared PVOH stock solution was added to clay solutions and mixed for 1 hour with a magnetic stirrer and then mixed with a high shear mixer (KadyMill-L , Kady® International, Scarborough, ME) for 10 minutes. Prepared PCN solutions were placed in a hood at ambient temperature for 3–10 hours depending on viscosity in order to allow entrained air bubbles to dissipate.

To prepare a PC2N solution, 8wt% polymer stock solution was prepared by dissolving PVOH in deionized water at 80°C and stirring with magnetic stirrer. Each clay solution was prepared in the same manner described in the preparation of PCN solution and placed at room temperature for the cation exchange reactions. Laponite JS solution was added to polymer stock solution with agitation. Vigorous agitation with a mechanical stirrer for 10 minutes was conducted to prepare an exfoliated Laponite JS in a PVOH matrix.

Prepared PCN solutions consisting of PVOH and Laponite JS are added to Cloisite Na^+ clay solutions. Further, strong shear force with a mechanical stirrer was required for the final insertion process. This process was done by inserting PVOH mixed with relatively smaller Laponite JS particles into the intergallery region of Cloisite Na^+. To investigate effects of the ratio between Cloisite Na^+ and Laponite JS in the PC2N system on OTR ($cc/m^2/day$) values, 10:0, 7:3, 5:5, 3:7, and 0:10 of ratios were used.

Preparation of Coated Samples

Atmospheric pressure plasma (APP) treatments were performed using a Dyne-A-Myte VCP (Enercon Industries Co., Menomonee Falls, WI). Air and nitrogen gas (about 50/50) were used to create plasma. The ranges of flow rate of nitrogen gas, working distance, times of treatment, and the speed of conveyer belt are 10 – 25 (l/min), 5 – 25 (mm), 2 – 4, and 20-30, respectively. Modified surfaces of substrate films were coated using coating rods with PCN solution. Coated samples were dried for 24 hours at 40°C in a vacuum oven to abstract micro bubbles.

OTR Measurements

Oxygen transmission rates of substrate, PVOH, PCN, and PC2N samples were measured at 0 RH% and 23°C in accordance with the procedure described in ASTM D3985-05[46] and ASTM F1927-98[47] using a Model OX-TRAN 2/20MH (Mocon Corporation, Minneapolis, MN). Permeation cell area was 50 cm^2. Following figure 3-1 is schematic of OTR measurement facility.

Results and Discussions

OTR measurements of three commercially produced multi-layered films were examined to determine which would be best suited for observing effects of PCN and PC2N coatings on OTR. Figure 3-2 shows results for base films which are three double layered film constructions including oriented poly propylene / linear low density polyethylene (OPP/LLDPE), polyethylene terephthalate / polyethylene (PET/PE) and biaxially oriented nylon / polyethylene (BON/PE). The substrate with the greatest initial OTR (OPP/LLDPE) was chosen for this work..

Figure 3-3 shows effects of coating layers on OTR. OTR values of PVOH (P), PVOH with Laponite JS (PL), PVOH with Cloisite Na^+ and Laponite JS (PCL) coated samples were measured. OTR of PVOH-coated sample about 10 % of OPP/LLDPE substrate film.

Generally, increasing crystallinity of homo-polymers tends to decrease gas diffusion rates and therefore OTR as well. Practical limits to degree of crystallinity limit this benefit. Addition of nano particles simulates additional crystallinity, thus reducing OTR beyond what is possible by the polymer alone (Figure 3-3). In this work, PCL-coated sample showed the lowest OTR, with PL-coated samples showing slightly higher OTR than PCL-coated samples.

These results showed that a mixture of different sized particles (PCL-coated samples) offered only a slight improvement over one type of particle (PL-coated samples). This is likely due to the fixed filler volume of 8% filler by weight used to prepare all samples. Perhaps a greater benefit could be seen if particle packing density is shown to increase with the mixture of particles.

Effects of different aspect ratios in PC2N systems on OTR are identified by varying the ratio of Cloisite Na^+ to Laponite JS (Figure 3-4). There was no significant difference in OTR values based on weight percent (wt %). However, when the volume of Laponite is compared to that of Cloisite in terms of their densities, Laponite can occupy more space in the system than Cloisite for the same weight of clay used. This is contrary to results predicted from the model described in Chapter 2.

Figure 3-5. shows that lower OTR resulted from increasing clay weight percent. This tendency was confirmed by our previous work that examined Laponite JS as shown in Figure 3-6 [24]. Figure 3-6 shows OTR as a function of clay concentration loaded in the final dried PL film. The lowest OTR value was shown at 50 wt% of clay in the final dried film and, in the range of

20 to 40 wt% of clay concentration, there was no significant difference in OTR values. This plot also shows a dramatic increase in OTR values starting at 50 wt% of clay concentration which was likely due to particle aggregation and film stability as clay concentration increased.

In this study, enhanced barrier properties were shown to follow increased total effective volume of filler particles that were exfoliated in a PC2N system. Also increasing total volume fraction of filler within a practical range is a relatively simple way to improve barrier property by about one order of magnitude for relatively high transmitting films such as OPP/LLDPE. Although PC2N system did not show significant differences in barrier properties, PC2N composite films (mixture of particles) appeared to offer better optical clarity than Poly Vinyl Alcohol / Cloisite Na^+ (PC) films with comparable OTR.

Table 3-1. Specific information of material used for PCN and PC2N composite films

Polymer matrix LMW[1] PVOH		Inorganic filler Laponite JS	Cloisite Na^+
MW[2]	3,000	Density (g/cm^3)	0.95	2.86
Viscosity (CP)[3]	3~4 cp	Aspect ratio	25	75~150
		d-spacing[4] (nm)	0.001	1.17

1, Low molecular weight; 2, Number-average molecular weight; 3, 4% aqueous solution at 20 ^oC; 4, $d_{(001)}$

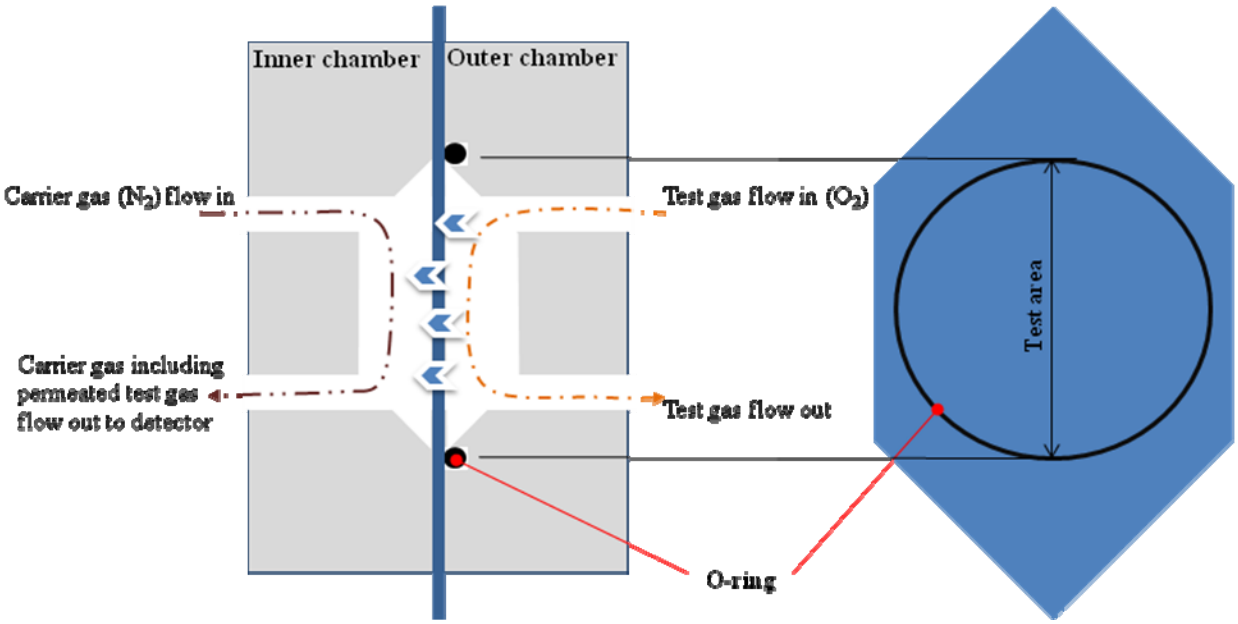


Figure 3-1. Oxygen Transmission Rate (OTR) instrument schematic

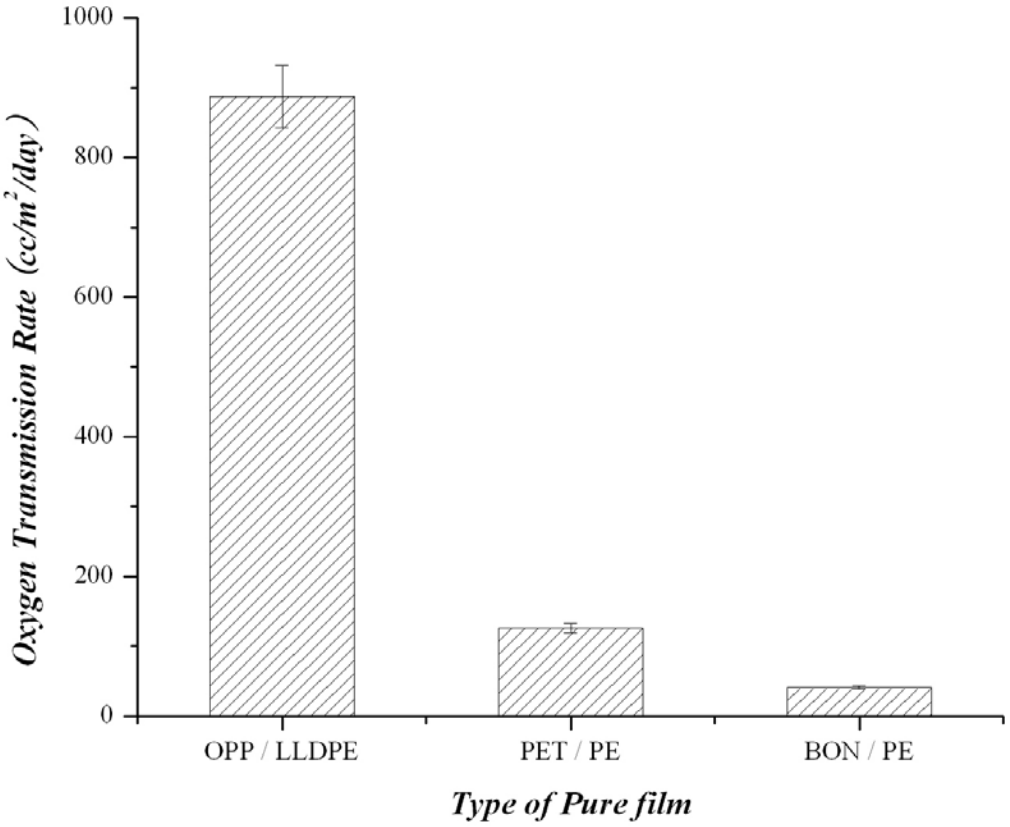


Figure 3-2. Substrate polymer film Oxygen Transmission Rate

(a)

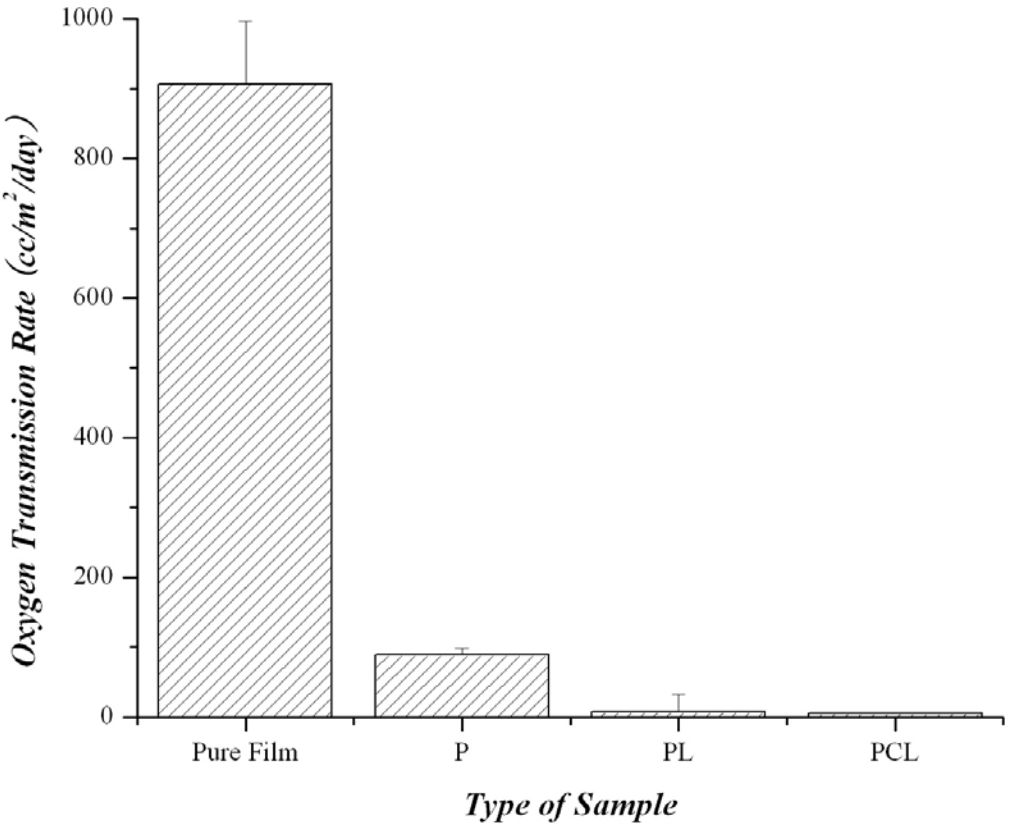


Figure 3-3. OTR and (a) Relative Permeability (b) of Samples; P (8wt% of PVOH), PL (8wt% of PVOH and Laponite JS), PCL (8wt% of PVOH, 4wt%of Cloisite Na+ and Laponite JS)

(b)

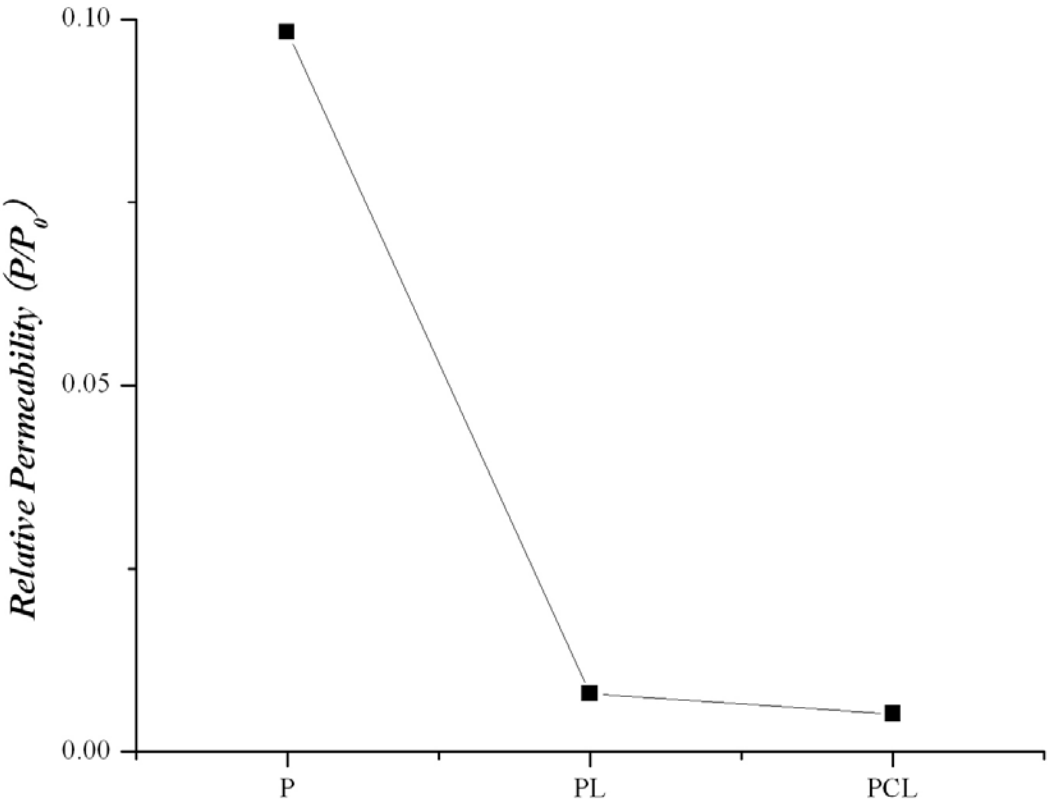


Figure 3-3. Continued

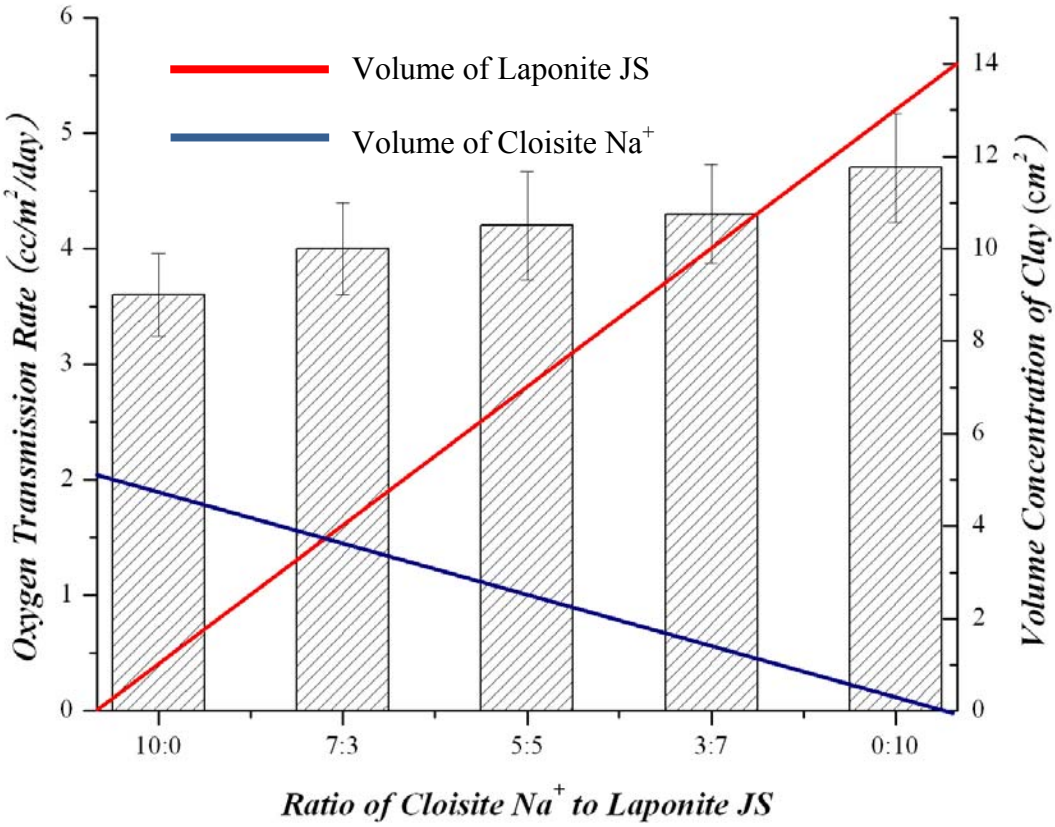


Figure 3-4. Oxygen Transmission Rate versus Ratio of Cloisite Na+ to Laponite JS

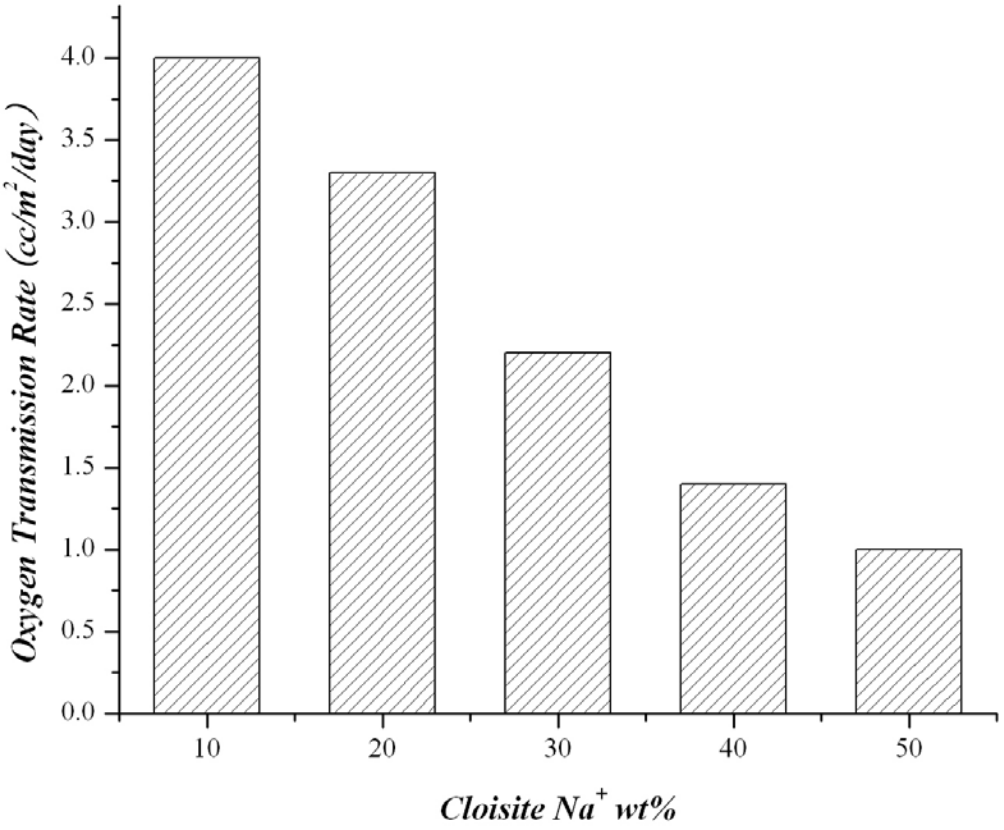


Figure 3-5. Oxygen Transmission Rate vs. PVOH with Cloisite Na^+ film according to Cloisite Na^+ wt%

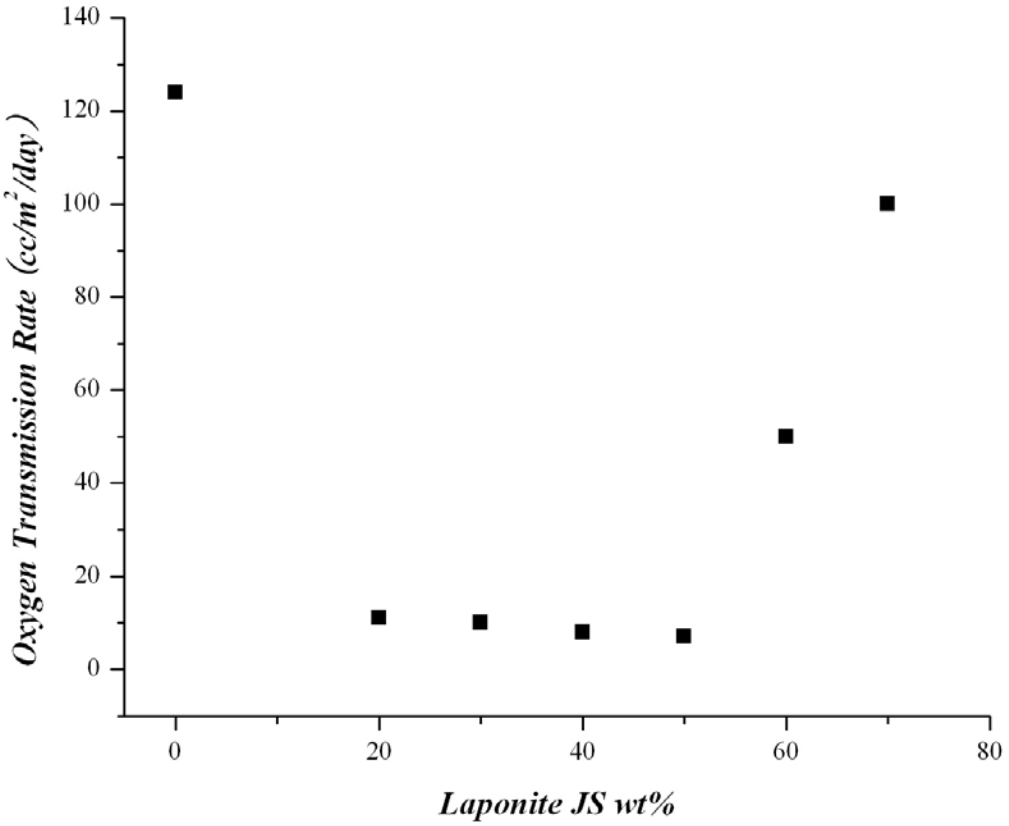


Figure 3-6. Dependence of clay content of loaded in PCN on OTR values

CHAPTER 4
CONCLUSIONS

Initially, it was believed that a mixture of two particles with different aspect ratios may provide longer tortuous paths and therefore, enhanced barrier properties than PCNs produced from just one particle variety. To investigate the effect of using a mixture of two particle types on barrier properties quantitatively, a model was developed. Several expectations were suggested based on the model. First, the relative size of the smaller particle (clay 2) has no effect. Second, the larger the d-spacing of the larger particle (clay 1) at constant volume fractions of two clays is in the system, the higher the Rp value is obtained. Third, when a constant number of platelets of the smaller particle (clay 2) at a fixed volume fraction are dispersed in increased intergallery of clay 1, more layers are formed, therefore reducing the number of clay platelets in each layer. Therefore, although d-spacing can be increased by creating more layers, the possibility that a diffusant encounters a platelet when passing by a layer is decreased. As a result, effects of increased tortuous path cannot exceed a critical Rp. Forth, a higher degree of aggregation results in higher Rp because the aggregates of particles that are not separated from the stacked agglomerate tend to lower N_1, shorten the detour length and even reduce the possibility of successful insertion of clay 2. Finally, the final Rp of PC2N was governed by total volume fraction rather than by the specific relative ratios between clay 1 and 2. The variance in Rp with degree of particle orientation was explored. Most models are based on the assumption that all clay platelets are dispersed in an orientation that is normal to the diffusant. The discrepancy from theoretical barrier models can have significant effect on Rp, especially for the PCN materials containing the filler with higher aspect ratio. To estimate the effect of the orientation of platelets on Rp, the orientation parameter (s) and related Rp equation reported by Bharadwaj et al., (2002)

were used for PC2N system and it was concluded that the higher volume fraction occupied in the system, the less important is orientation of clay platelets.

Initially, the effects of different coating layers (P, PL, and PCL) on OTR showed that addition of nano particles reduces OTR beyond what is possible by the homopolymer. Secondly, even though no significant difference in OTR values among all ratios for mixing two clays was obtained, the similar tendency that the clay having higher aspect ratio result in slightly lower OTR values was discovered. In conclusion, enhanced barrier properties were shown to follow increased total effective volume of filler particles that are exfoliated in polymer matrix and this tendency confirmed theoretical expectations for PC2N. Although PC2N system did not show significant enhancement in barrier properties, PC2N composite films with a moderate barrier property appeared to offer greater optical clarity than comparable PCN with just one, larger nanoparticle.

APPENDIX A
RAW OTR DATA

Table A-1. Oxygen Transmission Rate (cc/m^2/day) of Substrate Polymer Film

# of Trial	Type of Film		
	OPP/LLDPE	PET/PE	BON/PE
1	901.5	148	41.777
2	906.4	152.913	44.426
3	887.4	126.1	40.587
4	874	145.648	43.688
Average	892.3	143.2	42.6
SD	14.6	11.8	1.8

Table A-2. Oxygen Transmission Rate (cc/m2/day) of Substrate and PCN Film

# of Trial	Type of Film		
	P	PL	PCL
1	89.3	7.2	4.7
2	95.7	7.9	4.4
3	86.3	6.7	5.0
4	90.6	7.5	4.8
Average	90.5	7.3	4.7
SD	3.9	0.5	0.2

Table A-3. Oxygen Transmission Rate (cc/m2/day) of PC2N System

# of Trial	Ratio of Cloisite Na+ to Laponite JS				
	10:0	7:3	5:5	3:7	0:10
1	3.6	4.0	4.2	4.3	4.7
2	3.7	3.9	4.4	4.4	4.9
3	3.2	4.0	3.9	4.5	4.6
4	3.6	4.2	4.0	4.5	4.7
Average	3.5	4.0	4.1	4.4	4.7
SD	0.2	0.1	0.2	0.1	0.1

Table A-4. Oxygen Transmission Rate (cc/m2/day) of Cloisite

# of Trial	Cloisite concentration (wt%)				
	10	20	30	40	50
1	4	3.3	2.2	1.4	1
2	4.1	3.3	2.4	1.3	1.1
3	3.8	3.2	2	1.3	1
Average	5.5	7.5	9.2	11.0	13.3
SD	3.0	8.4	13.9	19.3	24.5

APPENDIX B
PC2N PROCEDURE

Table B-1. Procedure and Control Factor of PC2N Film

	Process	Factors
1	Making clay solutions	Clay quantity
		Clay ratio
2	Letting clay solutions 1day for cation exchange	Waiting time
		Temperature
3	Making PVOH solution	wt% of PVOH for adjusting viscosity
4	Mix Clay solution and PVOH solution	Mixing time
		Intensity of Shear force
5	Letting mixed solution 1day for remove bubbles	Waiting time
		Temperature
6	Substrate plasma treatment	The speed of conveyer belt
		Cycles of treatment
		Flow rate of Nitrogen gas
		Working distance
7	Coating	
8	Drying	Time
		Temperature
		Vacuum on/off
9	Measure thickness	
10	Test OTR	

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BIOGRAPHICAL SKETCH

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